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INSTITUTO SUPERIOR TÉCNICO

Children exposure to inorganic and organic chemical compounds in particulate matter: characterisation and source identification

Tiago Alexandre Ferreira Paes de Faria

Supervisor:	**Doctor Susana Marta Almeida**
Co-Supervisors:	**Doctor Célia dos Anjos Alves**
	Doctor Christos Housiadas

Thesis approved in public session to obtain the PhD Degree in Environmental Engineering

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Funding Institutions

Fundação para a Ciência e Tecnologia PhD grant (SFRH/BD/129149/2017)

LIFE Index-Air project (LIFE15 ENV/PT/000674)

Center for Nuclear Sciences and Technologies (UIDB/04349/2020+UIDP/04349/2020)

ExpoLIS project (LISBOA-01-0145-FEDER-032088 + PTDC/EAMAMB/32088/2017)

2022

Título: Exposição de crianças a compostos orgânicos e inorgânicos no material particulado: caracterização e identificação de fontes.

Resumo

A exposição à matéria particulada (PM, do inglês particulate matter) está associada a efeitos adversos na saúde, principalmente em grupos populacionais suscetíveis, como as crianças. Esta tese pretende (i) caracterizar as partículas amostradas nos microambientes mais utilizados pelas crianças; (ii) avaliar a exposição diária das crianças aos compostos químicos que constituem a PM e estimar a contribuição dos vários microambientes para essa exposição; (iii) avaliar a dose interna de PM aplicando modelos de dosimetria; e (iv) quantificar a contribuição das fontes de PM para a exposição pessoal através da aplicação de modelos no recetor. Os resultados mostraram que as concentrações médias de PM2.5 e PM10 medidas nas salas de aula (35.3 e 65.4 $\mu g/m^3$, respetivamente) excederam os valores-limite estabelecidos pela legislação portuguesa para a qualidade do ar interior. A PM amostrada nas escolas foi caracterizada por elevados teores de matéria orgânica e elementos minerais resultantes da ocupação, ressuspensão de poeira e giz. Nas casas, as concentrações foram significativamente inferiores, contudo também se verificou uma elevada contribuição da matéria orgânica para a PM. Os microambientes interiores foram os que mais contribuíram para a exposição diária das crianças a PM2.5 e PM10, com valores acima de 80% e 65%, respetivamente. Através da análise microbiológica da poeira sedimentada, foram encontradas nos quartos e salas, secções de *Aspergillus* (como *Nigri* e *Candidi*) que possuem potencial toxigénico, e exibiram suscetibilidade reduzida a um ou mais azóis. Através da aplicação de modelos de dosimetria, verificou-se que, em média, 3% da PM deposita-se na região brônquica, enquanto 5% a 8% se deposita na região bronquiolar. Por fim, foram estudadas as fontes de emissão que influenciam a exposição das crianças à PM. Nove fatores foram identificados: emissões de escape e não escape do tráfego, partículas secundárias, combustão de fuel, indústria, sal marinho, solo, poeira urbana e uma fonte interior caracterizada por níveis elevados de carbono orgânico.

Palavras-chave: Crianças; Qualidade do Ar; Matéria Particulada; Exposição; Dose, Identificação de Fontes.

Title: Children exposure to inorganic and orgnic chemical compounds in particulate matter: characterisation and source identification**.**

Abstract

Exposure to particulate matter (PM) is associated with adverse health effects, especially in susceptible population groups such as children. This thesis aims to (i) characterise the particles sampled in the microenvironments (MEs) mostly frequented by children, using complementary techniques; (ii) assess the daily exposure of children to PM chemical compounds and estimate the contribution of the different MEs for this exposure; (iii) assess the internal dose of PM by applying numerical dosimetry models; and (iv) quantify the contribution of the sources of PM to the personal exposure using receptor models. The results showed that the average concentrations of PM2.5 and PM10 measured in classrooms (35.3 and 65.4 $\mu g/m^3$, respectively) exceeded the limit values established by the Portuguese legislation for indoor air quality. The PM sampled in schools was characterised by high levels of organic matter and mineral elements resulting from occupation, resuspension of dust and chalk. In the houses, the concentrations were significantly lower, however, there was also a high contribution of organic matter to PM. Indoor MEs were the main contributors to the children's daily exposure to PM2.5 and PM10, with values above 80% and 65%, respectively. The microbiological analysis of settled dust showed the presence of sections of *Aspergillus*, with toxigenic potential and reduced susceptibility to one or more azoles, in bedrooms and living rooms. Through the application of dosimetry models, it was found that, on average, 3% of PM is deposited in the bronchial region, while 5% to 8% is deposited in the bronchiolar region. Finally, receptor models were used to estimate the contribution of the sources to the children's exposure to PM. Nine factors were identified: exhaust and non-exhaust emissions from traffic, secondary particles, fuel combustion, industry, sea salt, soil, urban dust and an indoor source characterised by high levels of organic carbon.

Keywords: Children; Air Quality; Particulate Matter; Exposure; Dose; Source Identification.

Acknowledgments

I would like to express my sincere gratitude to all the people who directly and indirectly contributed to the preparation of this work. With whom I learned, grew, and lived, in my scientific and personal life.

I especially want to thank Dr Marta Almeida, my supervisor at the Center for Nuclear Sciences and Technologies (C^2TN) at Instituto Superior Técnico, for always being a source of inspiration, advice and guidance, and for providing me with a unique opportunity to develop my studies. For all the motivation, patience and knowledge. Thank you!

To my co-supervisors Dr Célia Alves from the Department of Environment, Centre for Environmental and Marine Studies (CESAM), University of Aveiro and Dr Christos Housiadas from the THEMLab, Institute of Nuclear and Radiological Science & Technology, Energy & Safety, NCSR "DEMOKRITOS", for all their help, knowledge and guidance over these 4 years.

To all my colleagues from the Life Index-Air project, especially to Dr Evaggelia Diapouli and Dr Manousos-Ioannis Manousakas, for everything they taught me and for their fundamental contribution to this thesis.

To Dr Marika Pilou (NCSR “DEMOKRITOS”) for all the help from the beginning and for having “received” me so well, by Skype (since the covid-19 came to change our lives), where she shared her knowledge and gave essential tools to develop part of this thesis.

To my colleagues in the Air Quality group at C^2TN, namely Nuno Canha, Joana Lage, Carolina Correia, Inês Lopes, Vânia Martins, Joana Coutinho and Isabel Dionísio for all their companionship, availability and interest. A special word to Vânia Martins, part of this work since the beginning, for all the help and advice. And to Inês Lopes, my office partner, for her friendship and constant availability.

I also gratefully acknowledge Fundação para a Ciência e Tecnologia (FCT) for funding me with the PhD fellowship (SFRH/BD/129149/2017). To LIFE Index-Air project (LIFE15 ENV/PT/000674) and C^2TN for all the resources.

Last but not least, I would like to thank my family and friends for their time, unconditional support, motivation and good ideas. Especially to my parents and grandparents, for all the teachings and conditions that allowed me to be who I am today. They are a pillar and a source of inspiration. And to Patrícia Neves for her constant encouragement and companionship all the time.

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Nomenclature

AI	Alveolar-interstitial
APA	Portuguese Environment Agency
BB	Bronchial
bb	Bronchiolar
BC	Black carbon
CCDR	Regional Coordination and Development Commission
CFU	Colony-forming unit
DALY	Disability-adjusted life-years
DG18	Dichloran glycerol
Dp	Aerodynamic particle diameter
EC	Elemental carbon
EDC	Electrostatic dust collector
EEA	Environment European Agency
ET	Extrathoracic
EU	European Union
GDE	General dynamic equation
HRT	Human respiratory tract
IAQ	Indoor air quality
ICP-AES	Inductively coupled plasma - atomic emission spectrometry
ICP-MS	Inductively coupled plasma mass spectrometry
INE	Portuguese National Institute of Statistics
IR	Inhalation rate
LOD	Limit of detection
MD	Mineral dust
ME	Microenvironment

MEA	Malt extract agar
OC	Organic carbon
OM	Organic matter
PCIS	Personal cascade impactor sampler
PM	Particulate Matter
PM10	Particulate matter with an aerodynamic diameter of less than 10 μm
PM2.5	Particulate matter with an aerodynamic diameter of less than 2.5 μm
POM	Particle organic matter
PTFE	Politetrafluoretileno
qPCR	Real-time polymerase chain reaction
SDA	Sabouraud dextrose agar
SIA	Secondary inorganic aerosol
SOA	Secondary organic aerosol
SS	Sea salt
TOT	Thermo-Optical transmittance method
TSA	Tryptic soy agar
TSP	Total suspended particle
UM	Unidentified matter
USA	United States of America
VOR	Voriconazole
VRBA	Violet red bile agar
WHO	World Health Organisation
XRF	X-Ray fluorescence

Chapter 1

Chapter 1. Introduction

1.1 Problem statement and research questions

The effects of Particulate Matter (PM) have been observed even at low levels of exposure and there is no certainty of a safe level or a threshold below which no adverse health effects occur (WHO, 2006).

There has been a significant improvement concerning anthropogenic emission control strategies, which has been reflected in the decrease of ambient PM concentrations in Europe to levels below EU limit values. However, emissions are also susceptible to economic fluctuations and the financial crisis that affected Europe between 2008 and 2014 contributed to a trend towards a reduction in the concentration of air pollutants. This trend began to reverse in 2015, with an increase in annual average concentrations for several European urban centres, although it seems that in the last years, the concentrations have slightly declined or stabilised (EEA, 2019). In 2020 the coronavirus disease (Covid-19) has spread worldwide giving rise to a pandemic. In order to reduce the spread of the new SARS-CoV-2 coronavirus, most European countries have implemented restriction measures that significantly decreased the circulation of road transport, aviation, and international maritime transport and, consequently, reduced the air pollution emissions. Spain and Italy have estimated reductions of PM10 in the order of 30 to 40% (EEA, 2020). With the return to the new normality, this trend is expected to change again. Probably the emissions will return to their previous values or even increase, due to the need to compensate for the loss of productivity caused by the successive lockdowns. Europe will try to rebuild its economy and increase its competitiveness; therefore, specific and effective environmental strategies are needed to avoid the increase of anthropogenic emissions. However, if the quantitative impact of these strategies on health is not well known for each of the emission sources, the definition of effective strategies may be compromised.

This brings us to the considerable importance of assessing the integrated personal exposure to airborne mixtures of chemical compounds, as it is the main determinant of the dose received by an individual and therefore directly influences health impacts. Measuring outdoor air levels and pollutant trends at fixed ambient air quality monitoring stations along with modelling outdoor air concentrations has been the traditional way of evaluating urban air quality and pollution abatement programs. However, this logic has been altered by a series of recent developments in scientific knowledge. Weak correlations have been found between ambient PM concentrations and personal exposure and therefore this approach fails to consider all components of exposure (Michikawa et al., 2014; Tran et al., 2020)

Since people spend more than 90% of their time indoors, individual exposure to PM is dominated by indoor air pollution, which is partially outdoor air pollution that has penetrated indoors and partially indoor air pollution. However, available data for indoor air pollution risk assessment are scarce and often insufficient. Information is available for the indoor air concentrations of some well-known pollutants, but

lacking for others whose effects are unclear, such as the chemical components of indoor PM that are poorly characterised.

In recent years, indoor air has been set as an essential part of a complete integrated strategy on air pollution. The World Health Organisation (WHO) has recognized the Indoor Air Quality (IAQ) as a fundamental human right, declaring that "everyone has the right to breathe healthy indoor air". However, the EU has not set guidelines for indoor air pollutants, in particular, because a systematic assessment of the health risks for these pollutants has not yet been made available.

In conclusion, future air quality management should require quantitative estimates for the integrated exposure of the population and measures should be oriented to both outdoor and indoor environments.

As a basis for designing this investigation and for directly addressing the challenges posed, the following research questions were formulated to guide the research contained in this thesis:

1) What are the main characteristics of the indoor PM?
2) What is the daily exposure to the PM and respective dose?
3) What are the main MEs, sources and activities affecting the exposure to PM?
4) What measures can be implemented to reduce the exposure to PM?

1.2 Aim and specific objectives

The inadequate quality of indoor air arises from a poor articulation, appreciation and understanding of the basic principles underlying the processes, policies and needed actions related to IAQ. As a result, this PhD work aims to contribute for a better understanding of some identified gaps in the IAQ knowledge:

1) Despite up to 30% of the burden of disease from PM exposure could be attributed to indoor-generated particles (Morawska et al., 2013), signifying that those indoor environments are likely to be a dominant factor affecting human health, indoor concentrations of PM chemical compounds have been sparsely investigated;

2) Personal integrated exposure to PM chemical compounds is of considerable importance as it is the key determinant of the dose received by an individual and thus directly influences any impact on health; however, so far, the majority of the works focused on the determination of outdoor pollutant concentrations and the human integrated exposure and dose to PM chemical compounds was poorly addressed to date;

3) Although source apportionment has been an active research subject for outdoor air quality, few studies on indoor and exposure source apportionment have been conducted.

Considering these aspects, this PhD study aims to understand the characteristics of the PM affecting the children exposure by:

a. characterising the particles sampled in the MEs mostly frequented by children, using complementary techniques;

b. assessing the daily exposure of children to PM chemical compounds and estimating the contribution of the different MEs for this exposure;

c. assessing the internal dose of PM by applying numerical dosimetry models;

d. quantifying the contribution of the sources of PM to the personal exposure using receptor models.

1.3 Organisation

The thesis is divided into ten (10) chapters. Chapter one (1) introduces the problem statement and the research questions, aim and objectives, and sets the scope of the thesis. Chapter two (2) presents the theoretical framework. Chapter three (3) describes the methodological approaches and techniques. In this section, the methodology of the entire thesis is presented in detail, although it is also described in a summarised way in each publication presented between chapter 4 and 9. Chapter four (4) to nine (9) outlines the research results based on the six research articles, which have already been published in peer-reviewed journals.

Chapter ten (10) presents a summary of the main findings in each article, and how these findings are interrelated, in light of the research questions, aim, and specific objectives of the thesis, and provides insights on potential future studies.

1.4 My contribution to the LIFE Index-Air project and scientific articles presented in the thesis

My contribution to the LIFE Index-Air project and to the scientific articles that are part of this thesis is summarised in the following list:

- I performed the quality assurance and quality control of the equipment before the sampling campaigns.

- I created the time-activity questionnaires and applied it to 6096 children. I was responsible for all data processing.

- I made all the field work in 5 schools, 40 homes and respective outdoors.

- I participated in the measurements performed in the transports.

- I carried out the gravimetric analysis of all the filters collected in homes and schools and was in charge of the logistics and articulation with the NCRD-Demokritos in Greece where the chemical analyses of the filters were carried out.

- I made the sampling of the EDCs in homes and schools and participated in the microbiological analysis of the samples.

- I analysed the presence of perfluoroalkylated substances (PFAS) and polybrominated diphenyl ethers (PBDE) in the filters sampled in schools and homes, in partnership with the Department of Environmental Science at Aarhus University in Roskilde, Denmark, through a 3-month Short Term Scientific Mission Grant (February 2020 - May 2020) funded by the COST Action CA17136 and by FCT (work in progress).

- I performed the data processing, statistical analysis, discussion of results, and wrote the scientific articles where I am the first author (articles 1, 2 and 5).

- I actively collaborated in the preparation of the scientific articles where I am a co-author (articles 3, 4 and 6). I have been mainly involved in the sampling campaigns, in the provision and statistical analysis of data, and in the review of the final drafts of the manuscripts.

- I communicated the results of the work in several awareness campaigns promoted in primary schools and in other dissemination actions (researcher's night, science fairs, etc.)

- I presented the results of my research in several scientific meetings, which are presented in Annex I.

Table 1.1 explains in detail the contribution for each published article presented in the thesis (chapters 4 to 8).

Table 1.1 - Summarized contribution to each published scientific article presented in the thesis.

Chapter / published article	CRediT (Contributor Roles Taxonomy) Author statement
Chapter 4 **Children's exposure and dose assessment to particulate matter in Lisbon**	Conceptualization, Methodology, Investigation, Formal analysis, Writing - original draft preparation.
Chapter 5 **Assessment of children's exposure to carbonaceous matter and to PM major and trace elements**	Conceptualization, Methodology, Investigation, Formal analysis, Writing - original draft preparation.
Chapter 6 **Relationship between indoor and outdoor size-fractionated particulate matter in urban microenvironments: Levels, chemical composition and sources**	Conceptualization, Methodology, Investigation, Formal analysis, Writing - Review & Editing.
Chapter 7 **Assessment of children's potential exposure to bioburden in indoor environments**	Methodology, Investigation, Formal analysis, Writing - original draft preparation.
Chapter 8 **Children's exposure to size-fractioned particulate matter: chemical composition and internal dose**	Conceptualization, Methodology, Investigation, Formal analysis, Writing - original draft preparation.
Chapter 9 **Source Apportionment of Children Daily Exposure to Particulate Matter**	Conceptualization, Methodology, Investigation, Formal analysis, Writing - Review & Editing.

Chapter 2

Chapter 2. Theoretical Framework

According to the WHO, air pollution is defined as the contamination of the indoor or outdoor environments by any chemical, physical or biological agent that modifies the natural characteristics of the air.

The perception of the existence of air with bad quality came with the beginning of cities, several centuries ago, where the "bad smell in the air" is documented. However, it was in the 20th century, several years after the industrial revolution, that some episodes occurred and alerted the population to the potential dangers of air pollution to human health. In an industrial area in Belgium, in the Meuse river valley, in 1930, a set of specific weather conditions (such as low temperatures, fog, little wind) caused the accumulation of pollutants that for three days caused several episodes of illness and death (Phalen and Phalen., 2013). In an industrialised valley in Donora, Pennsylvania, United States of America (USA) in 1948, a thermal inversion during some days also caused the accumulation of pollutants and several deaths. In London's Thames Valley, in December 1952, a rapid accumulation of PM and SO_2, due to a four-day thermal inversion phenomenon, killed approximately 4,000 people, with respiratory and cardiac problems (Ling and van Eeden, 2009; Sunyer et al., 2000).

These episodes brought awareness about the hazards of air pollution, and over the decades, several studies have been carried out and provided the basis for this area of knowledge. In the following chapters, part of this knowledge is summarised, in order to provide sufficient bases for a clear perception of the thesis.

2.2. Air quality

2.2.1 Outdoor air quality

Ambient air pollution has natural and anthropogenic origins, and its impacts varies according to the concentrations and characteristics of the pollutants. It is in the urban areas that the main air quality problems are found, due to the displacement of the population to the cities over the years, which increased the sources of anthropogenic pollution in urban areas. Among the various sources of pollution, exhaust and non-exhaust emissions from road traffic stand out (Amato et al., 2014; Karagulian et al., 2015). The amount of exhaust pollutants emitted by a motor vehicle varies with the type of vehicle, fuel used, treatment devices installed, type of road, among other (Amato et al., 2014; Padoan and Amato, 2018; Piscitello et al., 2021; Zhang et al., 2017). On the other hand, road traffic is an emission source of PM from tyre and brake wear, and road dust resuspension (Amato et al., 2014; Belis et al., 2013; Demir et al., 2022; Padoan and Amato, 2018; Zhang et al., 2017). These emissions are designated as “non-exhaust”. Still linked to transports, ambient air can be also contaminated by pollutants emitted by rail vehicles, such as trains and subways (Abbasi et al., 2013; Martins et al., 2017; Wang and Gao, 2011), nautical vehicles, whether tourism (cruises), recreational

and fishing activities (Jonsson et al., 2011; Merico et al., 2016; Mueller et al., 2011; Mar Viana et al., 2014) and air transport, especially when airports are located close to cities (Mazaheri et al., 2011; Stettler et al., 2011; Yim et al., 2013). In addition to traffic, urban ambient air is impacted by industry (Brewer et al., 2016; Espitia-Pérez et al., 2018; María Cruz Minguillón et al., 2012; Owoade et al., 2015; Xu et al., 2017), biomass burning, agriculture, and forest fires (He et al., 2016; Keywood et al., 2015; Wigder et al., 2013).

In the case of Portugal and more specifically Lisbon, several scientific studies identified the main origins of PM: natural dust, either from local emissions of bare soil, or from long range transport due to the influence of dust events from the Sahara (Almeida et al., 2008), marine aerosols, which have an important impact in the Portuguese coastal areas (Almeida et al., 2013), traffic (Almeida et al., 2009a), industrial activities (Farinha et al., 2004; Freitas et al., 2005), and the frequent summer wildfires (Martins et al., 2012).

As ambient air quality plays a fundamental role in the health and well-being of the population, the European Union and its Member States have introduced legislation through European Directives, which set targets for the reduction of certain pollutants to curb air pollution.

The EU Directive 2015/1480, published on 28 August 2015, on ambient air quality and cleaner air in Europe is currently in force. This directive amends several annexes of the Directive 2008/50/EC, which aggregates the provisions of Directive 96/62/EC, Council Decision 97/101/EC, and the provisions of the first three daughter directives (Directive 1999/30/EC, Directive 2000/69/EC, Directive 2002/3/EC). The Directive sets objectives and rules to guarantee the prevention or reduction of the harmful effects of air pollution, such as the assessment of the air quality based on common methods and criteria and the promotion of the cooperation and sharing of information between member states.

At a national level, the EU Directives were transferred to the national law through the Decree-Law No. 47/2017, of 10 May, and the Portuguese Environment Agency (APA) and the Regional Coordination and Development Commission (CCDR) are the entities responsible by its implementation.

2.2.2 Indoor air quality

The change in the habits of the population (increasingly “indoor” and in cities), the evolution of the technology, together with the need for greater energy conservation in buildings, led to a change in the way new buildings are built. However, frequently these changes do not take air quality into account, leading to inadequate ventilation in buildings and impacts on the health of their occupants. With the increase of the health complaints, in the 80s the Sick Building Syndrome designation emerged, which sought to explain the impact of IAQ problems on the health of occupants (Jaakkola et al., 1994).

There is a wide variety of MEs, such as homes, offices, schools, factories, gyms, and transpors, which have their internal sources and are influenced by the type of activities performed inside (Viana et al., 2011). Activities such as smoking, cleaning, cooking, painting or walking generate new particles or lead to

resuspension of deposited ones (Abdullahi et al., 2013; Arku et al., 2015; Custódio et al., 2014; Kang et al., 2019; Ni et al., 2020; Qian et al., 2014; Rivas et al., 2019). Other factors influencing indoor air pollution are the type of ventilation, air exchange rates, penetration factors, construction materials, furniture, products and equipment used in the space, temperature and relative humidity (Canha et al., 2013; MacNeill et al., 2012; Rivas et al., 2019; Urso et al., 2015; Younes et al., 2012; Zhang et al., 2021). These factors are influenced not only by the characteristics and geographic location of the building, but also by the socioeconomic status of country where it is located (Ferguson et al., 2020; Mannan and Al-Ghamdi, 2021).

Although IAQ plays a fundamental role in the health and well-being of its occupants, there are no mandatory limit values for indoor air pollutants established by the European Commission. Despite that, Portugal defined IAQ limit values for some chemical, physical and microbiological parameters in the IAQ in the Ordinance nº 138-G/2021, which was published in July 1st 2021 and obliges some building typologies, such as primary schools, to carry out periodic audits.

2.3. Particulate Matter

2.3.1 Origin and properties

Particulate matter is a complex mixture of extremely small particles composed of various organic and inorganic compounds, including organics and metals, that can be liquid or solid (Seinfeld and Pandis, 2006; Vallero, 2008). PM vary in size, physical, chemical, and biological characteristics, depending on their origin and source.

Sources that contribute to PM are classified as natural (emitted by natural processes) or anthropogenic (emitted by processes arising from human activities). Natural sources are dominant on a global scale and their main origins are volcanic eruptions, forest fires, sea salt particles formed, resuspension of particles from deserts carried by the wind, among others (EEA, 2020). Portugal, due to its geographical location, is occasionally affected by large concentrations of particles from the Sahara Desert in North Africa (Agência Portuguesa do Ambiente, 2017; Bozlaker et al., 2013; Wagstrom and Pandis, 2011).

The principal anthropogenic sources are transport, domestic heating, energy generation through fossil sources, industrial processes, biomass burning, and fugitive sources (EEA, 2021; Karagulian et al., 2015). Some of these human activities, which are carried out in or near cities, have a greater impact on local and regional concentrations. According to the report by the European Environment Agency, in Europe and Portugal, transport and energy production are the main sources of PM emissions (EEA, 2020).

Particles emitted directly into the atmosphere in liquid or solid form are called primary particles. Those that originate from nucleation or condensation reactions in the atmosphere between reactive species and primary pollutants are considered secondary particles (Singh and Tripathi, 2021). In addition to sources,

other factors such as meteorology, geography, city obstacles and seasonal patterns affect PM levels in a given location (Adams et al., 2015; X. Zhao et al., 2019).

One of the most important characteristics of PM is the size, since it affects the transport, removal, and deposition capacity of the particles and interferes in the impact of the PM on health and climate. PM size is defined by the aerodynamic particle diameter (Dp), which is equivalent to the diameter of a sphere of unit density (1 g/cm^3) with the same particle deposition speed under the action of gravity (Seinfeld and Pandis, 2006). Particles are generally classified as PM10 ($Dp \leq 10$ μm), PM2.5-10 or coarse particles (2.5 μm < Dp < 10 μm), PM2.5 or fine particles ($Dp \leq 2.5$ μm) and ultrafine particles ($Dp \leq 0.1$ μm).

Fine particles can be divided into nucleation mode, Aitken mode and accumulation mode (Zhang et al., 2016). The nucleation mode (ultrafine particles) encompasses particles with diameters less than 0.01 μm. They are generated from the condensation of vapours at high temperatures during combustion processes or from the nucleation of gaseous compounds in the atmosphere (Seinfeld and Pandis, 2006). On the other hand, particles can increase in size by condensing or coagulating the particles to other gases or particles (Kwon et al., 2020). The Aitken mode (ultrafine particles) encompasses particles with diameters between 0.01 and 0.1 μm and most Aitken nuclei are the result of primary emission, coagulation, or condensation onto pre-existing particles (Seinfeld and Pandis, 2006; Zhang et al., 2016). These particles mostly come from incomplete combustion from diesel-engine vehicles. The accumulation mode (fine particles) comprises particles with diameters between 0.1 and 2.5 μm and are the result of primary emissions, coagulation of small particles and condensation of secondary sulphates, nitrates and organics from the gas phase (Seinfeld and Pandis, 2006). Thermodynamic properties have a considerable influence on secondary particle formation processes, such as nucleation and condensation. These have greater mobility but also greater surface area. In addition to the small contribution of mineral origin, these particles are made up of sulphate, nitrate, organic and elemental carbon, metals formed in combustion processes, and microorganisms.

The coarse fraction of PM consists of biological material, marine salts, and minerals from the earth's crust and secondary particles, formed essentially by the chemical interaction of gases with primary particles of mineral or marine origin (Rogula-Kozłowska, 2016). While globally this fraction is mainly emitted by natural sources (Gieré and Querol, 2010), at urban level there is a large anthropogenic contribution. These can be long range transport of dust (Athanasopoulou et al., 2016; van der Does et al., 2018), a phenomenon that is evident in Portugal.

2.3.2 Chemical composition

The knowledge about the chemical composition of the PM is essential to explain their formation mechanisms, source apportionment and health impact assessment. PM are composed of a complex mixture

of chemicals that can be classified according to their origin as: carbonaceous matter, mineral dust, sea salt, secondary (in)organic aerosol, and anthropogenic elements.

- Carbonaceous matter

Carbonaceous matter in PM is essentially composed of organic carbon (OC) and elemental carbon (EC). OC (also expressed as organic matter (OM) to consider the masses of O, N, H and other atoms, besides carbon) refers to a complex mixture of different classes of organic compounds that can be emitted in its primary form by industry, road dust, pavements, residential biomass combustion devices, forest fires, biogenic material (pollen, microorganisms, and insect remains), fossil fuels, and cigarettes (Alves et al., 2014; Amato et al., 2014) or can exist as secondary organic aerosol, SOA, which is formed through photochemical reactions in the atmosphere from gaseous precursors (Seinfeld and Pandis, 2006). In urban and industrial areas, the predominant sources of OC are anthropogenic (Hussein et al., 2022), or biogenic, but transformed into SOA (Hoyle et al., 2011). OC affects air quality, climate, and human health (Zhang and Zhu, 2012; Zhang et al., 2013).

EC has a chemical structure similar to impure graphite (Evangeliou et al., 2018) and results mainly from combustion processes, such as burning coal and wood, some industrial processes and vehicle emissions, particularly from diesel engines (Briggs and Long, 2016; Waheed et al., 2011; Wang et al., 2019). EC has an impact on climate change, due to its capacity to absorb radiation in the atmosphere (Bahadur et al., 2012; Evangeliou et al., 2018; Kelly and Fussell, 2012; Ostro et al., 2015) and on the health of the population (Kelly and Fussell, 2012; Ostro et al., 2015; Sehlstedt et al., 2010). The study performed by Patel et al. (2009) found a relationship between exposure to EC and coughing in children. In the work developed by Ostro et al. (2009) it was possible to verify a link between exposure to OC, EC, and PM2.5 and the increase in hospitalisations of children with respiratory diseases.

- Mineral dust

Particles associated with mineral (or crustal) matter are one of the main components of the total mass of PM in the atmosphere (Gieré and Querol, 2010; Lozano, 2010). They are mainly generated by the action of wind on the earth's surface, causing soil erosion and its resuspension. The main sources of mineral dust are the arid and semi-arid regions, namely the deserts in the northern hemisphere and from where the PM is transported over long distances (Calvo et al., 2013; Choobari et al., 2014; Goudie, 2014). Portugal is particularly affected by mineral dust from the Sahara desert in the North of Africa (Almeida et al., 2005). The mineral aerosol is fundamentally composed of quartz (SiO_2), carbonates such as calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$), clay especially kaolinite ($Al_2Si_2O_5(OH)_4$), illite ($K(Al, Mg)_3SiAl_{10}(OH)$), feldspar ($KAlSi_3O_8$) and smectite $(Na,Ca)(AlSi)_4O_8$, and in smaller amounts, calcium sulphate ($CaSO_4.2H_2O$) and

iron oxides (Fe_2O_3). However, its composition varies depending on the geological characteristics of the area of origin. The elements that make up the mineral aerosol are mainly Si, Al, Ca, Ba, Sr, Fe, and Ti in the form of oxides and carbonates (Marconi et al., 2013; Zeb et al., 2018). At the local level, mineral particles are mainly the result of human activities, such as traffic, agriculture, construction and demolition, and industrial activities with mineral material (Reche et al., 2011).

- Sea Salt

Marine aerosol is produced by the rupture of air bubbles on the marine surface by the action of the wind that transfers them to the atmosphere and through the breaking of waves (Calvo et al., 2013). Marine aerosol is most evident in coarse particles, yet they are small enough to travel long distances and remain in the atmosphere for a few days (Seinfeld and Pandis, 2006). Its chemical composition consists mainly of sodium chloride (NaCl), but also of sulphates (Na_2SO_4, $MgSO_4$ and K_2SO_4), with geographic location (close to the coast) and meteorology having a decisive role in the concentration of this aerosol.

- Secondary inorganic aerosol

Secondary Inorganic Aerosols (SIA) mainly include sulphate (SO_4^{2-}), nitrate (NO_3^-), and ammonium (NH_4^+), which are formed from the gaseous precursor species sulphur dioxide (SO_2), nitrogen oxides (NOx), and ammonia (NH_3), respectively (Amato et al., 2016; Squizzato et al., 2013). The SO_4^{2-} can react with ammonium (NH_3), calcium carbonate ($CaCO_3$) and sodium chloride (NaCl), giving rise to other sulphates, such as ammonium sulphate, calcium sulphate and sodium sulphate. The main emission sources of the precursors are traffic, industrial processes, power generation, and residential emissions (Amato et al., 2014; Calvo et al., 2013). The production of secondary sulphates and nitrates depends on the concentrations of their atmospheric precursors, their characteristics and weather conditions (Kong et al., 2014). Several studies demonstrated the impacts of the SIA on climate, visibility, and human health (Lin et al., 2016; Wichmann et al., 2010; Xu et al., 2015).

- Trace elements

Although trace elements have a small contribution to the PM mass and some are necessary for living organisms, their presence in the atmosphere is a concern due to their potential adverse effects on human health and the ecosystems (Olumayede et al., 2021). Trace element concentrations are strongly influenced by local sources such as fossil fuel (Al, Fe, Ca, Mg, K, Na, As, Pb, Cd, Sc, Hg), tyre and brake wear (Cu, Sb, Fe, Zn, and Ba), vehicle exhaust (Cd, Cr, Cu, Ni, Pb, Zn), industrial emissions (Cu, Pb, Ni, Cd, Cr, Al, Fe As and Zn), among others (Calvo et al., 2013; Duan et al., 2012; Gietl et al., 2010; Piscitello et al., 2021).

2.3.3 Impacts of Particulate Matter

Air pollution with PM is a complex problem affecting all regions, ages, and socioeconomic groups (EEA, 2020). These impacts have been increasing since the industrial revolution and the migration of people to large urban centres have become an important topic of debate in the public sphere. Particulate matter has been declared by the WHO as the greatest threat to air quality, due to the various harmful chemical species detected in its composition (Nasser et al., 2015). PM have thus become, over time, one of the most important indicators of air pollution (Alves, 2005) due to their impacts in the ecosystems, climate, and population health.

- Ecosystems

The wet or dry deposition of atmospheric particles on ecosystems can cause a series of toxic effects, depending on their chemical composition and the type of ecosystem in which they deposit (Manisalidis et al., 2020). Some of these impacts are the acidification of aquifers with changes in their composition, changes in soil composition with significant impacts on agriculture, increase of deforested areas, disturbance of biogeochemical cycles and changes in the earth's energy balance. Besides that, PM can increase the acid rains, which damage statues and monuments (Akpo et al., 2015; Singh et al., 2016).

While wet deposition results from precipitation (rain or snow) of atmospheric particles and gases that have been incorporated into cloud droplets, dry deposition includes all the processes of transferring particles to the various environments in the absence of rain (Singh et al., 2016; Y. Wu et al., 2018). Wet deposition is more effective for fine particles of secondary origin, while dry deposition is more effective for coarse particles, being a slower process than wet deposition (Chen et al., 2012; Coz et al., 2011).

- Climate

Particulate matter has direct and indirect impacts on the climate depending on its origin and characteristics. Particles can interact with energy from the sun. PM warms by absorbing sunlight (e.g., black carbon) or cools by scattering sunlight (e.g., sulfates), contributing to the warming of the environment around them (Fiore et al., 2015). PM can also change the characteristics of clouds, through the interaction of particles with water vapour (they act as condensation nuclei), compensate the greenhouse effect, counteracting the increase in heat, through the action of sulphate particles and influence the circulation patterns at local, regional and global levels, due to the transboundary transport of pollutants (Fiore et al., 2015).

- Human health

Considering that daily human beings inhale between 10,000 and 20,000 litters of air and that this air contacts directly with the respiratory tract (with about 350 litters entering the bloodstream) (Salvi, 2007), it is easy to understand that harmful substances such as particles and their constituents can cause or aggravate cardiovascular and respiratory diseases, and ultimately lead to death.

The size is the PM property that most influences the way how particles circulate along the airways, and the impact on health (Almeida et al., 2014; Guarieiro and Guarieiro, 2013). Coarse particles deposit essentially in the upper airways (extrathoracic region), from the nasal/oral cavity to the pharynx/larynx (Nemmar et al., 2013). These can be removed through coughing or saliva (Jang, 2012). PM2.5 tends to be deposited in the lower airways (tracheobronchial region) and may reach the pulmonary alveoli (Guarieiro and Guarieiro, 2013). Ultrafine particles are deposited in the alveolar region and can enter the bloodstream (Sturm, 2016), reaching the various organs (Choobari et al., 2014; Schraufnagel, 2020). Therefore, the finest particles can penetrate deeper into the respiratory system and cause more serious impacts on health.

Several epidemiological studies associated high levels of pollution with a higher rate of hospital admissions (Morakinyo et al., 2016; Pascal et al., 2014). Effects such as dyspnoea, increased mucus and persistent cough (Hamanaka and Mutlu, 2018; Kim et al., 2015), asthma and rhinitis (Fukutomi and Taniguchi, 2015; Querol et al., 2007), lung cancer and chronic obstructive pulmonary disease (Hooper and Kaufman, 2018; Jang, 2012; Kelly and Fussell, 2012; Ristovski et al., 2012; Sax et al., 2013), gestational hypertension and premature birth (Kampa and Castanas, 2008; Kim et al., 2015) can be caused by exposure to PM.

Inhalation of PM may also imply a reduction in average life expectancy (Correia et al., 2013). According to the report of the European Environment Agency (EEA), in 2019, long-term exposure to PM2.5 was responsible for approximately 307 000 premature deaths in the EU- 27 (EEA, 2021). Over the past decade, the number of deaths in the world attributable to ambient PM2.5 globally increased by 23.3% even as attributable death rates declined about 4%. Similarly, the numbers of ambient PM2.5-attributable Disability-adjusted life-years (DALYs) have increased by 17.1% despite declines in DALY rates (Health Effects Institute, 2020).

These impacts are felt with greater intensity in risk groups and highly depend on the characteristics of the particles, their concentration, and the exposure time.

Studies have found an association between increased risk for cardiovascular and respiratory hospitalisations, cancer, or even increased mortality with the carbonaceous matter in PM or elements such as Al, As, B, Cr, Ni, Si, V, and Zn (Hamanaka and Mutlu, 2018; Kirrane et al., 2019; Sacramento et al., 2020). The studies point out that trace metals can exacerbate health effects, especially if there is an interaction between them (Slezakova et al., 2014; Tchounwou et al., 2012). Exposure to high amounts of

lead and manganese can trigger neurological and haematological effects in children (Manalis et al., 2005; Neal and Guilarte, 2013) and vanadium compounds are associated with health effects on the human respiratory tract (HRT) (Fortoul et al., 2015; Rojas-Lemus et al., 2021).

In addition, exposure to airborne microorganisms leads to the emergence of infectious diseases such as influenza (virus) and legionellosis (bacteria), itchy eyes, stuffy nose, headache, and general fatigue or severe allergic reactions such as allergic bronchopulmonary aspergillosis, most commonly caused by the fungus *Aspergillus fumigatus* (Black et al., 2013; Fröhlich-Nowoisky et al., 2016; Mousavi et al., 2016; Sabino et al., 2019).

Some studies indicated that the drastic decrease in PM2.5 and PM10 concentrations would bring clear public health benefits (Castro et al., 2017; Lepeule et al., 2012). The study developed by Correia et al. (2013) demonstrated that a decrease of 10 $\mu g/m^3$ in the concentration of PM2.5 would be associated with an increase in mean life expectancy of 0.35 years.

- Susceptible groups - children

The health impacts associated with the exposure to PM are not equal to all the population. Pre-existing respiratory and cardiovascular problems and certain stages of life (children, elders, pregnant) are factors that make people more susceptible to air pollution (Mead, 2011). Children are considered a susceptible group (Mead, 2011; Mendell and Heath, 2005) due to three main reasons. Firstly, children are growing, their immune system is still immature and their lungs are still developing, so their ability to fully recover is compromised (Lee et al., 2010; Mendell and Heath, 2005). Furthermore, children are generally more physically active than adults, so their average daily inhalation rate is higher and consequently they inhale more PM relative to their lung size (Buonanno et al., 2012). Children are also more likely to breathe through their mouths, so there is no retention of part of the inhaled pollutants and PM penetrates deeper into the lungs, making clearance slower and more difficult when compared to nasal breathing (Bateson and Schwartz, 2008). Studies about the relation between exposure to air pollutants and children's health have been increasing, but remain scarce, which does not allow for the identification of strong cause-effect links (Brumberg and Karr, 2021).

The study developed by Sunyer et al. (2015) showed that children attending schools with higher levels of traffic-related air pollutants had slower growth in cognitive development, with implications for learning and school performance. Two other studies found evidence that air pollution can induce or aggravate respiratory and cardiovascular problems, affect concentration, cause headaches, and impact the learning and performance of exposed children (Mendell and Heath, 2005; Oliveira et al., 2019), which may also affect their neurological function (Xu et al., 2016). According to the study developed by Gilliland (2009), asthmatic children when exposed to certain pollutants in the air have an increase in symptoms, such as

wheezing, decreased lung function, and more often resort to medical services or equipment. School absences also increase. The same applies to children with cystic fibrosis. Due to exposure to high concentrations of pollutants in the air, they are at risk for pulmonary exacerbations and need to resort to antibiotics more frequently (Goeminne et al., 2013). Other illnesses in children are associated with air pollution such as bronchiolitis and otitis (Karr et al., 2009; Macintyre et al., 2011), childhood leukaemia (Filippini et al., 2015), and obesity (Jerrett et al., 2014).

2.4. Individual exposure

The exposure to which each individual is subject depends on the concentration of pollutants and the time spent in a certain place (Watson et al., 1988) and is defined as an event that occurs when a pollutant of a certain concentration enters into contact with the body surface, by dermal contact, ingestion, or inhalation for a certain period of time (Ott, 1982, Watson et al., 1988).

The assessment of the integrated exposure is an important contribution to a more accurate epidemiological study, resulting in a less erroneous classification of individuals' exposure and allowing the application of more effective strategies. In order to understand the consequences of the exposure to air pollutants on human health it is essential to take into account the magnitude, duration, and frequency of the exposure (Watson et al., 1988). The magnitude is relative to the concentration of pollutants. Duration refers to the time that exposure lasts, and frequency specifies the regularity of that exposure. Its quantification is not an easy process, since it varies from individual to individual and the concentration of pollutants is subject to high temporal and spatial variability (Steinle et al., 2013). There are three methods to assess human exposure – the indirect method, the direct method, and the biological method (Steinle et al., 2013). The indirect method consists of measuring the concentration of pollutants through fixed equipment in the MEs frequented by the individuals. It takes into account the time spent in each of these MEs. The direct method consists of portable monitoring equipment that each individual uses during their daily routine, thus obtaining personal exposure. The biological method consists of measuring contaminants or their consequences in the body after entering body tissues or fluids (through exposure/effect markers).

2.4.1. Microenvironments and time activity pattern

A microenvironment is any three-dimensional space that a person occupies for a finite time (Duan, 1982), namely outdoor or indoor spaces, such as the school and home. Integrated personal exposure is the sum of personal exposure in all MEs experienced in one day, taking into account the time spent in each one of them and the existing concentrations. For individual exposure calculation, the relevant MEs are those

where the individual spends most of his/her time or that have higher concentrations of a particular pollutant (Janssen et al., 2012).

The activity-time pattern allows obtaining information on the time and duration that each individual spends in each ME. Exposure can vary widely between people, as each individual has its activity-time pattern and attends different MEs.

Risk assessments and studies of individual exposure have been carried out using outdoor concentrations of pollutants through air quality monitoring networks. However, not only do people spend most of their day indoors, but concentrations of air pollutants are often higher inside buildings than outside (Van Tran et al., 2020). In the study developed by Morawska et al. (2013), it was concluded that up to 30% of the burden disease of exposure to PM can be attributed to particles generated in indoor sources; therefore, it is extremely important to assess the integrated personal exposure, taking into account the various indoor environments visited during the day.

2.4.2. Main indoor microenvironments frequented by children

In industrialised countries, including Portugal, children spend most of their time indoors, especially at home and school. During the week, the house is inhabited in a nocturnal schedule and the school in a daytime schedule, where they usually spend about 7 to 8 hours a day.

Air pollution in homes, originated from indoor sources and from the penetration of outdoor pollutants into the indoor space, can have an important impact on children's health (Jang, 2012). The main indoor sources in homes are tobacco smoke, cooking and heating food, biomass burning for heating and cooking purposes, cleaning products, pets, and excessive moisture that contributes to the appearance of microorganisms (Langer et al., 2016; Nasir and Colbeck, 2013; Vardoulakis et al., 2020; Zhang et al., 2021). Other factors such as the age of the buildings, the utilisation of unappropriated materials, the geographic location, the socio-economic conditions of the residents and their behaviour, the climatic conditions, the ventilation and infiltration conditions, among others, influence the air quality in the indoor of the houses (Ashmore and Dimitroulopoulou, 2009; Buonanno et al., 2012; Langer et al., 2016). Although only in recent years there has been an increase in studies about air quality in homes and its effects on the health of the population and in particular children, some associations between household exposures with asthma and allergies have already been found (Joana Madureira et al., 2016a; Salvi, 2007; Sundell et al., 2011).

Due to the long period spent in the classrooms, a good air quality in schools is essential for the health, well-being, concentration, and performance of children (Almeida et al., 2011; Bakó-Bíró et al., 2012; Haverinen-Shaughnessy et al., 2011; Twardella et al., 2012). The studies developed by Fraga et al. (2008), Madureira et al. (2016, 2009) and Selgrade et al. (2008) found a link between the presence of certain pollutants and the prevalence of allergic and respiratory symptoms. The study of Mendell and Heath (2005)

explains that poor air quality in schools can affect not only children's growth and learning performance but also their cultural and social development. Poor air quality in classrooms is associated with the inexistence or inadequate maintenance of ventilation systems, the overcrowding of spaces due to the excess of students in relation to the size of the room, and the lack of cleanliness of the surfaces (Almeida et al., 2011). The main sources of air pollutants in the classrooms are the resuspension of particles due to children's activities, the accumulation of CO_2 through breathing, chalk dust, cleaning products, deterioration of construction materials and mineral materials. Geiss et al. (2011) carried out a study in schools from 11 European cities and found higher indoor air pollution levels than in the respective outdoor environment, a behaviour that was also found in the studies conducted by Almeida et al. (2011), Pegas et al. (2012) and Wichmann et al. (2010). These results showed the importance of the indoor sources for the air quality inside schools but also the relevance of the location of schools in the city centres to avoid the penetration of traffic related pollution in the classrooms (Almeida et al., 2011; Qian et al., 2014; Vieira, 2011; Weschler, 2016). Projects such as the SINPHONIE (Baloch et al., 2020) and SEARCH (Csobod et al., 2010) or the study carried out by Annesi-Maesano et al. (2012) highlighted that, besides the indoor sources and the insufficient ventilation, the location of schools highly contributes to the degradation of air quality.

2.5. Inhaled dose

The dose is the amount of a pollutant that enters in the respiratory system and reaches target tissues. In the literature, there are two different ways to calculate the dose: inhaled dose and deposited dose. The inhaled dose is evaluated through the time spent in each microenvironment, the concentration of pollutants in that microenvironment, and the inhalation rate (IR) (Cunha-Lopes et al., 2019). The inhalation rate varies with age and activity performed (Buonanno et al., 2011). The deposited dose is calculated by applying a numerical model (Lazaridis et al., 2001; Mitsakou et al., 2007, 2005), which estimates the dose in each part of the HRT. The dosimetry models use the concentrations and time spent in each ME, the physicochemical characteristics of the PM, and the physiological parameters of the exposed population that varies with age (Almeida-Silva et al., 2018). The model details the deposited dose of particles in different regions of the respiratory tract. Thus, two individuals exposed to the same concentrations in a given environment during the same time, may have different inhaled and deposited doses.

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Chapter 3

Chapter 3. Methodology

The experimental method of this thesis was designed to assess children's exposure and dose to PM and its constituents and to study the contribution of the various factors affecting the levels of these pollutants indoors and outdoors.

The assessment of personal exposure and dose was performed through the direct and the indirect methods. Figure 3.1 resumes the entire methodology of this thesis, which is specified throughout this chapter and in each one of the presented articles.

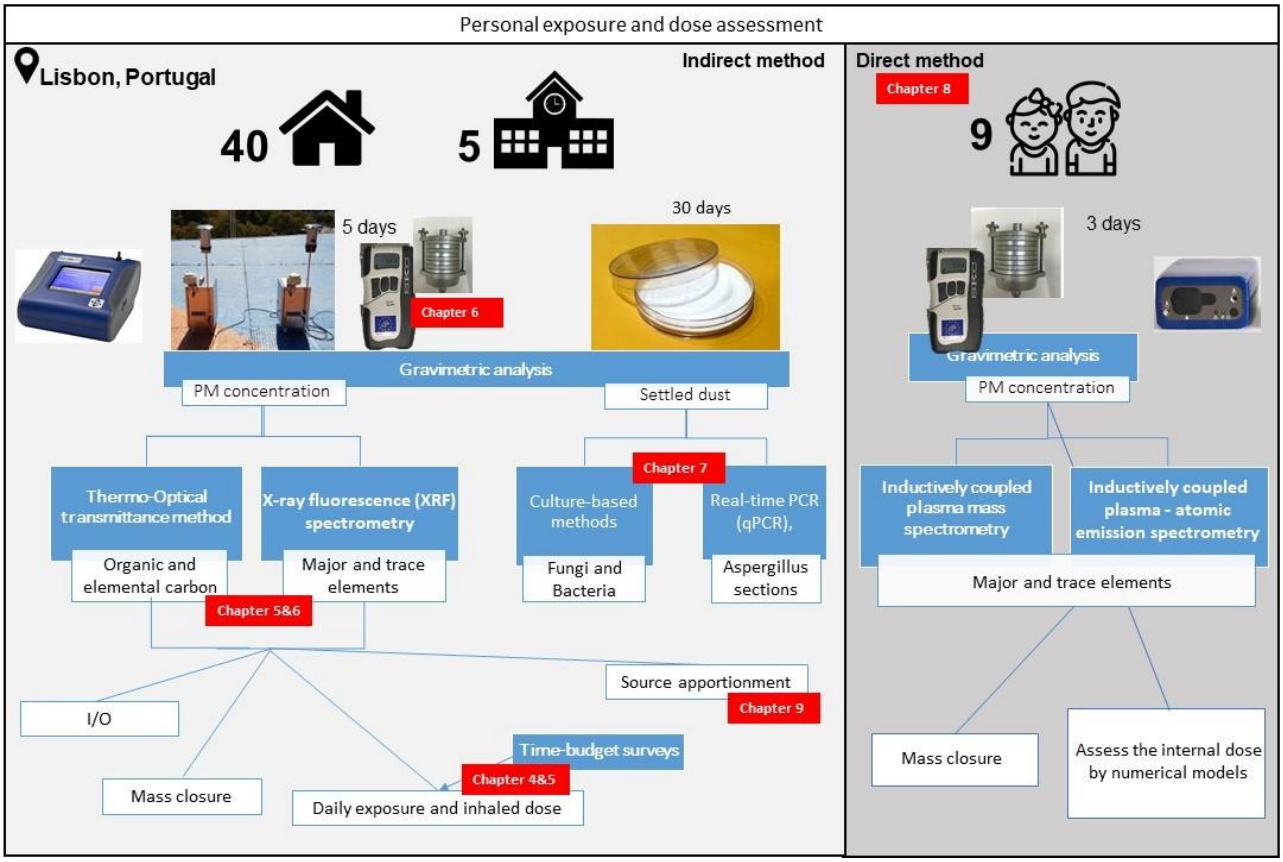

Figure 3.1 - Personal exposure and dose assessment methodology

3.1 Study design

3.1.1 Studied area

This study was carried out in Lisbon, which is the capital and largest city in Portugal. The city of Lisbon has 24 parishes, covering a total area of 100 km^2, with the city centre made up of seven hills. Lisbon is located in the west of the Iberian Peninsula, on the coast of the Atlantic Ocean, at the mouth of the Tagus

River that flows into the Atlantic. Lisbon is surrounded by the Tagus river (south and east), the Monsanto forest park (west), and neighbouring municipalities (north and northwest).

According to the 2021 census, the metropolitan area of Lisbon with 3,015 km^2 has about 2.9 million inhabitants, which represents around 28% of the country's population. More specifically, the municipality of Lisbon is the most populous city in Portugal, with about 545,923 inhabitants, of which 71,245 are children between 0 and 14 years old (INE, 2022).

The climate in the region is Mediterranean, mild, influenced by the Gulf Stream. Average temperatures range between 16 and 35°C in summer (hot and dry), and between 8 and 18°C in winter (wet and cold).

The main source of air pollutants in the city is road traffic (CCDR-LVT, 2020). However, since Lisbon is located along the Tagus River/Atlantic Ocean and has a dominant western wind regime, the marine aerosol presents a significant contribution to the air quality of the city (Almeida et al., 2013). In addition to this natural source, the air mass transport phenomena from North Africa contributes significantly to the load of atmospheric mineral dust (Almeida et al., 2008).

Furthermore, Lisbon has an important cruise port and the principal airport of the country. In 2017, the cruise port was considered the ninth European port with the highest emission of PM from cruise ships (Transport & Environment, 2019). Regarding the airport of Lisbon, a study carried out in 2019 concluded that people who work or live in its vicinity (up to about 1.5 km) are exposed to high values of ultrafine particles (Lopes et al., 2019).

In adverse weather conditions, low dispersion conditions, and thermal inversions, especially in winter, high concentrations of air pollutants can be registered in Lisbon (Alves et al., 2010).

3.2 Time activity pattern survey

A self-report questionnaire on time-activity patterns was developed to identify the different MEs attended by children during the week/weekend and to quantify the time spent on each one of them. The questionnaire included 17 indoor and outdoor MEs and the time was divided into 30-minute intervals (Annexe II).

The questionnaire was applied in 26 primary schools in the city of Lisbon, to 6096 children (5-10 years old), residing in Lisbon. 1251 questionnaires were returned, but only 1189 were correctly filled out, representing a 20% response rate. The survey was carried out between October 2016 and June 2017.

To increase the interest of the school community and the response rate, the awareness campaign "The air belongs to everyone" was put in practice. This campaign was designed for students (5-9 years) and aimed to make the school community aware of the problem of air quality. Sixty awareness sessions were made.

Of the total number of children who answered the questionnaire correctly, 54% were female and 46% were male. About 6% of the children were 5 years old, 14% were 6 years old, 22% were 7 years old, 21% were 8 years old, 24% were 9 years old and 13% were 10 years old.

3.3 Sampling campaigns

3.3.1 Indirect method

The particulate matter was sampled in five schools, forty houses, and their respective outdoors located in Lisbon from September 2017 to October 2018. The five primary schools (first to the fourth year of schooling) were public, used natural ventilation, and were located in different parishes of the municipality of Lisbon.

All schools were monitored for five days - Monday to Friday and during school hours (about 8 hours a day, depending on the school). The locations chosen in each school for sampling were a classroom with classes in progress (indoor) and the school's courtyard/playground (outdoor environment).

The residences selected fulfil three requirements: i) being in Lisbon, ii) having a balcony with space for equipment, and iii) having at least one child between five and ten years old. All homes were monitored for five days - four days a week and one day at the weekend, always during the occupation period, that is, 15 hours a week (from 6:00 pm to 9:00 am) and 24 hours at the weekend (9:00 am on Saturday to 9:00 am on Sunday). The indoor sampling was carried out in the living room and the outdoor one was carried out on the balcony. In both MEs, sampling took place in parallel, with samplers in the indoor and outdoor environment working for the same time.

The occupants of the studied MEs performed their regular activities to ensure that the measurements reflected real-life conditions. In addition, residents of the houses filled out a diary to record the activities performed over the time they were at home, also indicating the start and end times of each activity. Teachers were asked to record the number of students present in the room, the main activities carried out, as well as the ventilation conditions in force during the day.

The location of the samplers was chosen in order to meet the conditions for an undisturbed measurement and to minimise inconvenience for the participants.

Three different types of equipment were used to collect PM in these MEs:

- Medium volume particulate matter sampler

Four medium volume samplers (MVS6, Leckel, Sven Leckel, Germany) were used simultaneously to collect PM2.5 and PM2.5-10 in filters (Figure 3.2), at a flow rate of 2.3 m^3/h, which were used for subsequent gravimetric analysis and chemical characterisation (Chapter 4, 5, 7 and 9).

The MVS6 collected particles in sampling filters in accordance with EN 123414. A vacuum pump pulled the air and the sampler fractionated airborne particles in a sampling inlet. The air containing the desired fraction of particulates passed through the filters, where the particles were collected.

For the simultaneous collection of PM2.5 and PM2.5-10 in only one equipment, a new sampling head was designed and developed by the Institute of Nuclear and Radiological Sciences and Technology, Energy and Safety, NCSR Demokritos.

At each site, one sampler collected PM2.5-10 and PM2.5 on 25 mm and 47 mm quartz fibre filters (Pall), respectively. The other sampler collected PM2.5-10 on 25 mm Nuclepore filters (Whatman) with a pore size of 0.4 μm and PM2.5 on PTFE filters of 47 mm (Whatman) with a pore size of 2 μm. All sampled filters were weighed on a microbalance (Sartorius R160P, Greifensee, Switzerland) before and after sampling to determine the mass concentration of PM2.5 and PM2.5-10. Before weighing, all filters were preconditioned at constant temperature and relative humidity for at least 24 hours.

Figure 3.2 - Medium-Volume sampler Leckel MVS6 outside and inside a school

- Aerosol Monitor for continuous PM measurements

DustTrak is a laser light scattering photometer (DustTrak, Model 8533, TSI Inc., USA) that was used to perform continuous PM measurements in homes and classrooms (24 h/day, with 1-minute resolution) to identify the contribution of the different daily activities to the concentration of the PM in classrooms and living-rooms (Chapter 4). DustTrak measured the mass concentration of PM1, PM2.5, PM10, and total suspended particle (TSP) fractions (Figure 3.3). The concentrations of PM2.5 and PM10 provided by the DustTrak monitor were corrected with *in situ* and simultaneous gravimetric samples. To assess the daily PM pattern, seven homes and three schools were selected. Occupied and unoccupied periods were considered in this analysis.

Figure 3.3 - DustTrak DRX Aerosol Monitor 8533 in a living room

- Personal Cascade Impactor Sampler

Three Personal Sioutas Five-Stage Cascade Impactor Samplers (PCIS, SKC Inc.) connected to a SKC Leland Legacy pump (Figure 3.4), operating at 9.0 L/min, were placed inside (2) and outside (1) classrooms and homes to obtain size distributed PM concentrations and composition, which was essential to understand the main factors affecting the PM levels in the MEs and quantify the doses (Chapter 6).

The PCIS is a cascade impactor consisting of five impaction stages followed by a filter. Particles larger than a stage's cut-off size cross the airflow lines and are collected on the filter. The finer particles with less inertia do not cross the flow lines and continue to the subsequent stage where the nozzles are tighter, the air velocity through the nozzles is higher, and the finer particles are collected. This continues through the cascade impactor until smaller particles are collected in the last filter. Particles were separated into the following aerodynamic particle diameter ranges: <0.25; 0.25 to 0.5; 0.5 to 1.0; 1.0 to 2.5.

Particles were collected in PTFE and quartz filters to allow the subsequent determination of elements and carbonaceous species, respectively. In the indoor and outdoor, particles at the <0.25 μm stage were collected on 37 mm diameter polytetrafluoroethylene filters with a pore size of 2.0 μm (PTFE; SKC Inc.). The remaining stages, used 25 mm diameter PTFE filters with 0.5 μm pore size. In the indoor, an additional PCIS was used to sample particles in quartz fibre filters (Whatman).

The flow rate (≈9.0 L/min) was verified at the beginning of each sample using a flowmeter (Bios Defender 510, MesaLabs). The flow was always adjusted to ±0.05 L/min of the desired flow rate.

The collection of particles was carried out during the period of occupation of the MEs. In order to guarantee the gravimetric representativeness of the sample, a cumulative sampling was performed for 5 days. For the evaluation of the particle size distribution, 4 houses and 4 schools were selected.

Figure 3.4 - Personal Cascade Impactor Sampler/SKC Leland Legacy pump in the classroom.

- Bioburden characterisation

In addition to the active measurements of the suspended particulate matter, sampling of settled dust was carried out with electrostatic dust collectors (EDC) in thirty-three homes and four schools to characterise the bioburden (Chapter 7). The EDC is a passive collection device consisting of an electrostatic polypropylene cloth (Figure 3.5). The EDC is placed on an elevated surface where it can capture airborne dust. In contrast to conventional methods (plates with selective culture media), this method allows dilutions to be carried out during the laboratory procedure, avoiding the problem of overloaded plates. The dilution of a single EDC can be applied to a huge variety of media cultures and allows the collection of contamination for a longer time (Badyda et al., 2016; Normand et al., 2009).

Dust was collected for thirty to forty-four days. In homes, EDCs were displayed in the children's living room and bedrooms, and in schools, EDCs were placed in classrooms. Each EDC was weighed before and after sampling to determine the mass of collected dust.

Figure 3.5 - Electrostatic dust collector.

- Measurements in transports

Transport measurements - car, metro, and bus - were taken on a pre-defined route, passing through the city centre of Lisbon (Chapter 4). The route starting in Telheiras and ending in Praça dos Restauradores travels 6700 meters. This route was chosen because is representative of the daily commutes of the citizens.

Measurements were performed five times a day (8:00 am, 10:30 am, 1:00 pm, 6:00 pm, and 8:00 pm) in 21 weekdays from June to October 2018. A more detailed description of these measurements can be found in the study performed by Correia et al. (2020).

Due to the characteristics of these MEs, personal environmental monitors were used to sample PM2.5 (PEM for PM2.5 No. 761-203B, SKC Inc., USA) and PM10 (PEM for PM10 No. 761-200B, SKC Inc., USA). The PEMs were connected to an air suction pump (Leland Legacy, SKC Inc., USA), whose flow (10 L/min) was checked at the beginning of each sampling period with a DryCal primary flowmeter (Bios Defender 510, MesaLabs, USA). In each PEM, the PM was collected on 37 mm diameter polytetrafluoroethylene (PTFE) filters, with each filter being used for a whole day of measurements (Figure 3.6). Before and after sampling filters were weighted to determine the PM2.5 and PM10 concentrations.

Figure 3.6 - Personal Cascade Impactor Sampler in metro and car sampling.

3.3.2 Direct method

Nine children that live and study in the metropolitan area of Lisbon were selected for personal sampling. Sampling took place for three days per child (72 uninterrupted hours) between May and June. 2018.

Each child carried the five-stage Sioutas Cascade Impactor SKC (described before) with an air intake tube placed in the breathing zone, to obtain the particle size distribution information, which was used to assess the dose through the use of a dosimetry model (Chapter 8).

At the same time, the children carried with them a MicroAeth AE51 model aethalometer (AethLabs, USA) to assess real-time black carbon (BC) mass concentrations. The pump flow rate was adjusted to 100

mL/min and the data was recorded every 60 s. This instrument collected air through a 3 mm diameter filter, where the particles were trapped. Optical transmission by a stabilised 880 nm LED light source through this point was measured by a photodiode detector. With the gradual accumulation of particles, the light at this point was attenuated (absorbance) progressively, being measured every 60 seconds compared to an adjacent portion of the filter (considered reference). These measurements were stored and converted to BC mass concentration expressed in ng/m^3. The data obtained was corrected using the "Optimised Noise-Reduction" software to reduce signal noise.

Children carried the trolley with them throughout the day while performing their regular activities (Figure 3.7). However, children were allowed to place the trolley aside but close to them while playing sports, bathing or sleeping to avoid discomfort and to protect instruments from moisture and vibration.

Figure 3.7 - Child carrying the trolley with the MicroAeth AE51 and the Personal Cascade Impactor Sampler/SKC Leland Legacy pump.

3.4 Chemical analysis

3.4.1 Indirect method

- Major and trace elements

PM2.5-10 and PM2.5 samples collected in the MEs 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 (Chapter 5, 6 and 9). The analysis was performed using an Energy Dispersive X-ray Spectrometer (ED-XRF) Laboratory Instrument (Epsilon

5, PANalytical, the Netherlands). This instrument, with Cartesian geometry, offers very efficient sample excitation. The recorded spectrum contains not only the sample spectrum but also a large amount of the scattered X-ray tube spectrum. With Cartesian geometry, the X-ray tube spectrum is eliminated by polarisation. The resultant reduction in the spectral background makes it possible for much lower detection limits to be achieved. The use of different polarising targets (secondary targets), placed along the first axis of the optical path employing a three-dimensional geometry, offers further analytical advantages. Whereas some target materials merely scatter the X-ray tube irradiation of the sample, other materials fluoresce, yielding intense, almost monochromatic X-rays that irradiate the sample. By using targets of different materials, it is possible to optimise the excitation source specifically for elements of interest. The instrument was calibrated for aerosol filters by utilising 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 3.1.

Table 3.1 - Detection limits (in ng/m^3) for all elements measured by XRF.

Element	**Detection limit (ng/m^3)**	**Element**	**Detection limit (ng/m^3)**
Al	5.1	Mn	0.6
As	0.8	Na	10.3
Ba	2.1	Ni	0.4
Br	1	Pb	0.6
Ca	1.2	S	1.6
Cl	0.6	Sb	2
Cr	0.2	Si	10.3
Cu	0.2	Sr	0.8
Fe	0.6	Ti	0.6
K	0.4	V	0.4
Mg	3.1	Zn	0.6

- Organic and elemental carbon

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 (Chapter 5, 6 and 9). A punch of 1x1.5 cm was cut from all quartz filters for the analysis and was placed in a quartz oven. 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 EUSAAR2 thermal protocol

(Cavalli and Putaud, 2008), consists of 4 temperature steps in the He atmosphere and 4 temperature steps in the He/O_2 atmosphere. The limit of detection was 0.02 $\mu g/m^3$. 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 characterisation methodology is detailed in Manousakas et al. (2018) and Popovicheva et al. (2019).

- Bioburden characterisation

Settled dust collected by the EDCs was analysed by culture-based methods and using real-time Polymerase chain reaction (qPCR), targeting 4 different *Aspergillus* sections (*Flavi, Fumigati, Circumdati,* and *Nidulantes*) (Chapter 7). The target fungi were selected based on the classification as indicators of harmful fungal contamination. EDC samples were subjected to extraction and bioburden characterisation by culture-based methods. Each EDC was washed and 0.15 mL seeded onto 2% malt extract agar (MEA) with 0.05 g/L chloramphenicol media and dichloran glycerol (DG18) agar-based media for yeasts and moulds assessment, tryptic soy agar (TSA) with 0.2% nystatin for total bacteria assessment, violet red bile agar (VRBA) for Gram-negative bacteria. Incubation of MEA and DG18 plates at 27 °C for 5 to 7 days and TSA and VRBA plates at 30 and 35 °C for 7 days, respectively, was performed.

Samples were also spread (0.15 mL) onto Sabouraud dextrose agar (SDA) media supplemented with 4 mg/L itraconazole (ITR), 1 mg/L voriconazole (VOR), or 0.5 mg/L posaconazole for the screening of antifungal resistance.

Molecular identification of the different fungal species/strains was achieved by qPCR using the CFX-Connect PCR System (Bio-Rad, Hercules, CA, USA). Reactions included 1x iQ Supermix (Bio-Rad), 0.5 µM of each primer, and 0.375 µM of TaqMan probe in a total volume of 20 µL. Amplification followed a three-step PCR: 50 cycles with denaturation at 95 °C for 30 s, annealing at 52 °C for 30 s, and extension at 72 °C for 30 s (Table 1). Nontemplate control was used in every PCR reaction. For each gene that was amplified, a nontemplate control and positive control were used, consisting of DNA obtained from a reference that belonged to the culture collection of the Reference Unit for Parasitic and Fungal Infections, Department of Infectious Diseases of the National Institute of Health, from Dr. Ricardo Jorge. These strains have been sequenced for ITS B-tubulin and Calmodulin.

3.4.2 Direct method

- Major and trace elements

The samples were analysed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS from THERMO, X Series II) and g (ICP-AES from THERMO, IRIS Advantage TJA Solutions) to determine

major (Al, Ca, Fe, K, Mg, Na, P, S) and trace elements (Li, B, Ti, V, Mn, Ni, Cu, Zn, Ga, As, Rb, Sr, Y, Zr, Nb, Mo, Cd, Sn, Sb, Ba, La, Ce, Nd, Pb, Bi, Th, among others, respectively (Chapter 8). Each filter was subjected to acid digestion (1.25 mL HNO_3: 2.5 mL HF: 1.25 mL $HClO_4$). For every batch of acid digested samples, the corresponding blanks followed the same analytical procedures. Three multi-elemental solutions Spec® 1 (rare earth elements, REE), Spec® 2 (alkalis, earth alkalis, and metals), and Spec® 4 (Nb) were used to elaborate external calibration curves. The detection limits were close to 0.005 μg m^{-3} for major elements and 0.05 ng m^{-3} for most trace elements. Repeated measurements were performed with quality control standard solutions and a standard reference material (SRM 1633b, fly ash). Additionally, a multi standard composed of the same elements was introduced in each batch of samples to check the accuracy of measurements. The methodology enabled quantification with relative errors < 5% for most elements and around 10% for Al and Na.

3.5 Quality assurance and control (QA&C)

The calibration and intercomparison of the different equipment used during the sampling campaign were carried out.

- QA&C – Medium volume PM samplers

Measurements in both outdoor and indoor were performed to test the samplers and the new Leckels' sampling inlets developed by NCSR Demokritos. These sampling inlets were compared with the commercial (reference) inlets to ensure the quality of the data obtained. The intercomparison results showed that the use of the new sampling inlets yields equivalent results to those obtained by the use of commercial inlets (mentioned as reference Leckel in Figure 3.10), as results are within the expected uncertainty. A good correlation was obtained in the intercomparison study (R^2=0.86 – 0.97, see Figure 3.10). Occasional outliers were flagged and removed from the statistical analysis (red points). With the development of the sampling inlets, the sampling campaigns were less intrusive in home and school environments, as the use of a single instrument for both PM2.5-10 and PM2.5 sampling allowed a significant reduction in noise emission and in the use of space. Moreover, all efforts were done to minimise artefacts and contamination in the samples. It must be noted that several variables independent of the sampling inlet may affect the results, including variability in the sampled aerosol and weighting and handling of filters.

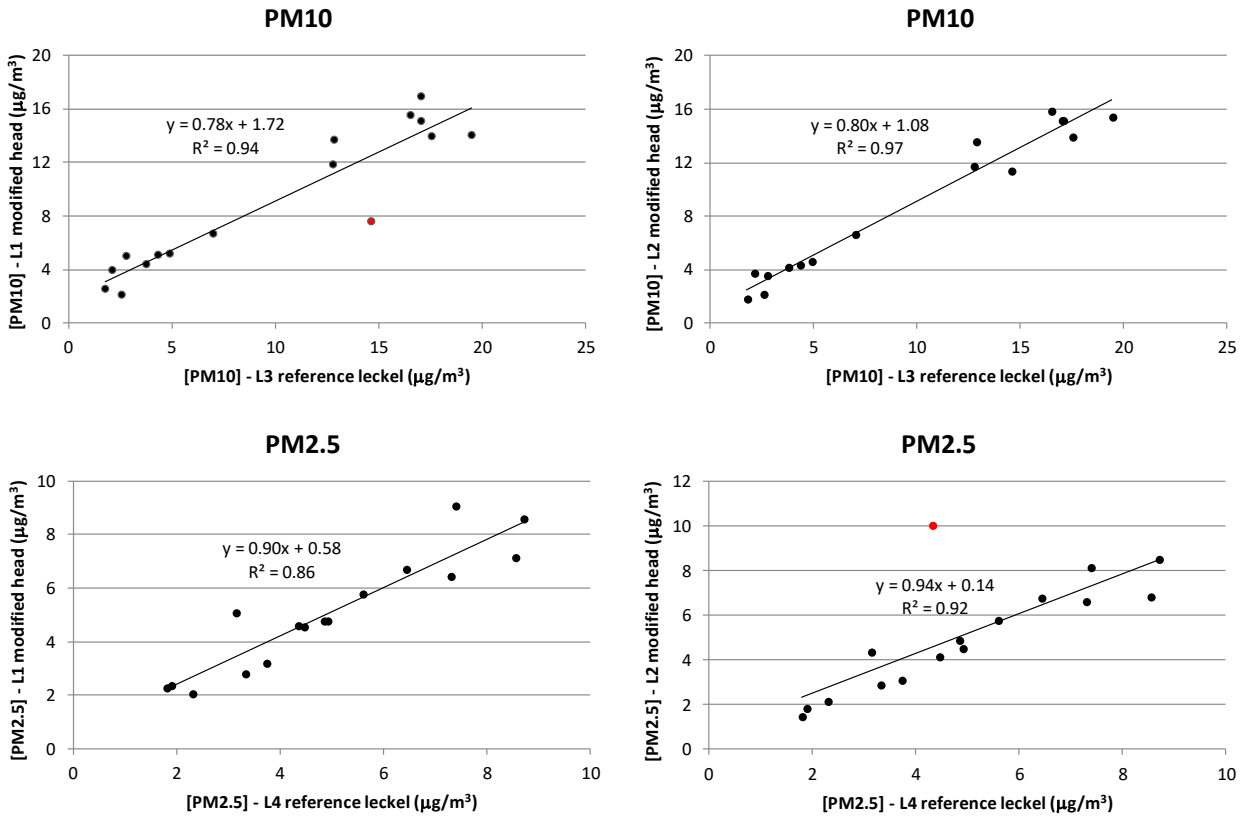

Figure 3.8 - Results of the inter-comparison study with the sampling heads

- QA&C – DustTrak

As the DustTrak does not provide actual gravimetric mass, the PM2.5 and PM10 readings provided by the real time monitor were corrected against the *in situ* and simultaneous gravimetric PM2.5 and PM10 measurements, respectively. The Leckel sampler that was used to collect the filters for the gravimetric analysis is certified by the European Committee for Standardisation as a reference sampler for PM10 and PM2.5 measurements according to CEN EN 12341 and CEN EN 14907. Figure 3.11 displays the comparison of PM2.5 and PM10 concentrations measured with the DustTrak and those determined gravimetrically in the homes and schools. A good correlation was obtained in the intercomparison between the DustTrak and Leckel data (R^2=0.80 – 0.92). The DustTrak PM10 and PM2.5 concentrations were corrected based on the linear regression equations shown in Figure 3.11.

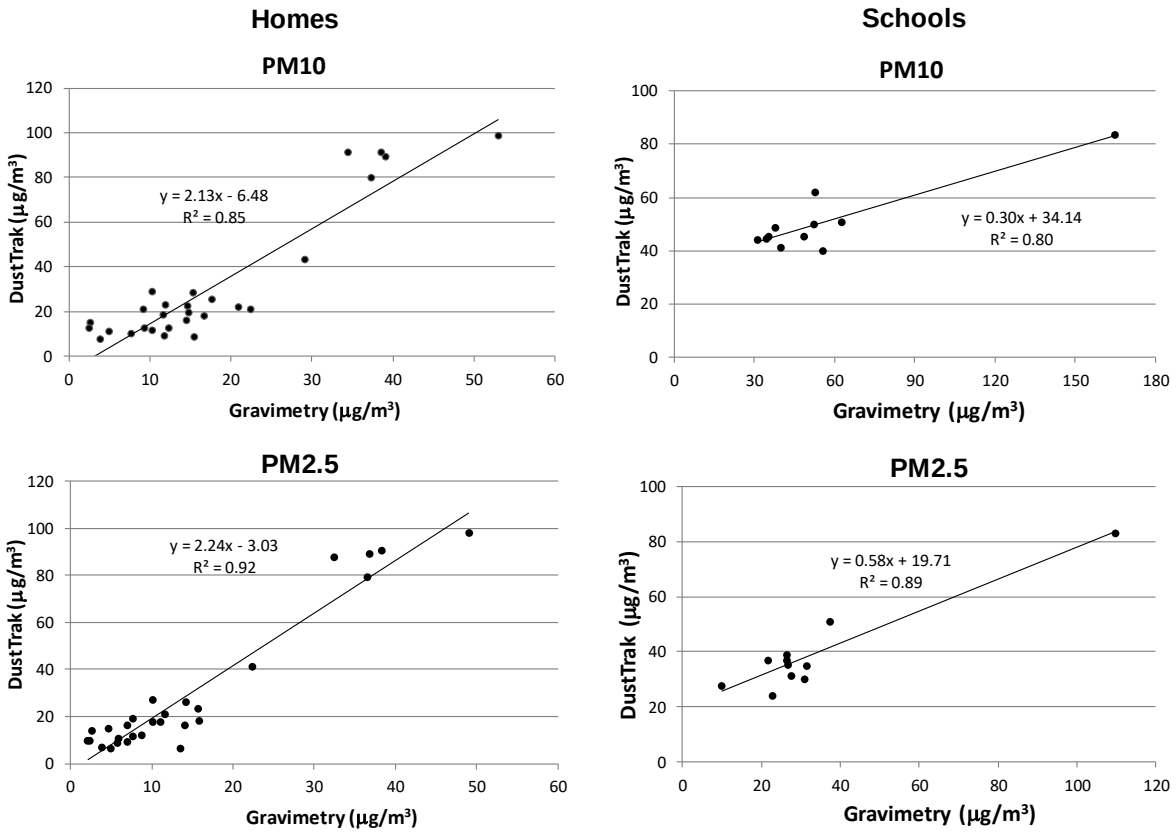

Figure 3.9 - PM concentrations (µg/m^3) measured with the DustTrak vs. those determined gravimetrically in the homes and schools

3.6 Data processing

3.6.1 Children's exposure and dose assessment

The children's daily exposure was estimated using the indirect method, by integrating the temporal activity data with the average concentrations measured in each ME (Chapter 4 and 5), according to equations in Table 3.2.

Table 3.2 - 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)	$\frac{\sum_{j=1}^{m} C_j . t_j}{\sum_{j=1}^{m} t_j}$	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)	$\sum_{j=1}^{m} (C_j . t_j . IR_j)$	
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 (%)	$\frac{C_a \times t_a \times IR_a}{\sum_{j=1}^{m} C_j \times t_j \times IR_j} \times 100$	

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 (Chapter 4 and 5). The IRs used for the different activities were based on the study performed by Buonanno et al. (2011) and are displayed in Table 3.3.

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

Table 3.3 - Inhalation rate (m^3/h) for the 6-10 age group as a function of the activity performed (Buonanno et al., 2011)

Activity	IR (m^3/h) for 6-10 age group
Sleeping and rest	0.31
Studying and sedentary activities	0.42
Walking (not along a road)	0.58
Physical activity indoor and playing outdoor	1.27
Physical activity outdoor	1.44
Commuting - walking	0.91
Commuting – public and private vehicles	0.58

3.6.2 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 to better understand the chemical composition and aerosol type sampled in the different MEs (Chapter 5 and 8). The sum of the chemical species in the aerosol with values lower than the total mass concentration indicates the existence of unidentified mass (UM). Adjustments were made in the application of the mass closure between the direct method and the indirect method, due to the availability of measured elements, as can be seen in the respective chapters. The contribution of each aerosol type was calculated according to the equations presented in Table 3.4.

POM was calculated by multiplying OC by a factor of 1.6. This factor is consensual for outdoor urban background locations (Wu et al., 2017; 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 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 with the trace elements group (Calvo et al., 2013). EC and $nssSO_4^{2-}$ were considered separately from any group.

Table 3.4 - Equations used in the mass closure assessment for indirect method and replicated with adjustments for the direct method.

	Equations	**Where**
POM	1.6 x [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 x Mn + 1.12 x Ba + 1.18 x 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-} - $ssSO4^{2-}$	

3.6.3 Transport and deposition in the respiratory tract

A mechanistic numerical model based on a Eulerian approach that describes aerosol dynamics was employed to determine particle deposition in the HRT of the children as a whole and in its regions: the extrathoracic (ET) and the main thoracic regions, i.e., the bronchial (BB), the bronchiolar (bb) and the alveolar-interstitial (AI) (Chapter 8). The model predicted the temporal variation of particle concentration and the regional deposition of the inhaled particles during a breathing cycle by solving the aerosol general dynamic equation (GDE), taking into account breathing dynamics:

$$\overbrace{\frac{\partial}{\partial t}(A_t\, n_i)}^{\text{temporal variation}} = \overbrace{-\frac{\partial}{\partial x}(A_A\, u\, n_i)}^{\text{convection}} + \overbrace{\frac{\partial}{\partial x}\left(A_t\, D_i\, \frac{\partial n_i}{\partial x}\right)}^{\text{diffusion}} - \overbrace{U_{d_i}\, \Gamma\, n_i}^{\text{deposition}} + \overbrace{\left(\frac{\partial}{\partial t}(A_t\, n_i)\right)_{\text{growth}}}^{\text{condensation}} + \overbrace{\left(\frac{\partial}{\partial t}(A_t\, n_i)\right)_{\text{coagulation}}}^{\text{coagulation}}$$

where t is the time, n_i the particle number concentration in section i of the size distribution, u the fluid velocity, D_i the diffusion coefficient of particles with size i, A_i and A_A the time dependent and constant cross-section of all air ducts, respectively, at distance x from the respiratory system entrance, Γ the circumference of air ducts and U_{di} the particle deposition velocity. The GDE is considered in a one-dimensional form and describes the different external (convection, axial diffusion, deposition) and internal (growth, coagulation) processes acting simultaneously on the inhaled particle population. The description of the above deposition mechanisms is based on standard theory for the respective aerosol processes. The thoracic region of the respiratory tract is described with the help of the classical morphometric model “A” by Weibel (Weibel, 1963). The volume of the alveolated section of the lung is left to vary with time to accommodate effects due to breathing dynamics. A simplified morphological scheme that consists of sequential cylindrical airways describes the extrathoracic region through the mouth pathway. The air velocity along the airways of the respiratory tract is determined by solving the equation of continuity.

A detailed description of the model, its validation against experimental data, as well as its application potential have already been published (Almeida-Silva et al., 2018; Mitsakou et al., 2007, 2005; Pilou, 2020; Pilou et al., 2015).

3.6.4 Source identification and quantification

Source apportionment was implemented through the multilinear engine-2 (ME-2) solver and controlled via SoFi (Source Finder), which allows for a comprehensive and systematic PMF analysis (Canonaco et al., 2013) (Chapter 9).

Source apportionment of PM was performed by receptor modelling that is based on the mass conservation principle:

$$xij = \sum gikfik + eij \; i = 1, 2, \ldots m \; j = 1, 2, \ldots . n \; p \; k=1$$

where xij is the concentration of the species j in the $i\ th$ sample, gik is the contribution of the $k\ th$ source in the $i\ th$ sample, fik is the concentration of the species j in the source k, and eij is the uncertainty of each individual measurement result.

Data below the limit of detection (LOD) were substituted by half of the LOD and the uncertainties were set to 5/6 of the LOD. Missing data were substituted by the geometric mean of the measured concentrations and the corresponding uncertainties were set as 4 times these geometric mean (A. Polissar et al., 2001).

Chemical species with high noise were down-weighted based on their signal-to-noise (S/N) ratio to reduce the influence of poor variables on the analysis. Species with S/N lower than 0.5 were considered as bad variables and excluded from the analysis, and species with S/N between 0.5 and 1 were defined as weak variables and down-weighted by increasing the uncertainty.

ME-2 (Paatero, 1999) allows exploring the rotational space around the base solution by introducing limits into the PMF model for deviation from predetermined values for gik and/or fkj for one or more factors. This approach is referred to as constraining. In the current study a constraining technique that is called a-value approach in used. In this approach one or more output factor profiles are required to be within predefined limits of a reference profile, with the tightness of constraint defined by the scalar a ($0 \leq a \leq 1$). The scalar a defined the degree of freedom (a=0 means 0% allowed deviation from the anchor profile, and a=1 means 100% allowed deviation).

For identifying the indoor and outdoor sources, four different datasets were used: PM2.5 indoor and outdoor combining data from schools and houses in each case, as wells as PM10 indoor and outdoor combining data from schools and houses in each case. The total number of variables used was 22 (OC, EC,

Na, Al, Si, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Br, Sr, Ba, Pb). To estimate the factor contribution, PM was also used as species in the analysis with a 300% uncertainty assigned.

A novel methodology was used for the identification of indoor and outdoor sources, based on the *a* value approach. First, the outdoor sources for both PM10 and PM2.5 datasets were identified by performing fully unconstrained analysis on the datasets. Then, the factor profiles that were obtained from the analysis of the outdoor data, were used to constrain the indoor data analysis. In particular, the indoor data source apportionment analysis was performed by constraining the outdoor profiles on the indoor runs with an *a* value of 0.2 (all species except PM were constrained), and adding an additional unconstrained source. Since the indoor PM levels are the sum of outdoor contributions plus indoor contributions, by using this approach we were able to successfully characterize the influence of the outdoor sources in the indoors environment, to those that are exclusively indoor. Since, due to infiltration or/and other processes that can take place in an indoor environment, the chemical profiles of the outdoor sources cannot remain unchanged, the *a* value of 0.2 (20% change allowed), provides enough space to the model to adapt the outdoor source profiles to those changes. By following this approach two main goals are achieved: a) the contribution/effect of outdoor sources to the indoor environment are accurately estimated, b) the contribution of exclusively indoor sources is accurately estimated.

A sensitivity analysis was performed to determine the used a value and the number of extra sources indoors in comparison to the outdoor ones. As was stated before an *a* value equal to 0.2 and one extra indoor source provided the optimum results. Including more indoor sources did not lead to extra sources with reasonable source profiles (more OC sources with no other tracers were produced), while increasing the a value did not lead to significant changes in the factor profiles. The small change in the Q values (<1%) before and after the application of the constraints, indicates that the solutions are mathematically equal and the model is not forced to deviate too much from the unconstrained solution.

Three main reasons are the cause of uncertainties in SA analysis: random errors in data values, rotational ambiguity, and modeling errors. Modeling errors are identified by monitoring the residuals of the solution. The residuals were normally distributed, unstructured over time and variables throughout all ranges as suggested by Reff et al. (2007). The rotational ambiguity was investigated using the methodology described in Canonaco et al. (2021). This method is based on a combination of the a value approach (information about the rotational ambiguity) and the classical bootstrapping approach (information about the statistical uncertainty and random errors) (Ulbrich et al., 2009). All mathematical indicators suggest SA solution with low uncertainty. The optimum number of factors was decided by examining the mathematical diagnostics (Q/Qexp, scaled residuals, structure of the residuals, unexplained variation), as well as the physical meaning of the factors.

The contribution of each source for the exposure was calculated by integrating the time-activity data with the contribution of the source in the different MEs, according to the following equation:

$$S = \frac{\sum_{j=1}^{m} S_j . t_j}{\sum_{j=1}^{m} t_j}$$

Where S_j is the source contribution in the ME (j) and t_j is the time spent in the ME (j).

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Chapter 4

Chapter 4 - Children's exposure and dose assessment to particulate matter in Lisbon

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Keywords: Exposure, dose assessment, particulate matter, air quality

Published in: Building and Environment 171, (2020). DOI: 10.1016/j.buildenv.2020.106666

Accepted: 11 January 2020

Journal Impact Factor (2020): 6.90

Citations: 24

Abstract

Exposure to Particulate Matter has been associated with adverse health effects. The main objective of this study is to quantify children's exposure to PM and the respective inhaled dose in Lisbon. For that, a time activity pattern survey was performed with the participation of 1189 children. In addition, PM was sampled inside 5 schools, 40 homes, 4 modes of transportation and in the respective outdoor environments. Time-activity pattern records showed that children spent 86% of their time indoors, especially at home and in the classroom. The PM2.5 and PM10 concentrations in classrooms (35.3 μg/m^3 and 65.4 μg/m^3, respectively) were more than double than in homes (14.5 μg/m^3 and 18.2 μg/m^3, respectively) and highly exceeded the limit values established by the Portuguese legislation for indoor air quality. The high indoor-to-outdoor concentration (I/O) ratios calculated in schools for PM2.5 (1.8) and PM10 (2.1) suggest that a substantial fraction of particles was generated by indoor sources. PM daily patterns for classrooms showed the importance of occupancy, resuspension of dust and cleaning activities for the elevated levels of particles. The average daily children exposure was 20.6 μg/m^3 for PM2.5 and 31.5 μg/m^3 for PM10. During weekdays, the classrooms contributed with 42% and 50% to the PM2.5 and PM10 daily exposure, and with 36% and 41% to the PM2.5 and PM10 inhaled dose, respectively. This work quantitatively demonstrated that indoor microenvironments are the main contributors to personal exposure to PM and respective inhaled dose.

4.1. Introduction

Exposure to Particulate Matter is associated with increased morbidity and mortality (Almeida et al., 2014; Martinelli et al., 2013). PM is usually classified as coarse particles, with aerodynamic diameter between 2.5 and 10 μm (PM2.5-10), and fine particles with aerodynamic diameter smaller than 2.5 μm (PM2.5) (Jakovljevi et al., 2018). The coarse particles can reach the upper respiratory tract (trachea) and come from the processes of abrasion of surfaces, resuspension of industrial dust, roads works, natural sources such as ocean spray and desert dust transport events. The fine particles reach the lower respiratory tract (lungs) and may be originated from combustion processes of products such as gasoline, oil, coal and diesel fuel, as well as from secondary aerosols and high-temperature processes such as smelters and steelworks (Jakovljevi et al., 2018; Wilson et al., 1997). The effects of PM were observed even at low levels of exposure and there is no evidence of a threshold below which no adverse health effects occur (Almeida et al., 2016; Jakovljevi et al., 2018; Lazaridis et al., 2012; World Health Organization, 2013).

People's exposure is usually assessed from the ambient concentrations measured by national air quality networks, assuming that the corresponding monitoring stations are representative of the population exposure across a given city. Nevertheless, this approach fails to account for all components of exposure (Almeida et al., 2016). Firstly, there is a significant variability in the PM concentrations within a city, including hot spots that are often not covered by the air quality networks. Secondly, there is a heterogeneity in the time activity patterns of the different population subgroups. And thirdly, people spend approximately 90% of the time indoors, rendering indoor air quality more relevant for population exposure than ambient concentration levels. This brings us to the considerable importance of assessing the personal integrated exposure to air suspended particles, as it is the key determinant of the dose received by an individual and thus directly influences the health impacts.

Acknowledging the importance of the indoor air quality for the human health, in the last decades, several researchers focused their work on indoor microenvironments, such as schools (Almeida et al., 2011; Canha et al., 2016, 2010), homes (Canha et al., 2018; Simoni et al., 1998), elderly care centers (Almeida-Silva et al., 2016), offices (Faria et al., 2016; Mandin et al., 2017), gymnasiums (Ramos et al., 2015) and transports (Almeida et al., 2012; Martins et al., 2015; Ramos et al., 2016). These studies showed that indoor air quality is affected by outdoor air pollutants that has penetrated indoors but it is also largely influenced by indoor sources. However, few studies evaluated the integrated human exposure to PM, considering all the ME visited daily by the population.

Children are more susceptible to the potential health effects induced by air pollution because their immune, respiratory, central nervous, digestive and reproductive systems are still in development (Burtscher and Schüepp, 2012; WHO, 2005). Moreover, due to their physiology, size and activity level, children inhalation rates are higher than adults. Education is a fundamental part of children's social

development, which means that they spend a significant part of their time in schools (Oliveira et al., 2019). Several studies have reported high particle concentrations in classrooms (Hermann Fromme et al., 2007; Goyal and Khare, 2009; Tippayawong et al., 2009) and have shown that poor air quality has negative impacts on students' health, performance and attention, highlighting the need to study the air quality in the MEs frequented by the children (Canha et al., 2013; Daisey et al., 2003; Haverinen-Shaughnessy et al., 2011; Lin and Zhu, 2018; Mendell and Heath, 2005; Sunyer et al., 2015).

This work was developed in the framework of the LIFE Index-Air project (www.lifeindexair.net) and aims 1) to assess the daily time-activity pattern of children in Lisbon, 2) to evaluate the PM2.5 and PM10 mass concentration in the MEs mostly frequented by them, 3) to study the diurnal variability of PM to assess the impact of the occupancy and emission sources, and 4) to quantify children's daily integrated exposure and dose to PM, reducing the uncertainty in assessing exposure and allowing stronger associations with health outcomes (Rivas et al., 2016).

4.2. Methodology

4.2.1 Studied area

Lisbon is the capital of Portugal and the most populous city in the country (Figure 4.1). Lisbon is located on the right side of the Tagus River. The center of the city consists of seven hills and the western part is occupied by the Forest Park of Monsanto. The climate in Lisbon is mild, Mediterranean, heavily influenced by the Gulf Stream. The summer is generally hot and dry with temperatures ranging from 16°C to 35°C and the winter is typically rainy and cool with average temperatures between 8°C and 18°C. Lisbon has a population of 547733 inhabitants, from which 70494 are children between 0-14 years (INE, 2022). The dominant source of air pollutants in the city is the road traffic (Almeida et al., 2009b). Moreover, Lisbon is highly influenced by the marine aerosols due to its geographic position and the dominant western wind regime (Almeida et al., 2013; Cruz et al., 2015). Furthermore, the city is frequently affected by North African air mass transport, which contributes significantly to the atmospheric mineral dust load (Almeida et al., 2008). Under adverse meteorological conditions, low dispersion conditions and thermic inversions, particularly in the winter, high concentrations of air pollutants can be registered in Lisbon (Alves et al., 2010).

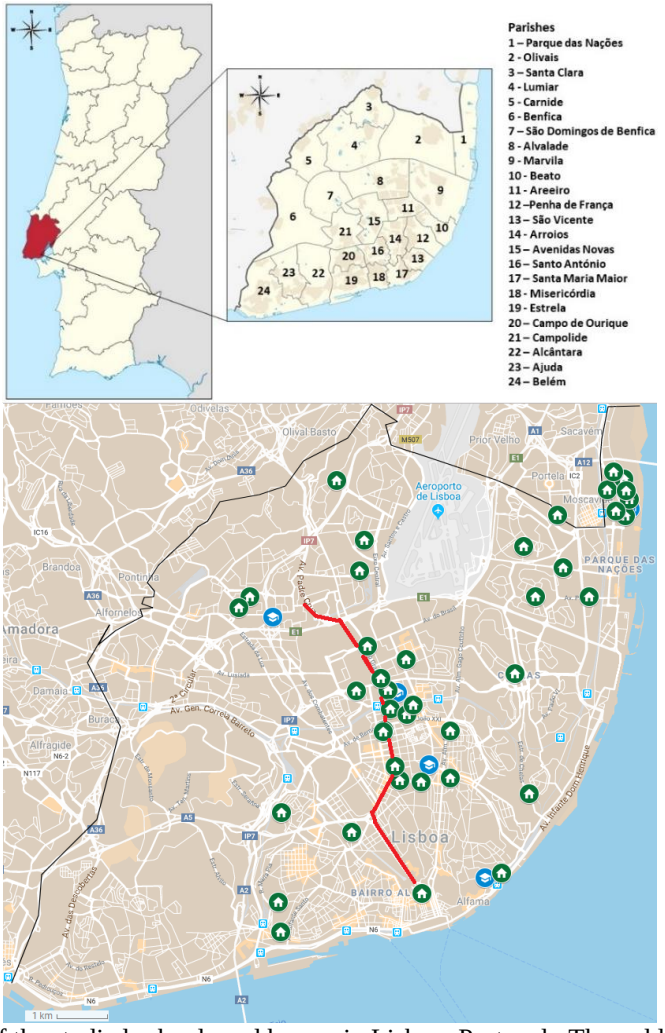


Figure 4.1 – Location of the studied schools and homes in Lisbon, Portugal. The red line represents the route selected for the transport measurements.

4.2.2 Time Activity Pattern Survey

A self-report questionnaire on time-activity patterns was developed to identify the different MEs frequented by the children during the weekday and weekend and to quantify the time spent in each one of them. The questionnaire included 17 indoor and outdoor MEs and the time was divided into intervals of 30 minutes. The questionnaire was applied in 26 schools, to 6096 children (5-10 years old) of both gender, who live in Lisbon. 1251 of the questionnaires were returned, but only 1189 were completed, representing a response rate of 20%. The survey was conducted between October 2016 and June 2017.

4.2.3 Air quality monitoring

PM was sampled in 5 schools and 40 homes located in the city of Lisbon (Figure 4.1), during the period September 2017 - October 2018. In the schools, samples were collected concurrently in the indoor

(classroom) and in the outdoor (playground) MEs. All schools were monitored for 5 days – from Monday to Friday and during the teaching hours (for about 8 hours per day, depending on the school). In the homes, the indoor sampling was performed in the living room while simultaneous measurements were performed in the outdoor (balcony). All homes were monitored for 5 days - 4 days during the week and one day during the weekend, always during the occupied period, i.e. 15 hours during the week (from 18:00 to 9:00) and 24 hours during the weekend (from 9:00 on Saturday to 9:00 on Sunday).

PM samples were conducted using two medium volume samplers (MVS6, Leckel, Sven Leckel, Germany) that worked in parallel in indoor and outdoor of homes and schools. The Leckel samplers were equipped with a new sampling head designed and developed by the Institute of Nuclear and Radiological Sciences and Technology, Energy and Safety, NCSR. Demokritos, for the simultaneous collection of PM2.5 and PM2.5-10 at a constant flow rate of 2.3 m^3/h. The quality assurance and control of the new heads was performed before the sampling campaign. The PM2.5-10 samples were collected onto Nuclepore filters (Whatman) 25 mm in diameter and with 0.4 μm pore size and the PM2.5 were collected in Polytetrafluoroethylene (PTFE) membrane filters (Whatman) 47 mm in diameter and with 2 μm pore size. The gravimetric analysis of the filters was performed pre and post sample collection on a microbalance (Sartorius R160P, Greifensee, Switzerland). Prior to weighing, all filters were preconditioned at a constant temperature and relative humidity (20°C and 50%) for at least 24 hours. PM mass concentrations were determined by dividing filter loads by the volume of air filtered.

Continuous measurements of PM in homes and classrooms (24 h/day, with a 1-minute time resolution) were performed using a light-scattering laser photometer (DustTrak, Model 8533, TSI Inc., USA). This photometer is an optical instrument that simultaneously measures the mass concentration of ambient particles across the PM1, PM2.5, PM10 and total suspended particle fractions. PM2.5 and PM10 concentrations provided by DustTrak monitor were corrected against the in-situ and simultaneous gravimetric samples. For the assessment of the PM daily pattern 7 houses (H1, H2, H3, H4, H9, H11 and H12) and 3 schools (SA, SB and SC) were selected and the periods of non-attendance were also considered in the analysis.

The occupants of the studied MEs performed their regular activities, in order to ensure that the measurements reflected real-life conditions. Furthermore, homes' occupants were requested to complete a diary in order to record the activities they carried out throughout the day, indicating also the start and end times for each activity. Teachers were asked to record the number of pupils in the room, the main activities carried out, as well as the ventilation conditions prevailing during class hours and breaks.

The location of the aerosol instrumentation was chosen as a compromise between meeting conditions for undisturbed measurement and minimizing the annoyance to participants. The aerosol inlets were placed at roughly 1 m above the floor, corresponding to the breathing level of the children.

In addition, PM2.5 and PM10 sampling was carried out in 3 means of transportation, inside cars (3 diesel, 2 gasoline, 1 electric), subway and buses. The measurements were conducted in a route that is representative of the commutes performed by Lisbon citizens. The selected route includes 6.7 km, starting in Telheiras, a residential area, and ending in Praça dos Restauradores located in the city center (Figure 4.1). PM was collected in PTFE filters using a Personal Environmental Monitor (PEM) connected to an air suction pump (SKC Leland Legacy) with a flow rate of 10 L/min. Before and after sampling, filters were weighed with a microbalance using the methodology described above. Details about the methodology used in the different transport modes can be found in Correia et al. (2019).

4.2.4 Children's exposure and dose assessment

Exposure is often confused with concentration, the latter being the most frequently quantified (Morawska et al., 2013). Exposure incorporates the duration of the contact to a certain concentration by integrating over time. Therefore, children's average daily exposure was assessed by integrating the time-activity data with the PM concentrations measured in the different MEs, according to Equation 4.1:

$$E = \frac{\sum_{j=1}^{m} C_j . t_j}{\sum_{j=1}^{m} t_j} \qquad \text{(Equation 4.1)}$$

Where C_j is the PM concentration measured in the ME (j) and t_j is the time spent in the ME (j).

The potential inhaled dose was estimated by multiplying the exposure in each ME by the inhalation rate (IR, m^3/h), as described in Equation 4.2:

$$D = \sum_{j=1}^{m} (C_j . t_j . IR_j) \qquad \text{(Equation 4.2)}$$

The IRs used for the different activities was based on the study performed by Buonanno et al. (2011) and are displayed on Table S4.1, Supplementary material.

The contribution of the different MEs to the daily exposure and daily inhaled dose was calculated by Equations 4.3 and 4.4, respectively (Cunha-Lopes et al., 2019).

$$\text{Daily exposure contribution (\%)} = \frac{C_j \times t_j}{\sum_{j=1}^{m} C_j \times t_j} \qquad \text{(Equation 4.3)}$$

$$\text{Daily inhaled dose contribution (\%)} = \frac{C_j \times t_j \times IR_j}{\sum_{j=1}^{m} C_j \times t_j \times IR_j} \qquad \text{(Equation 4.4)}$$

4.2.5 Statistical analysis

Statistical calculations were performed using the STATISTICA software. Wilcoxon Matched pairs and Mann–Whitney U tests were used. These tests are non-parametric – hence they do not consider any assumptions related to the distribution – and basically are the same in that they compare between two medians to suggest whether both samples come from the same population or not. When the two samples were not entirely independent of each other and had some factor in common, the Wilcoxon Matched pairs test was applied. When the samples were independent Mann–Whitney U test was used. Statistical significance refers to $p < 0.05$.

4.2.6 Quality assurance and control

Leckels head-sampling test: The new sampling heads were tested at the beginning of the experimental campaign, in order to allow for data quality assurance, by comparison with the commercial (reference) heads. The tests were performed in both outdoor and indoor environments. The inter-comparison results showed that the use of the new sampling heads yield equivalent results to those obtained by the use of commercial heads (mentioned as reference Leckel in Figure S4.1, Supplementary material), since deviations were within the expected uncertainty. A good correlation was obtained in the inter-comparison study (R^2=0.86 – 0.97, see Figure S4.1, Supplementary material). Occasional outliers were flagged and removed from the statistical analysis (red points). The deployment of the new sampling heads resulted in sampling campaigns more efficient and less intrusive in the home and school environments, since the use of a single instrument for both PM2.5 and PM2.5-10 sampling allowed significant reduction in the noise emission and space usage.

DustTrak data correction**:** Optical instruments, such as DustTrak, provide good time resolution, fast response signal, excellent signal-to-noise ratio, and simplicity (Moosmüller et al., 2001). However, the calibration process is critical since the response of the DustTrak monitors may vary for different types of measured aerosol (Moosmüller et al., 2001). As the DustTrak does not provide actual gravimetric mass, the PM2.5 and PM10 readings provided by DustTrak monitor were corrected against the in-situ and simultaneous gravimetric PM2.5 and PM10 measurements, respectively. The Leckel sampler that was used to collect the filters for the gravimetric analysis is certified by the European Committee for Standardization as a reference sampler for PM10 and PM2.5 measurements according to CEN EN 12341 and CEN EN 14907. Figure S4.2, Supplementary material displays the comparison of PM2.5 and PM10 concentrations measured with the DustTrak and those determined gravimetrically in the homes and schools. A good correlation was obtained in the inter-comparison between the DustTrak and Leckel data (R^2=0.80 – 0.92). The DustTrak PM10 and PM2.5 concentrations were corrected based on the linear regression equations shown in Figure S4.2, Supplementary material.

4.3. Results and Discussion

4.3.1 Daily time-activity patterns

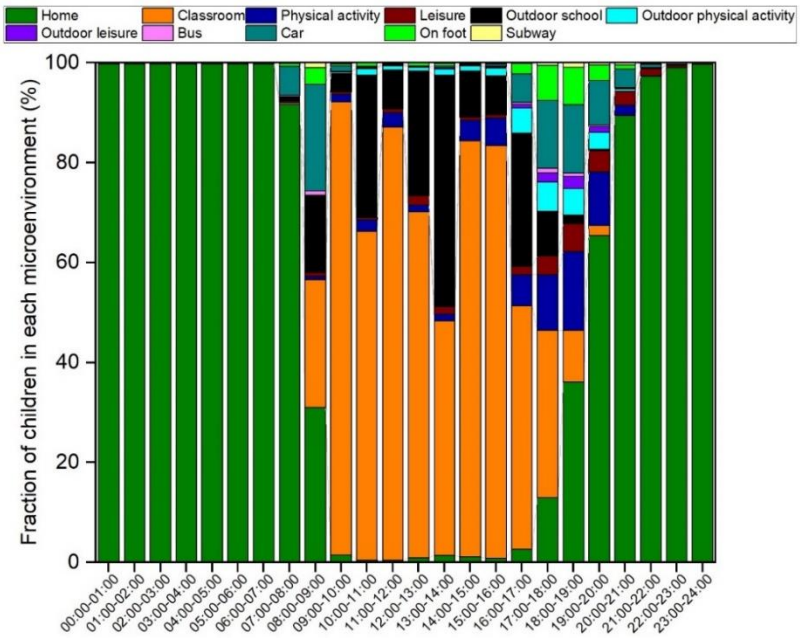
From the 1189 questionnaires received, 52% were answered by females and 45% by males (Table S4.2, Supplementary material). The typical children's time-activity pattern was characterized by a substantial amount of time spent indoor, evidencing that risk assessment should focus on indoor MEs (Table 4.1).

Table 4.1 - Time spent by children on each microenvironment.

	Weekday		Weekend	
	Minutes	%	Minutes	%
Indoor	**1242**	**86.3**	**1251**	**86.9**
Home	800	55.6	1102	76.5
Classroom	387	26.9	10	0.7
School	370	25.7	0	0
Extra-curriculum activities	17	1.2	10	0.7
Physical activity	39	2.7	20	1.4
Gymnasium	25	1.7	11	0.8
Swimming-pool	14	1.0	9	0.6
Leisure	16	1.1	119	8.3
Shop/supermarket	3	0.2	24	1.7
Cinema/theatre	1	0.1	22	1.5
Restaurant/coffee	5	0.4	34	2.4
Other	6	0.4	39	2.7
Outdoor	**147**	**10.3**	**136**	**9.4**
School	109	7.6	2	0.1
Physical activity	17	1.2	23	1.6
Leisure	4	0.3	66	4.6
Garden/park/esplanade	4	0.3	62	4.3
Beach	0	0	4	0.3
Street (on foot)	17	1.2	45	3.1
Transports	**50**	**3.4**	**53**	**3.7**
Bus	2	0.1	0	0
Car	46	3.2	52	3.6
Subway	2	0.1	1	0.1

During the weekday, children spent 86.3% of their time indoors – 55.6% in home and 26.9% in classrooms. Only 10.3% of their time was spent outdoors. 4.6% of the time was spent commuting, either using transports or traveling by foot. The use of private car was the prevalent mode of transportation to and from school (69.1%), whereas public transportation, i.e. bus and subway, were used only by 3.4 and 2.9% of the children, respectively. Most of the children were at home between 19:00 and 8:00 and at school between 8:30 and 16:30 (Figure 4.2). During the weekend, children spent 86.9% of their time indoors, increasing the time spent in home and leisure places, in comparison to the weekdays. The time spent outdoors decreased to 9.4% with respect to weekdays.

(a)



(b)

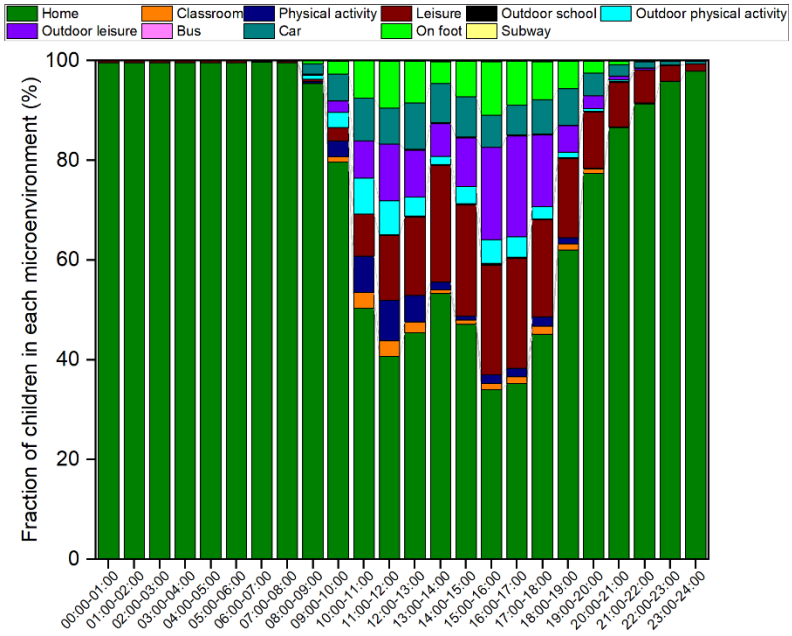


Figure 4.2 - Time activity pattern of children aged between 5 and 10 years old in Lisbon during weekdays (a) and weekend (b).

The results are similar to those found in Matz et al. (2015) in urban Canada, where children aged between 5-11 years were reported to spend about 89% of their time indoors, about 7-8% outdoors and 3-4% in transports. Children's exposure to ambient air pollutants occurs in the different MEs; the levels of exposure depend on the fraction of time that children spend in the various indoor and outdoor MEs, as well as the concentrations of air pollutants in those MEs. To calculate children's exposure and dose, the time-

activity patterns were used together with the average pollutant concentrations obtained in this study for each ME.

4.3.2 PM mass concentration

Table 4.2 presents the gravimetric PM2.5 and PM10 concentrations measured in the indoor and outdoor of 40 homes and 5 schools, as well as, the levels registered inside 3 means of transportation. The spatial distribution of PM2.5 and PM10 concentration levels measured inside and outside the homes and schools is presented in Figure 4.3.

Table 4.2 - Gravimetric PM2.5 and PM10 concentrations (μg/m^3) measured in homes, schools and transports during weekdays and weekends (SD – standard deviation; n – number of samples).

			Weekdays		Weekend	
			PM2.5	**PM10**	**PM2.5**	**PM10**
Homes	**Indoor (n = 192)**	**Mean**	14.5	18.2	14.3	18.6
		SD	12.3	13.3	11.8	12.9
		Min	2.1	2.5	4.2	5.1
		Max	91.9	97.6	66.6	75.5
	Outdoor (n = 194)	**Mean**	13.8	22.4	11.8	19.7
		SD	13.1	14.9	6.3	7.6
		Min	0.8	5.4	3.8	9.7
		Max	138.0	148.8	31.5	43.7
Schools	**Indoor (n = 25)**	**Mean**	35.3	65.4	-	-
		SD	24.9	38.9	-	-
		Min	10.0	22.2	-	-
		Max	112.2	164.5	-	-
	Outdoor (n = 25)	**Mean**	20.9	31.7	-	-
		SD	15.3	15.2	-	-
		Min	1.9	9.9	-	-
		Max	78.3	80.8	-	-
Transports	**Bus (n = 13)**	**Mean**	28.4	39.6	-	-
		SD	5.3	0.3	-	-
		Min	21.0	39.4	-	-
		Max	35.0	39.9	-	-
	Car (n = 32)	**Mean**	33.7	41.5	-	-
		SD	8.6	10.1	-	-
		Min	23.9	30.1	-	-
		Max	52.4	62.4	-	-
	Subway (n = 6)	**Mean**	37.8	84.1	-	-
		SD	20.8	34.0	-	-
		Min	23.1	52.6	-	-
		Max	61.6	120.2	-	-

- Schools

PM2.5 and PM10 average concentrations in the classrooms (35.3 and 65.4 μg/m^3) exceeded the 8-hr limit value established by the Portuguese legislation (Portaria 353-A/2013) for the indoor PM2.5 (25 μg/m^3)

and PM10 (50 μg/m^3). The indoor PM2.5 concentrations in the schools SA (28.7 μg/m^3), SC (52.0 μg/m^3) and SD (52.9 μg/m^3) (representing 60% of the schools) exceeded the PM2.5 limit value (Figure S4.3, Supplementary material). The PM2.5 levels measured outside the schools SA (25.9 μg/m^3) and SC (31.3 μg/m^3) exceeded the WHO 24-hr guideline (25 μg/m^3), which can affect the classroom air quality by indoor penetration of this pollutant.

The indoor PM10 concentrations in the schools SB (51.6 μg/m^3), SC (95.6 μg/m^3) and SD (109 μg/m^3) exceeded the Portuguese indoor PM10 limit value. The highest concentrations were measured in school SD which uses blackboard in chalk and the lowest levels were measured in SA and SE that use whiteboard. Previous studies have already showed the importance of the chalk for the indoor air quality in classrooms (Canha et al., 2014; Fromme et al., 2008; Mohammadyan et al., 2017).

The results obtained in this study were compared with concentrations measured in schools from other cities (Table 4.3). The levels of PM2.5 found at schools in Lisbon were similar than the ones measured in Barcelona (Rivas et al., 2014), Milan (Rovelli et al., 2014) and London (Wheeler et al., 2000) but higher than the concentrations measured in Cassino (Fuoco et al., 2015), Munich (Hermann Fromme et al., 2007), Stockholm (Wichmann et al., 2010) and Prague (Braniš et al., 2005). The PM10 levels measured in Oslo (Simoni et al., 2010), Uppsala (Simoni et al., 2010) and Prague (Braniš et al., 2005) were lower than the ones obtained in Lisbon. In Porto (J. Madureira et al., 2016), Athens (Diapouli et al., 2011) and Silesia (Mainka and Zajusz-Zubek, 2015) and in some Asian cities from India (Chithra and Nagendra, 2014; Habil et al., 2015; Jan et al., 2017), Iran (Mohammadyan et al., 2017), United Arab Emirates (Fadeyi et al., 2014) and China (Liu et al., 2004) higher PM2.5 and PM10 concentrations were registered (ratios Lisbon/other cities between 0.1 and 0.8).

Statistical analysis showed significant similarities between PM2.5 and PM2.5–10 concentrations measured inside ($p = 0.43$), representing an average PM2.5/PM10 ratio around 0.57, while the outdoor PM2.5/PM10 ratio was 0.65. The lower PM2.5/PM10 ratio found inside schools, indicating increased contribution from the coarse fraction, may be related to the resuspension and generation of coarse particles due to the movement and different activities of the children in the classroom.

The PM2.5 and PM10 concentrations were significantly lower ($p<0.05$) outdoors than indoors. The PM2.5 indoor-to-outdoor (I/O) ratio varied from 1.08 to 2.69, with a mean ratio equal to 1.79 and the PM10 I/O ratio ranged between 1.03 and 3.86 with an average of 2.14. A 112 primary school study performed in 22 European countries within the Sinphonie EU project reported PM2.5 I/O ratios ranging from 0.20 to 9.29 with an average of 1.44 (Kalimeri et al., 2019). PM I/O ratios above unity are common for schools due to resuspension of dust within classrooms associated with the students' movement and activities (frequently involving crafting).

Table 4.3 - Indoor average concentrations of PM2.5 and PM10 (μg/m^3) for various schools in world. * Ratio between the concentration of our study and the concentration found in the study to which it is compared.

Location	N. schools	PM2.5 (Our/Other)* μg/m^3	PM10 (Our/Other)* μg/m^3	Source
Stockholm, Sweden	6	8.0 (4.4)	-	(Simoni et al., 2010)
Oslo, Norway	3	-	54 (1.2)	(Simoni et al., 2010)
Uppsala, Sweden	4	-	33 (2)	(Simoni et al., 2010)
Arhus, Denmark	2	-	169 (0.4)	(Simoni et al., 2010)
Milan, Italy	7	33 (1.1)	134 (0.5)	(Rovelli et al., 2014)
Barcelona, Spain	36	37 (1)	-	(Rivas et al., 2014)
Cassino, Italy	3	25 (1.4)	-	(Fuoco et al., 2015)
Athens, Greece	7	82 (0.4)	229 (0.3)	(Diapouli et al., 2011)
Porto, Portugal	73	94 (0.4)	139 (0.5)	(J. Madureira et al., 2016)
London, United kingdom	1	27 (1.3)	79 (0.8)	(Wheeler et al., 2000)
Antwerp, Belgium	27	59 (0.6)	-	(Stranger et al., 2008)
Munich, Germany	64	14 (2.5)	72 (0.9)	(Hermann Fromme et al., 2007)
Prague, Czech Republic	1	22 1.6)	42 (1.6)	(Braniš et al., 2005)
Silesia, Poland	4	101 (0.3)	142 (0.5)	(Mainka and Zajusz-Zubek, 2015)
Pune, India	2	136 (0.3)	264 (0.2)	(Jan et al., 2017)
Agra, India	10	82 (0.4)	265 (0.2)	(Habil et al., 2015)
Chennai, India	2	68 (0.5)	262 (0.2)	(Chithra and Nagendra, 2014)
Malaysia	3	26 (1.4)	34 (1.9)	(Yang Razali et al., 2015)
Sari, Iran	6	47 (0.8)	397 (0.2)	(Mohammadyan et al., 2017)
United Arab Emirates	16	100 (0.4)	448 (0.1)	(Fadeyi et al., 2014)
Korea	34	19 (1.9)	36 (1.8)	(Park et al., 2020)
Beijing, China	7	44 (0.8)	133 (0.5)	(Liu et al., 2004)

- Homes

The concentrations measured inside homes were significantly lower than schools ($p<0.05$) for both size fractions and did not exceed the Portuguese limit values for indoor air quality, except for PM2.5 in homes H6 (31.3 μg/m^3), H12 (38.6 μg/m^3), H22 (68.0 μg/m^3) and H24 (29.3 μg/m^3) (representing 10% of the homes) and for PM10 measured inside home H22 (72.9 μg/m^3) (representing 2.5% of the homes).

The lowest PM2.5 average concentration was measured in home H2 (4.6 μg/m^3), which is located in the residential area of Parque das Nações. The highest PM2.5 concentrations (68.0 μg/m^3) was registered in home H22, which is occupied by a smoker (Figure S4.4, Supplementary material). In addition, measurements at this home were made during a week with rain that did not allow the opening of the windows, further promoting the accumulation of indoor-generated aerosols.

The lowest PM10 indoor average concentrations were measure in home H2 (9.9 μg/m^3) and H29 (9.1 μg/m^3), both located in residential areas of Lisbon with low traffic intensity. The highest PM10 indoor average concentration (72.9 μg/m^3) was registered again in home occupied by the smoker (H22). Langer et al. (2016) measured increased concentrations of PM2.5 and PM10 by a factor of 3 in homes with one or two smokers and by a factor of 7 in homes with three or more smokers. Nasir and Colbeck, (2013) measured, in the winter, PM2.5 and PM10 mean concentrations of 6 μg/m^3 and 13 μg/m^3 in non-smoking homes and of 37 μg/m^3 and 42 μg/m^3 in smoking homes, respectively (Nasir and Colbeck, 2013). Breysse et al. (Breysse et al., 2005) and Stranger et al. (Stranger et al., 2007) reported an increase of 58–130% in indoor PM2.5 mass concentration due to smoking.

The results obtained in this study were compared with concentrations measured in homes from other cities (Table 4.4). The PM2.5 and PM10 concentrations measured in homes from Lisbon were in general lower than the levels found in other cities except in Stockholm (Molnár et al., 2007; Wichmann et al., 2010), Helsinki (Hänninen et al., 2004), Athens (Hänninen et al., 2004), Colorado (Escobedo et al., 2014) and Essex (Nasir and Colbeck, 2013).

The PM2.5/PM10 ratios were always higher indoors (0.77) than outdoors (0.59), evidencing that the PM inside the homes is mainly found in the fine fraction. The calculated ratios in homes are within the typical range of values for developed countries (0.5–0.8) reported by WHO (World Health Organization, 2006).

The outdoor PM2.5 concentrations were lower than those measured in the respective indoor spaces for both weekdays and weekends, although the difference was only significant in the weekend. The PM2.5 I/O ratios ranged between 0.52 and 8.43 with an average of 1.23. The PM2.5 I/O mean ratio for Lisbon was higher than the ratio calculated in studies developed in homes from Hong Kong (0.92-1.09) (Chao and Wong, 2002), Birmingham (1.00) (Jones et al., 2000) and Southern California (1.03) (Geller et al., 2002). The PM10 I/O ratios varied between 0.40 and 3.84 with an average of 0.87. Lower PM10 I/O ratios were also registered by Chao and Wong, (2002) in Hong-Kong, Cattaneo et al. (2011) in Lodi, Italy, (Nasir and Colbeck, 2013) in Essex, UK and in Delhi, India (Khillare et al., 2004). The higher PM2.5 I/O ratios can be attributed to three factors: 1) the indoor particulate generation induced by smoking, cooking and the various human activities; 2) the highest penetration ratios of outdoor-generated fine particles indoors; 3) the low air change rate assisted in keeping the indoor PM accumulating in the indoor environment (Chao and Wong, 2002; Diapouli et al., 2011). The lower I/O ratio registered for PM10 evidenced the protection of the building envelopes against the coarser particles coming from outdoors. The maximum PM2.5 and PM10 I/O ratio was registered in the smoker's home (H22), indicating the dominance of the indoor source, which was most pronounced in the fine fraction. The same behaviour was found by Stranger et al, (2007) in 15 homes from Antwerp.

Table 4.4 - Indoor average concentrations of PM2.5 and PM10 (μg/m^3) for various homes in world. * Ratio between the concentration of our study and the concentration found in the study to which it is compared. **Non smoking house.

Location	N. homes	PM2.5 (Our/Other)* μg/m^3	PM10 (Our/Other)* μg/m^3	Source
Stockholm, Sweden	20	8.0 (1.8)	-	(Molnár et al., 2007)
Stockholm, Sweden	18	8.0 (1.7)	-	(Wichmann et al., 2010)
Helsinki, Finland	170	13 (1.1)	-	(Hänninen et al., 2004)
Athens, Greece	13	11 (1.3)	21 (0.9)	(Stamatelopoulou et al., 2019)
Porto, Portugal	12	89 (0.2)	92 (0.2)	(Joana Madureira et al., 2016a)
Athens, Greece	35	31 (0.5)	-	(Hänninen et al., 2004)
Rome, Italy	18	29 (0.5)	-	(Romagnoli et al., 2016)
Lodi, Italy	60	29 (0.5)	46 (0.4)	(Cattaneo et al., 2011)
Barcelona, Spain	54	24 (0.6)	-	(M.C. Minguillón et al., 2012)
France	567	16 (0.9)	26 (0.7)	(Langer et al., 2016)
London, UK	10	23 (0.6)	50 (0.4)	(Wheeler et al., 2000)
Antwerp, Belgium	15	36 (0.4)	39 (0.5)	(Stranger et al., 2007)
Essex, UK**	5	6.0 (2.4)	13 (1.4)	(Nasir and Colbeck, 2013)
Essex, UK	5	37 (0.4)	42 (0.4)	(Nasir and Colbeck, 2013)
Basel, Switzerland	40	26 (0.5)	-	(Hänninen et al., 2004)
Prague, Czech Republic	47	36 (0.4)	-	(Hänninen et al., 2004)
Agra, India	5	109 (0.1)	181 (0.1)	(Massey et al., 2012)
Delhi, India	1	98 (0.1)	179 (0.1)	(Khillare et al., 2004)
Harbin, China	21	92 (0.2)	112 (0.2)	(Wang et al., 2018)
Hong Kong	34	45 (0.3)	63 (0.3)	(Chao and Wong, 2002)
Bangladesh	174	-	155 (0.1)	(Dasgupta et al., 2006)
Colorado, EUA	30	7.0 (2.0)	-	(Escobedo et al., 2014)
Boston, EUA	4	14 (1.0)	20 (0.9)	(Abt et al., 2000a)
Baltimore, EUA	100	26 (0.5)	38 (0.5)	(Breysse et al., 2005)
South Africa	246	-	64 (0.3)	(Jafta et al., 2017)

The construction characteristics of the homes, the distance from traffic emissions, the existence of green spaces, among others, vary from parish to parish (Figure 4.1), affecting the indoor and outdoor PM concentrations across the city. Results showed that in the parishes of Parque das Nações and Olivais and in the parish of Lumiar the outdoor and indoor PM levels were below the WHO guidelines and the Portuguese limit values for Indoor Air Quality. Home H11 (located in the northernmost point in Figure 4.3) was the only one in Parque das Nações parish that registered PM2.5 outdoor concentrations between 10 and 25 μg/m^3, which may be related to increased traffic emissions due to the proximity of this site to the Vasco da Gama Bridge. The parishes previously described are the ones most recently populated in Lisbon, displaying

thus modern buildings, and ample and green spaces. These areas also display lower traffic density in comparison to the city center. In the city center, PM concentrations, especially PM2.5, increased considerably and results showed that homes located near busy or narrow streets, where increased vehicular traffic emissions and low dispersion conditions are observed, displayed the highest levels of PM. A study from Massey et al. (2012) in North-Central India also registered higher PM concentrations in homes located near heavy traffic roads. Massey et al., 2009 study reported PM10 and PM2.5 indoor concentrations of 247 ± 71 μg/m^3 and 161 ± 62 μg/m^3, respectively in roadside homes, and 181 ± 84 and 109 ± 48 in urban homes.

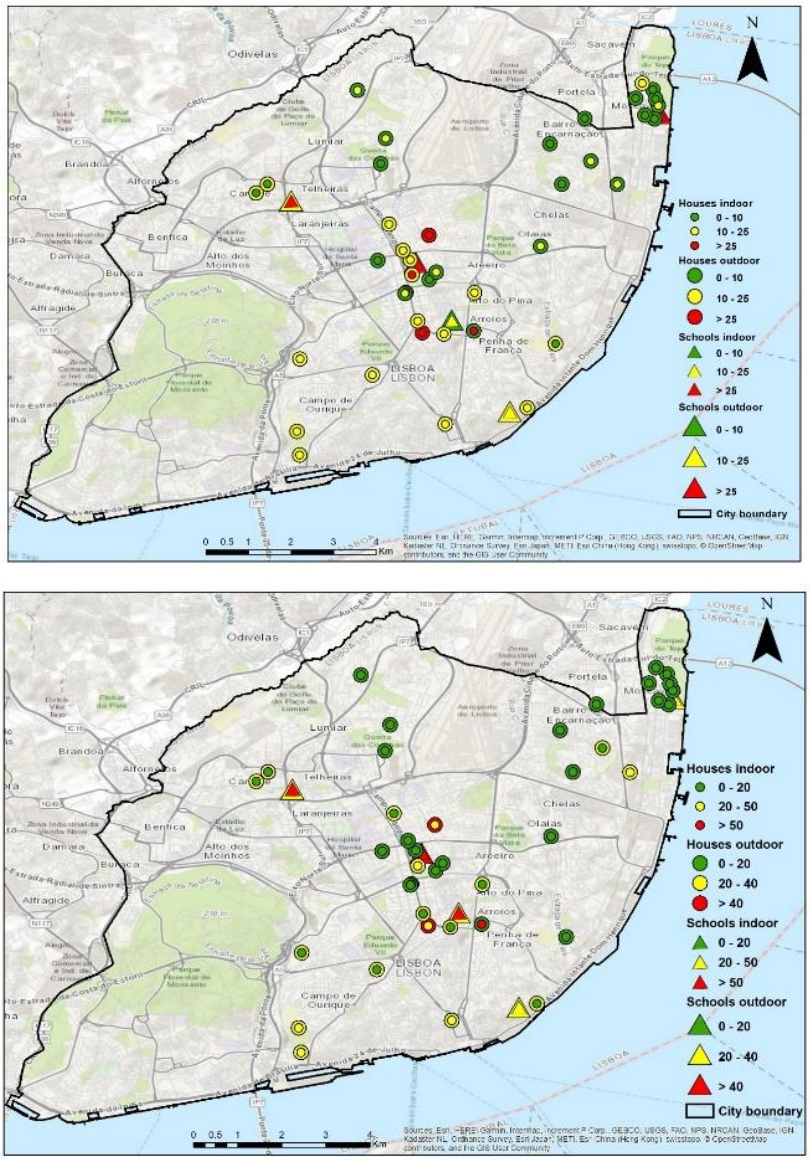


Figure 4.3 - PM2.5 and PM10 concentrations measured inside and outside homes and schools located across the city of Lisbon.

- Transport

Regarding to transport modes, the PM concentrations were higher inside the subway (PM2.5: 37.8 μg/m^3; PM10: 84.1 μg/m^3), followed by car (PM2.5: 33.7 μg/m^3; PM10: 41.5 μg/m^3) and bus (PM2.5: 28.4 μg/m^3; PM10: 39.6 μg/m^3). For all the transport modes, concentrations tended to exceed the PM2.5 guideline established by the WHO. For PM10, the WHO guideline of 50 μg/m^3 was exceeded in the subway. More details about the measurements performed in transports and the respective results are presented in Correia et al. (2019).

4.3.3 Indoor daily patterns

The real-time measurements of PM2.5 and PM10, measured with the DustTrak, provided information on the diurnal variability, as well as impact of the occupancy and emission sources.

The diurnal pattern varied from home to home and from school to school, although there was always a close relationship between the PM concentration and human indoor activities. Therefore, the cases of home H11 and SC are discussed, indicatively. Figure 4.4 shows the mean daily pattern of hourly PM2.5 mass concentrations in home H11 during weekdays (average of 4 days) and weekend (1 day) (a_1 and a_2, respectively) and in school SC during weekdays (average of 5 days) (a_3).

In homes, the daily trends of PM10 and PM2.5 concentrations were very similar. On the weekdays, two increments in the PM2.5 mass concentration occurred during the morning period (Figure 4.4 a_1). The first was associated with the movement and activities of the residents before going to work or school (≈ 08:00 h), depending on the age group. The second was caused by the presence of the housekeeper, between 09:30 and 13:30 h, performing the cleaning activities. In the afternoon, PM2.5 concentrations raised as the residents arrived home (≈ 18:30 h), towards the highest peak of the day at around 20:30 h. These findings are consistent with previous studies that have identified cleaning, cooking, and the movement of people as important contributors to indoor particle concentrations in homes (Bari et al., 2015; Diapouli et al., 2011; Li et al., 2017; Pekey et al., 2010; Secrest et al., 2017). People movement affects indoor air quality due to the resuspension of fine and coarse particles, as pointed out in prior indoor studies (Colbeck et al., 2010; Morawska et al., 2017; Qian et al., 2008; T. Wu et al., 2018).

On the weekend, the variability of the PM2.5 mass concentrations was also linked to the presence of people in the home and to their activities (Figure 4.4 a_2). Thus, the highest concentrations occurred during the occupied periods with activities while the lowest concentrations were measured in the unoccupied and sleeping periods.

In the classroom, there was an increase of PM2.5 concentrations before the beginning of the classes (9:00 h) due to the cleaning of the room, which takes place every day before the first class (Figure 4.4 a_3). Generally, the classroom floor is cleaned by sweeping, which promotes the resuspension of particles

deposited, as also stated by (Colbeck et al., 2010). PM concentrations tended to increase during the class-hours due to the presence of students and the teacher in the room, leading to the generation and resuspension of particles. During school-hours there was a decrease in PM concentrations between 11:30 and 13:30 h, which was attributed to the absence of students from the classroom. This absence relates to physical education classes taking place at the sports hall until 12:30 h in some days of the week, followed by lunch time. The PM2.5 concentrations decreased steeply after the end of the school day and remained at low levels during the non-school hours, clearly demonstrating the impact of school activities on the observed indoor air quality.

Figure 4.4 b) compares the indoor concentrations of PM2.5 and PM10 during the occupied and unoccupied periods at home H11 and school SC. The mean mass concentrations were higher when the MEs were occupied, while vacant periods were generally characterized by a decreasing trend of PM levels, down to a rather stable background concentration. This difference was more pronounced in the schools rather than the homes. The mean PM2.5 and PM10 concentrations in home H11 during the occupied period were approximately 1.2 and 1.1 times higher, respectively, than during the unoccupied period. PM2.5 and PM10 concentrations were slightly higher on the weekend than on the weekdays (Figure 4.4 b_1 and b_2). The mean indoor PM2.5 concentrations at school SC during class hours were on average 3.6 times higher than in the off-school hours (Figure 4.4 b_3). Zhang and Zhu, (2012) also found elevated indoor particle mass concentration when the classrooms were occupied. Furthermore, the PM2.5 concentrations were much more variable in the school than in the home ME (see interpercentile range in Figure 4.4 a_1, a_2 and a_3), with a mean variation of 13.4-39.1 versus 7.4-14.6 $\mu g/m^3$, respectively.

The highest coarse fraction (PM2.5-10) concentrations was observed during indoor occupancy, as also observed by Colbeck et al. (2010). The contribution of the coarser fraction to the PM10 mass concentration was much higher in the school than in the home (Figure 4.4 b_1, b_2 and b_3), both in the unoccupied (9.4 at school and 2.5 at home) and occupied (34.2 at school and 2.8 at home) periods. Kingham et al. (2008) also found that the students' activities cause the resuspension of coarse particulate matter inside the school buildings.

In sum, the variations of PM mass concentrations depended largely on the occupancy of the places and the people's activities, and therefore, the personal exposure to PM concentrations is largely dependent on the ME and time of the day.

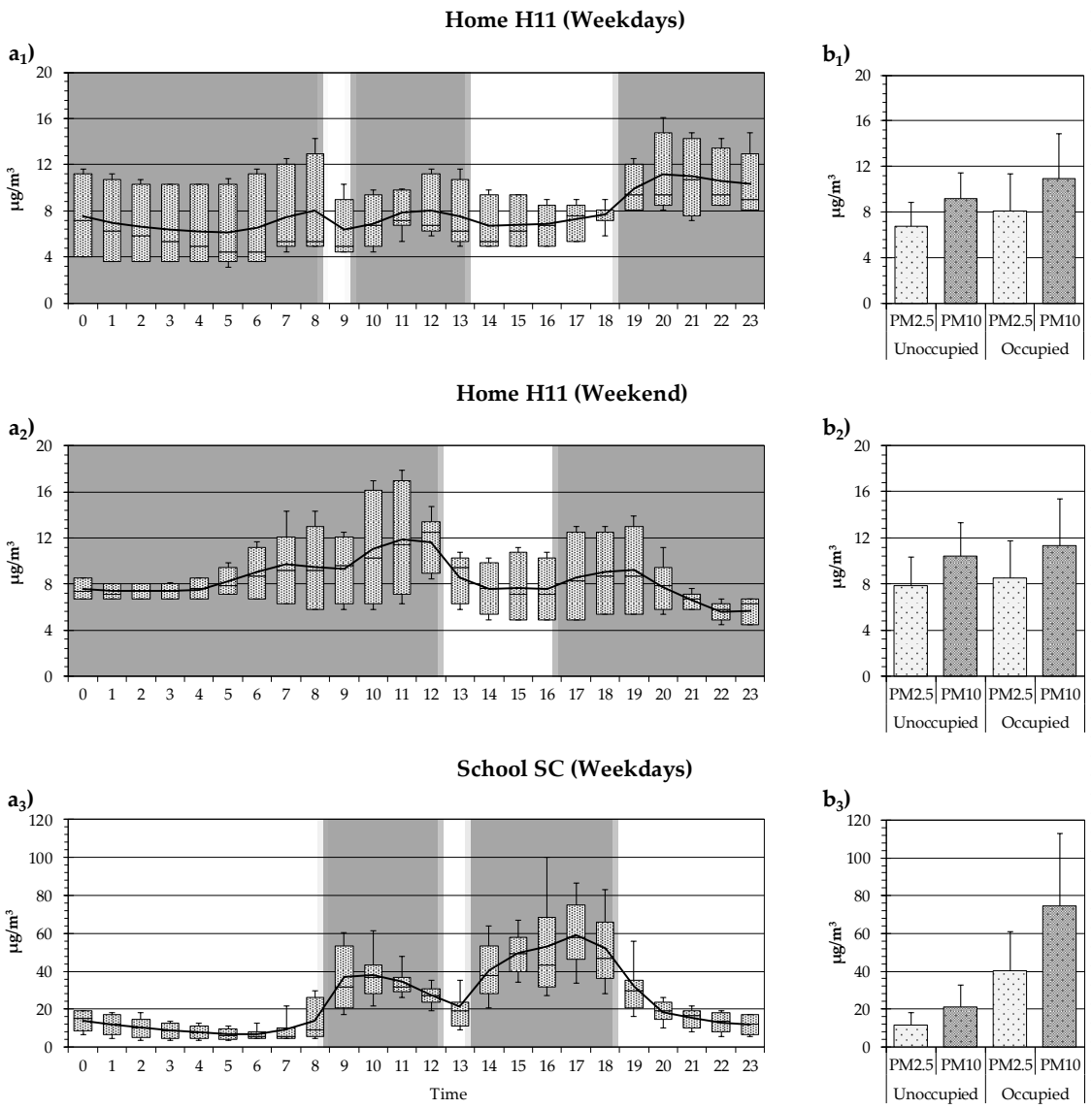


Figure 4.4 - Temporal variation of PM2.5 mass concentrations in home H11 on the weekdays (a1) and weekend (a2) and in school SC (a3). The box-plots represent the median, and the 25th and 75th percentile of hourly PM2.5 concentrations. The whiskers show the 10th and 90th percentile of hourly PM2.5 concentrations. The thick black line represents the mean of hourly PM2.5 concentrations. The period when the ME was occupied is shadowed in grey. Note the different scales between the plots in the home and the school.

Mean PM2.5 and PM10 mass concentrations during the occupied and unoccupied periods in home H11 during weekdays (b_1) and weekend (b_2) and in the school SC (b_3). The error bars indicate the standard deviation.

4.3.4 PM exposure and respective inhaled doses

The measurements in all MEs were always performed during the occupancy period, since the inclusion of unoccupied time underestimates the concentration relevant for personal exposure assessment (Morawska et al., 2013). The annual number of school days was taken into account when calculating the average daily exposure that was 20.6 μg/m^3 for PM2.5 and 31.5 μg/m^3 for PM10.

The highest exposure to PM during weekdays was registered in school (PM2.5 - 218 μg/m^3.h, PM10 - 404 μg/m^3.h), (Figure 4.5 (a)). The classroom was the second ME with respect to time spent (26.9%) but it was the ME where the highest concentrations of PM were measured. The home contributed 36.6% and 29.4% to the total daily exposure to PM2.5 and PM10, respectively. The high exposure estimated during the sleeping period (PM2.5: 141.4 μg/m^3.h; PM10: 177.4 μg/m^3.h) was due to the increased time allocated to this activity. Similarly, the lowest exposure levels for both PM fractions were found during outdoor leisure activities, due to the short duration of these activities. Zhang et al. (2018) reported an average daily exposure to PM2.5 of 155.7 μg/m^3 for children in Shanghai, China. On-campus exposure to PM2.5 (inside of the school and at the playground) was found equal to 1493.3 μg/m^3.h and off-campus exposure (indoor and outdoor of the house and in commuting) equal to 1926.8 μg/m^3.h.

During the weekend, the highest exposure to PM was registered in home, during the sleeping time (PM2.5 - 192.3 μg/m^3.h, PM10 – 245 μg/m^3.h), followed by indoor leisure activities (PM2.5 – 70.2 μg/m^3.h, PM10 – 130.0 μg/m^3.h). Home contributed 66.6% to the exposure to PM2.5 and 61.0% to PM10 (Figure 4.5 (b)).

Figure 4.5 (a) and (b) also depicts the exposure in different transport modes. During the weekdays, the highest exposure to PM2.5 was registered in cars (34.6 μg/m^3.h) while the highest exposure to PM10 was associated to the subway (65.1 μg/m^3.h). PM10 average mass concentration was higher for the subway (84.1 μg/m^3), in comparison to all other transport modes, due to the elevated levels of coarse particles, which may be associated with the resuspension of particles due to turbulence created by the train and commuter movement (Martins et al., 2015). In cars the PM2.5 concentration was slightly lower than in the subway (33.7 μg/m^3 in cars, 37.8 μg/m^3 in subway) but the travel time was higher leading to a higher exposure. During the weekend, children rarely used the bus or subway. The highest exposure to PM2.5 and PM10 was registered in cars (29 μg/m^3.h and 35.7 μg/m^3.h, respectively), followed by the time spent walking on the street (8.9 μg/m^3.h and 14.8 μg/m^3.h, respectively).

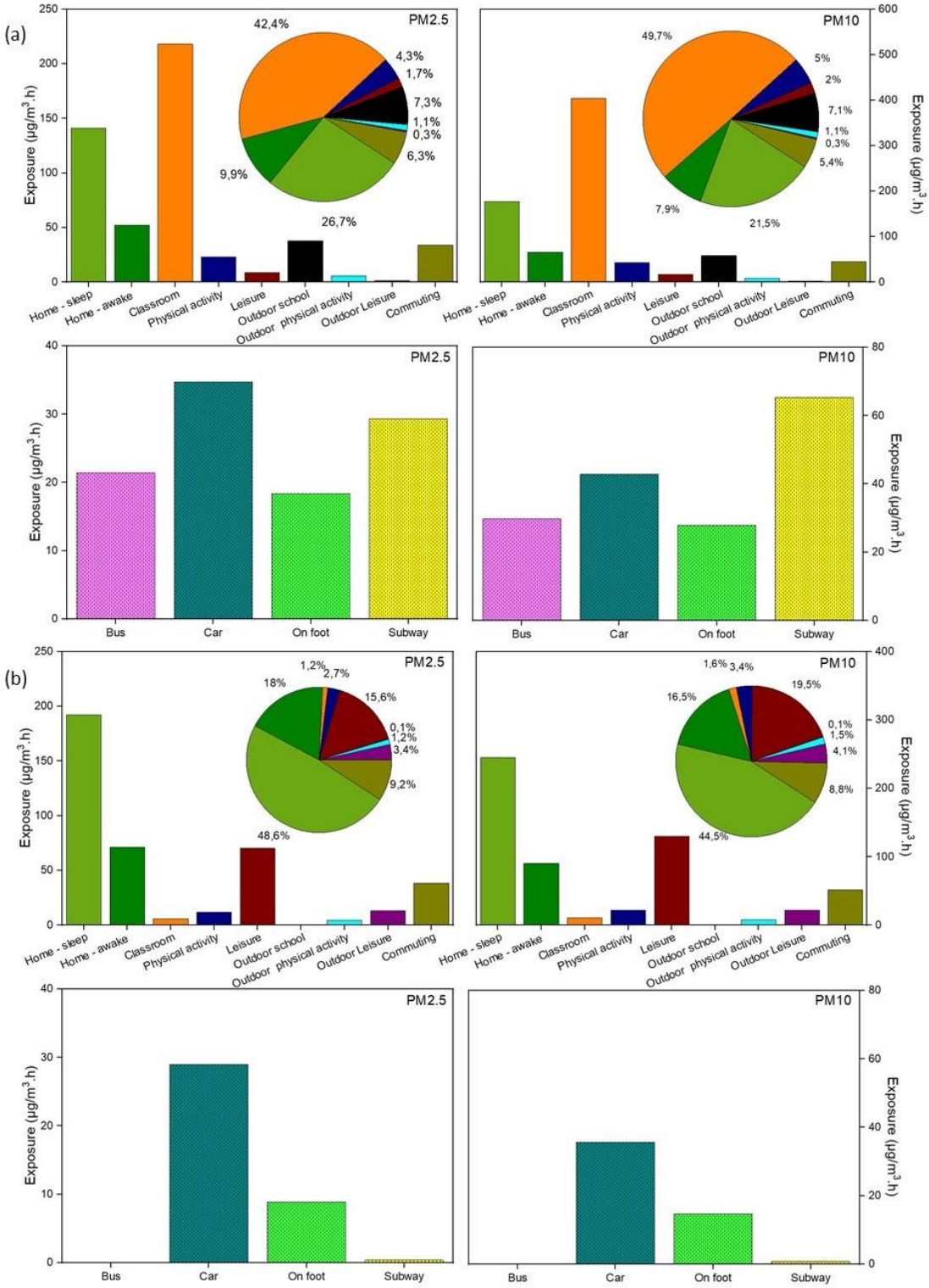


Figure 4.5 - Graphs at the top (a): PM2.5 and PM10 daily exposure in each ME during the weekdays and exposure within each transport mode. Graphs at the bottom (b): PM2.5 and PM10 daily exposure in each ME during the weekends and exposure within each transport mode.

The inhaled daily dose depends not only on the ME frequented by the child and time allocation but also on the activities performed that have an impact on the IR. The average daily inhaled dose was 243.5 µg for PM2.5 and 382.2 µg for PM10. During the week, classroom was the ME that mostly contributed to the daily PM2.5 and PM10 dose (PM2.5 – 96 µg, 36%, PM10 – 177 µg, 41%) despite the fact that children spend more time at home. This is because schools have important sources of particles such as the dust resuspension that contribute to higher PM concentrations (Figure 4.6 (a) and (b)). During the weekend, the ME that mostly contributed to the daily dose for both size fractions was the home (PM2.5 – 90 µg, 54%, PM10 – 114 µg, 49%).

The contribution to PM daily dose was higher while children were sleeping (weekdays: PM2.5 – 16%, PM10 – 13%; weekend: PM2.5 – 36%, PM10 – 32%) than awake (weekdays: PM2.5 - 8%, PM10 – 7%; weekend: PM2.5 – 18%, PM10 – 16%), because the time spent sleeping (73%) was higher than the time spent awake (27%).

Regarding the transport ME, the inhalation rate was the same for all the considered transport means. The dose inhaled during travel by foot increased in relation to other transport modes, because the associated IR is higher. During weekdays, children spent 3.4% of their time commuting; however they received 7.9% of their PM2.5 daily dose, due to co-occurrence with traffic rush hours and the proximity to the source during commuting, leading to increased concentrations in these MEs.

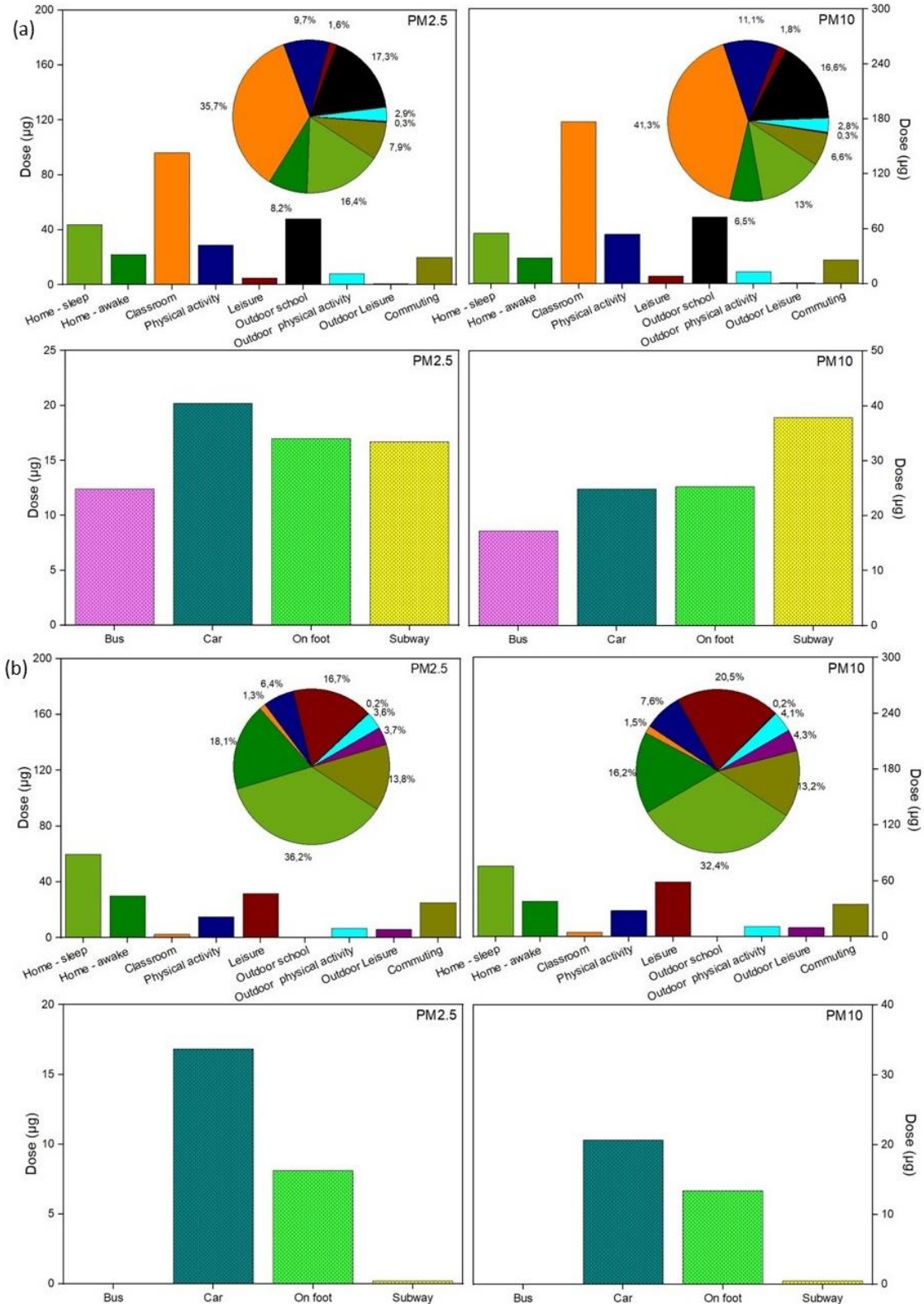


Figure 4.6 - Graphs at the top (a): PM2.5 and PM10 inhaled daily dose in each ME during weekdays and inhaled dose within each transport mode. Graphs at the bottom (b): PM2.5 and PM10 inhaled daily dose in each ME during weekends and inhaled dose within each transport mode.

4.4 Conclusions

Children spend more than 86% of their time indoors (55% at home, 27% in classrooms, 5% in commuting and 2.7% engaging in physical activities indoors), indicating that the risk assessment should focus on indoor MEs.

Measurements of PM10 and PM2.5 were performed indoors and outdoors, at 40 homes and 5 schools, as well as in 3 transport modes (cars, buses and subway). The highest PM2.5 and PM10 concentrations (35.3 and 65.4 $\mu g/m^3$) were registered in classrooms as result of the children's activity, PM resuspension and inadequate ventilation of the spaces. Generally in homes, the indoor concentrations followed the outdoor concentrations (I/O ratio of 1.23 for PM2.5 and 0.87 for PM10).

The spatial distribution of the concentrations revealed the importance of traffic emissions for indoor air quality. Homes located in the parishes most recently populated displayed lower concentrations in comparison to the ones located in older parishes and especially in the center of the city, where the traffic is more intense and the buildings are older. However, additional indoor sources were identified such as cleaning, cooking and smoking.

The classroom was the ME mostly contributing to children exposure to PM2.5 (42.4%) and PM10 (49.7%), followed by the home principally during the sleeping time (PM2.5 – 26.7%; PM10 – 21.5%). In transports, the highest exposure to PM2.5 and PM10 and respective doses were registered in cars (34.6 $\mu g/m^3.h$) and subway (65.1 $\mu g/m^3.h$), respectively.

This work quantitatively demonstrates that indoor MEs are the main contributors to personal exposure to PM and respective inhaled dose. The results highlight the need for indoor air quality assessment studies, in order to reduce uncertainty in exposure and dose assessment, to allow stronger associations between PM exposure and health outcomes and to identify mitigation measures to improve the health and wellbeing of the children.

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Supplementary material

Table S4.1 - Inhalation rate (m^3/h) for the 6-10 age group as a function of the activity performed

Activity	IR (m^3/h) for 6-10 age group
Sleeping and rest	0.31
Studying and sedentary activities	0.42
Walking (not along a road)	0.58
Physical activity indoor and playing outdoor	1.27
Physical activity outdoor	1.44
Commuting - walking	0.91
Commuting – public and private vehicles	0.58

Table S4.2 - General characteristics of study children.

Characteristics		**N**	**%**
Gender	Male	533	45
	Female	612	52
	Unknown	44	3.7
Age	5	68	5.7
	6	160	14
	7	251	21
	8	250	21
	9	285	24
	10	153	13
	Unknown	22	1.8

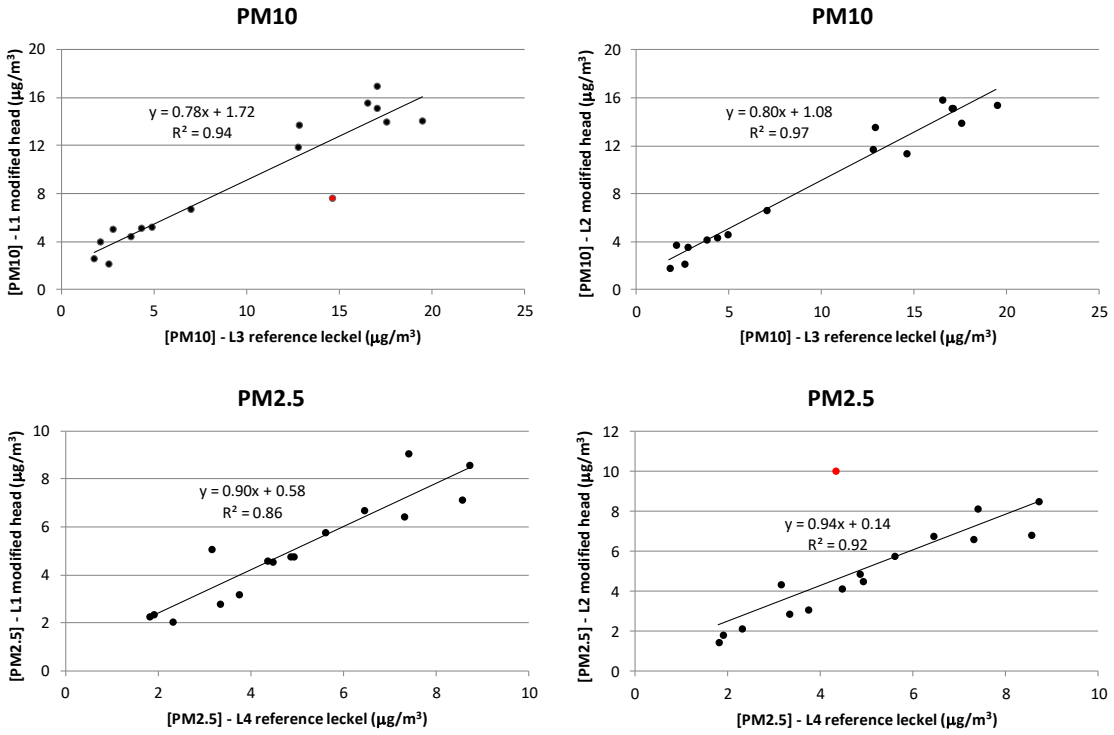

Figure S4.1 - Results of the inter-comparison study with the sampling heads

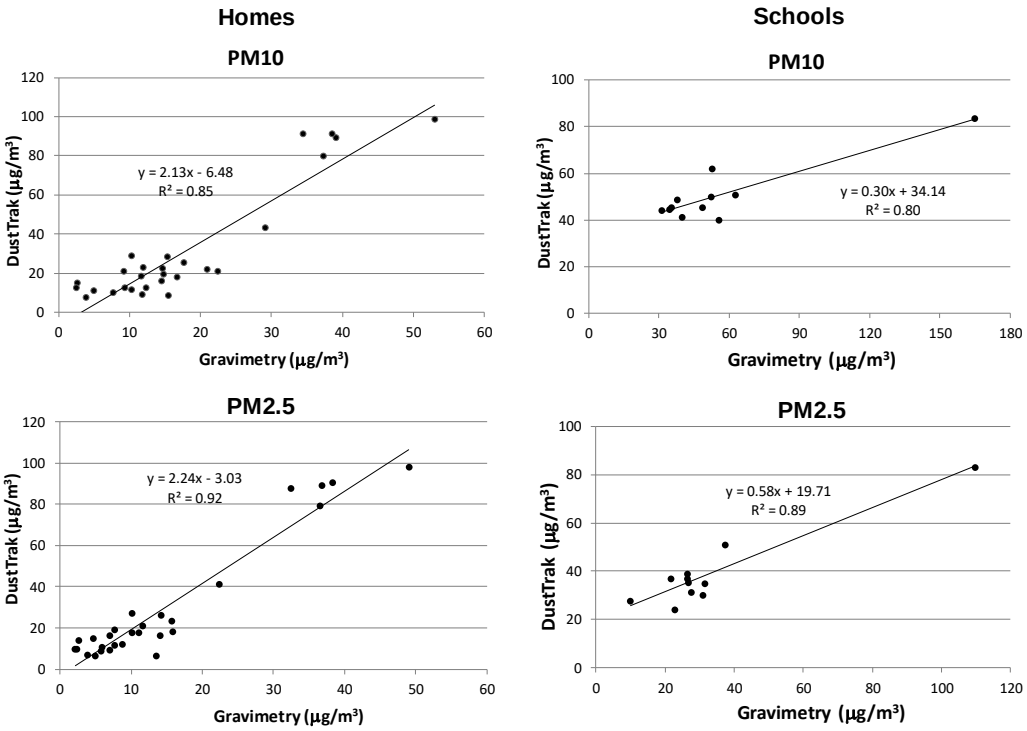

Figure S4.2 - PM concentrations (µg/m^3) measured with the DustTrak vs. those determined gravimetrically in the homes and schools.

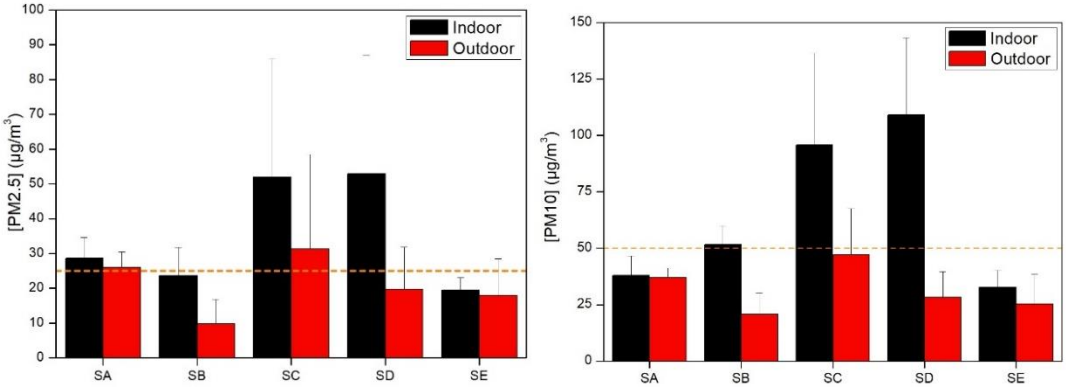

Figure S4.3 - PM2.5 and PM10 mass concentrations (µg/m^3) measured indoors and outdoors at schools. The dashed line represents the WHO guidelines and the Indoor Air Quality Portuguese limit values for PM2.5 and PM10.

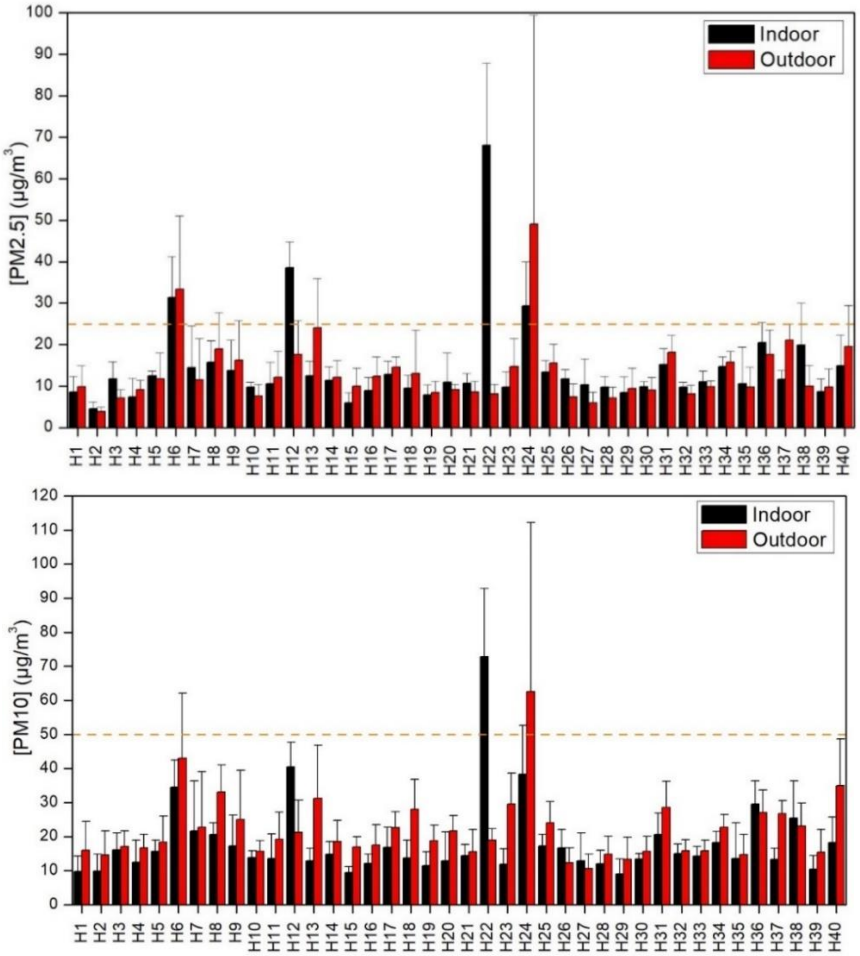

Figure S4.4 - PM2.5 and PM10 mass concentrations (µg/m^3) measured indoors and outdoors at homes. The dashed line represents the WHO guidelines and the Indoor Air Quality Portuguese limit values for PM2.5 and PM10

Chapter 5

Chapter 5. Assessment of children's exposure to carbonaceous matter and to PM major and trace elements

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Published in: Science of the Total Environment 807 (2022) DOI: 10.1016/j.scitotenv.2021.151021

Accepted: 12 October 2021

Journal Impact Factor (2021): 7.963

Citations: 0

Abstract

Particulate matter 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 microenvironments 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 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.

Keywords: Exposure, dose assessment, particulate matter, mass closure, air quality

5.1. Introduction

Particulate Matter 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; Davidson et al., 2005; Hauck et al., 2004; Sandström et al., 2005) and the European Environment Agency 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 microenvironments 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 and elemental carbon. 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; F. 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.

5.2. Methodology

5.2.1. 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 5,081 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., 2009b).

The sampling at each home and school lasted for 5 days, during the occupancy hours (schools: 9am-6pm only during weekdays; homes: 6pm-9am, during weekdays, and 24h 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).

5.2.2. Chemical characterization

PM2.5-10 and PM2.5 samples collected on Nuclepore and PTFE filters, respectively, were analysed by X-Ray Fluorescence 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 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 S5.1, in the supplementary material.

PM2.5-10 and PM2.5 samples collected on quartz filters were analysed by the Thermo-Optical Transmittance method for the determination of the OC and EC. A punch of 1x1.5 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).

5.2.3. Mass closure

Chemical mass closure was calculated including the assessment of the contribution of 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.

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; R. 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 5.1. 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 5.1). EC and $nssSO_4^{2-}$ were considered separately from any group.

Table 5.1 - Equations used in the mass closure assessment

	Equations	**Where**
POM	1.6 x [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 x Mn + 1.12 x Ba + 1.18 x 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-} - $ssSO4^{2-}$	

5.2.4. 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 5.2 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 5.2 - 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)	$\frac{\sum_{j=1}^{m} C_j . t_j}{\sum_{j=1}^{m} t_j}$	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)	$\sum_{j=1}^{m} (C_j . t_j . IR_j)$	
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 (%)	$\frac{C_a \times t_a \times IR_a}{\sum_{j=1}^{m} C_j \times t_j \times IR_j} \times 100$	

5.2.5. 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 $p < 0.05$.

5.3. Results and discussion

5.3.1. 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 S5.2, 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 (Diapouli et al., 2011; lai Chen 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., 2000a).

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 (Hermann 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).

5.3.2. 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 compounds in the analysis. Figure 5.1 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% to 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.

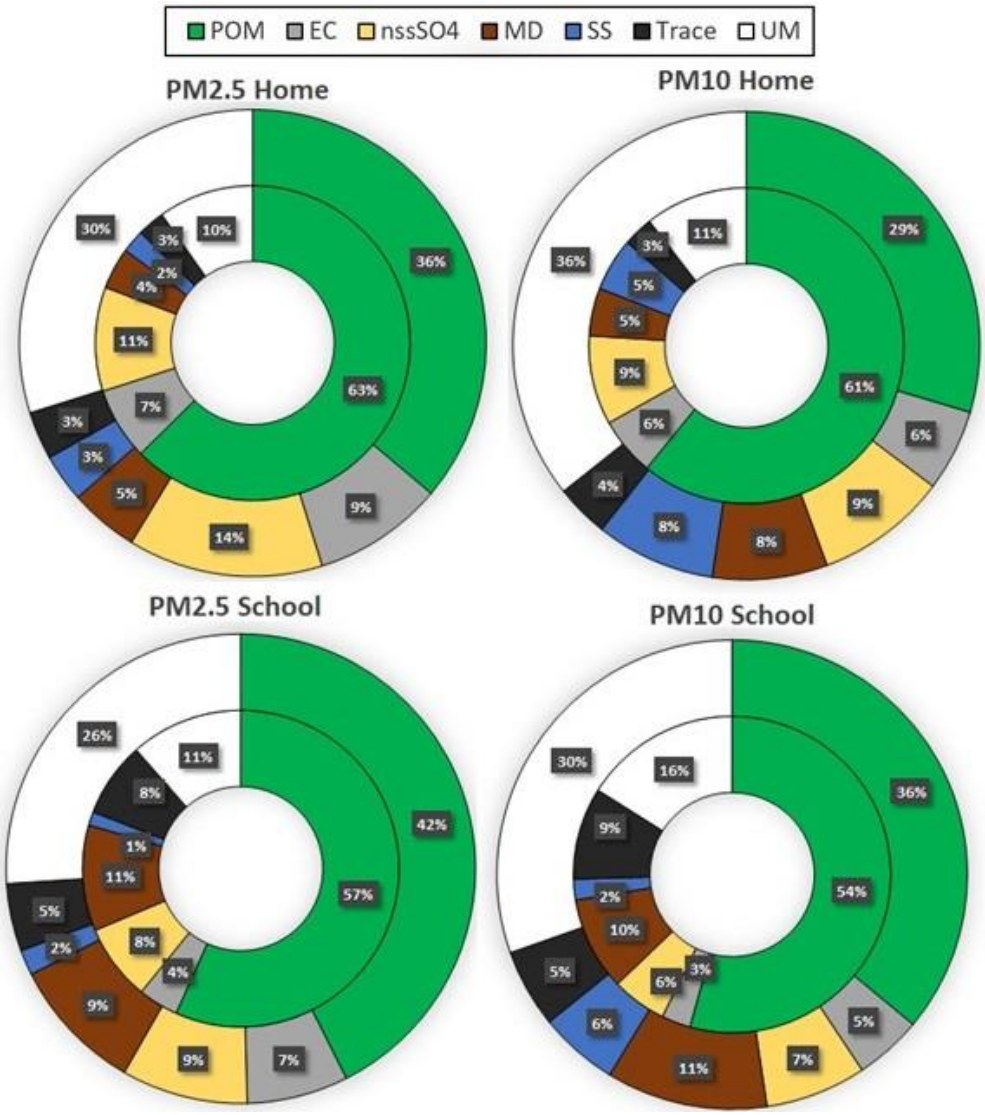

Figure 5.1 - Average indoor (inner circle) and outdoor (outer circle) PM2.5 and PM10 chemical composition in homes and schools

- 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; M. 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 suggests 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) (Figure 5.2 and 5.3).

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 and 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 9am and 6pm) while in homes occurred mainly during the night-time (from 6pm to 9am). 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. Figure 5.2 and 5.3 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.

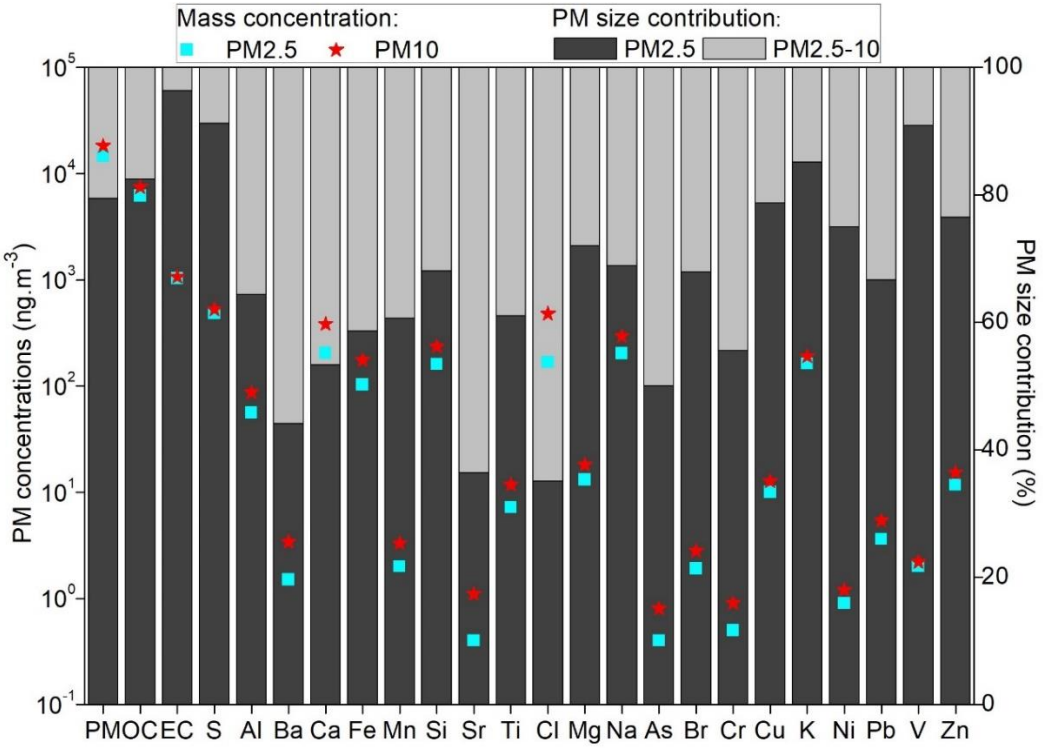

Figure 5.2 - Mass concentrations in PM2.5 and PM10 measured in homes (values in ng/m^3). Contribution of PM2.5 and PM2.5-10 to PM10 (values in percentage)

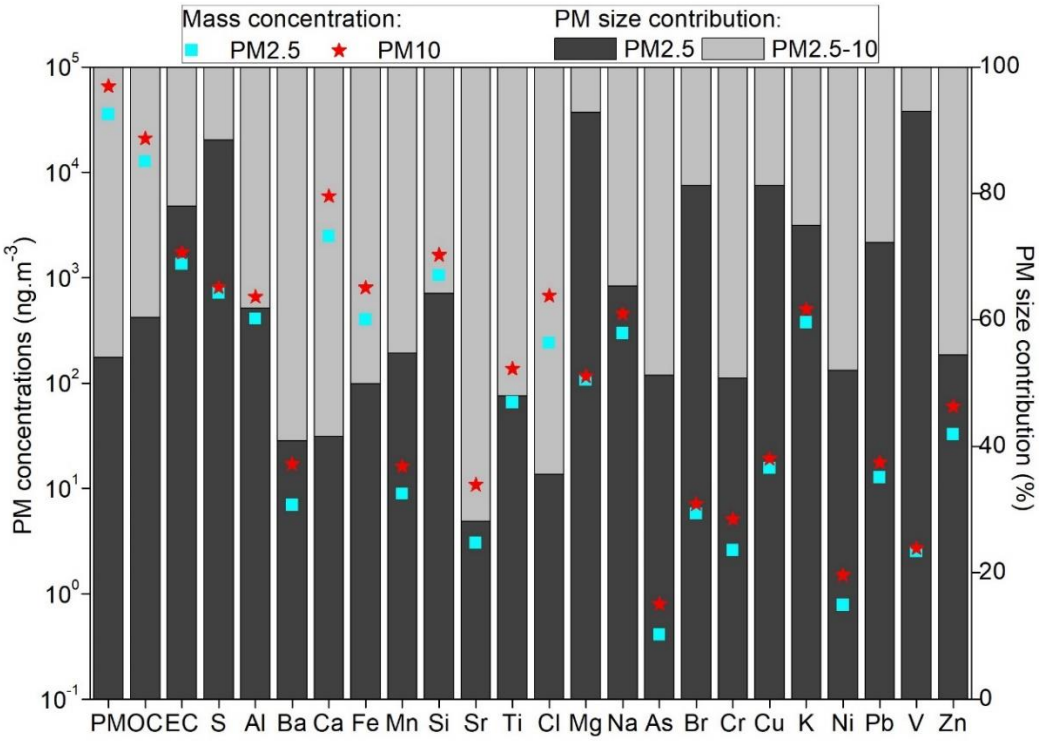

Figure 5.3 - Mass concentrations in PM2.5 and PM10 measured in schools (values in ng/m^3). Contribution of PM2.5 and PM2.5-10 to PM10 (values in percentage)

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; L. 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 to 9.1 indicating an association with the combustion of coal, burning of biomass (Almeida-Silva et al., 2015; L. 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).

- 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 (Figure 5.1). 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.

- 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).

- 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).

- 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).

5.3.3. Exposure and inhaled dose assessment

Figure 5.4 and Figure 5.5 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 38000 ng/m^3.h for PM10, while in the home was 5100 ng/m^3.h (Table S5.3, 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 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. (2005) 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. (2005) 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.

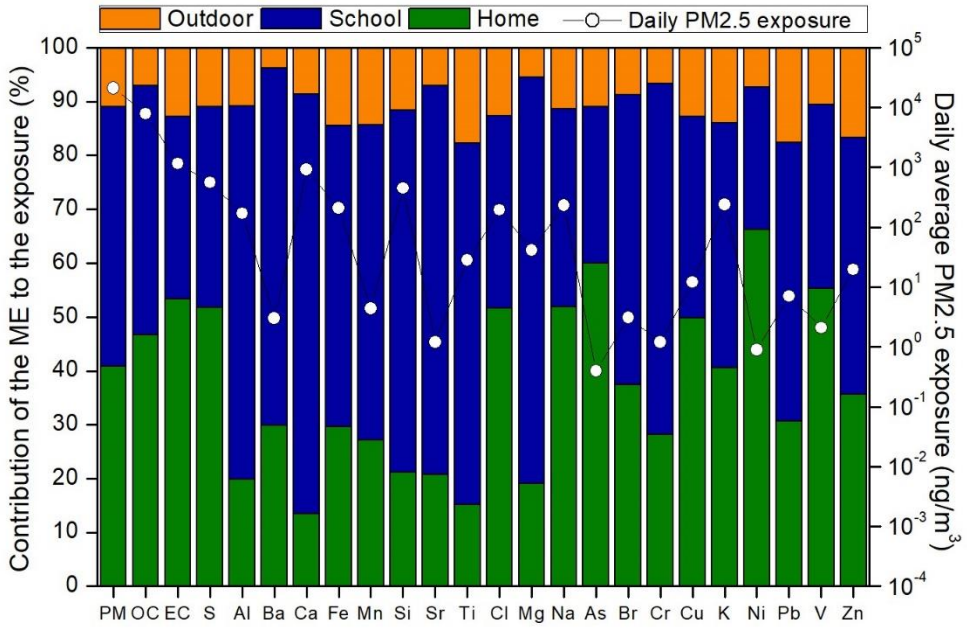

Figure 5.4 - Contribution of each ME to the daily PM2.5 exposure.

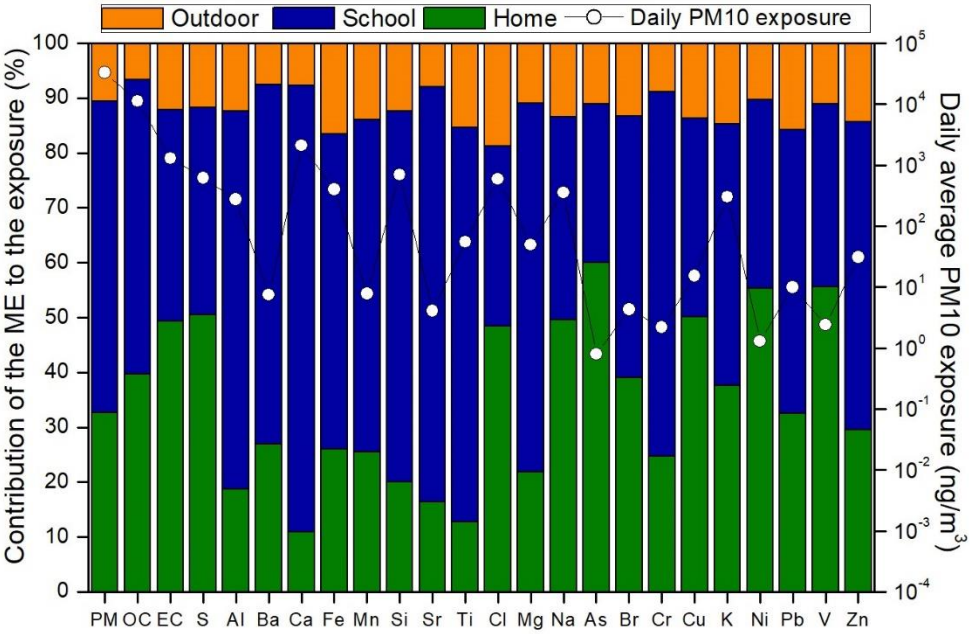

Figure 5.5 - Contribution of each ME to the daily PM10 exposure.

Figure 5.6 and Figure 5.7 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.

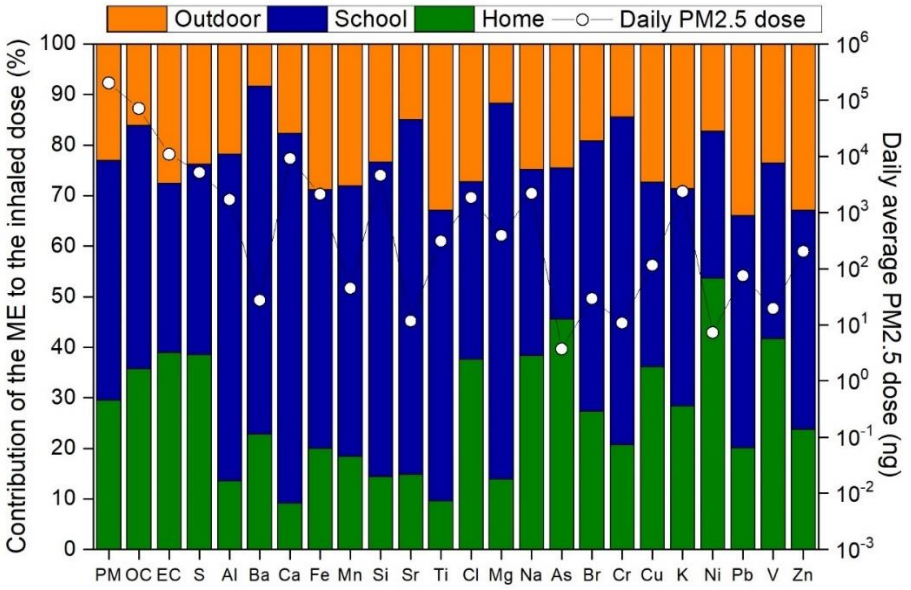

Figure 5.6 - Contribution of each ME to the PM2.5 inhaled daily dose.

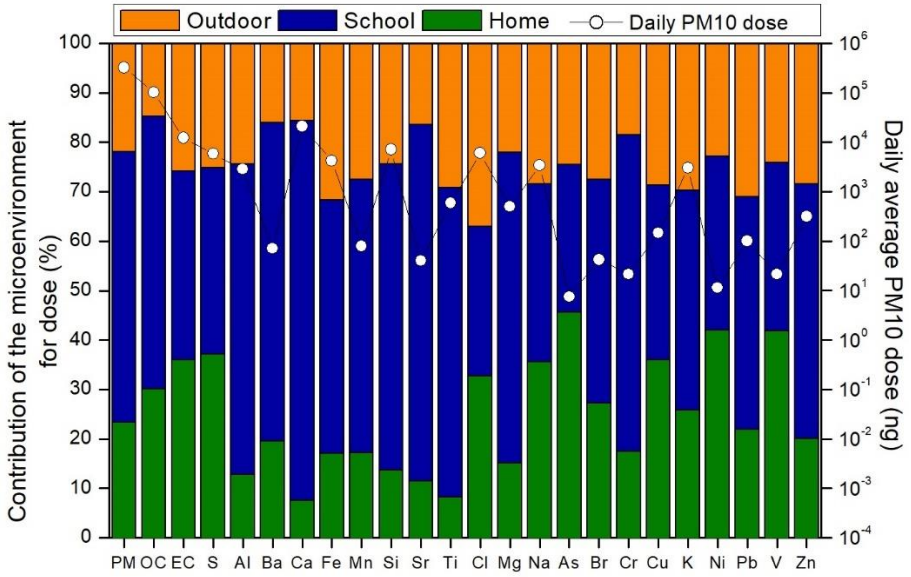

Figure 5.7 - Contribution of each ME to the PM10 inhaled daily dose.

5.4. 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 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.

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Supplementary material

Table S5.1 - Detection limits (in ng/m^3) for all elements measured by XRF.

Element	Detection limit (ng/m^3)	Element	Detection limit (ng/m^3)
Al	5.1	Mn	0.6
As	0.8	Na	10.3
Ba	2.1	Ni	0.4
Br	1	Pb	0.6
Ca	1.2	S	1.6
Cl	0.6	Sb	2
Cr	0.2	Si	10.3
Cu	0.2	Sr	0.8
Fe	0.6	Ti	0.6
K	0.4	V	0.4
Mg	3.1	Zn	0.6

Table S5.2 - PM (µg/m^3), OC (µg/m^3), EC (µg/m^3), major and trace elements (ng/m^3) concentration inside and outside of homes and schools.

Microenvironment				PM	OC	EC	S	Al	Ba	Ca	Fe	Mn	Si	Sr	Ti	Cl	Mg	Na	As	Br	Cr	Cu	K	Ni	Pb	V	Zn
Houses	Indoor	PM2.5	Average	14	6.2	1.0	480	56	1.5	200	100	2.0	160	0.4	7.2	170	13	200	0.4	1.9	0.5	10	160	0.9	3.6	2.0	12
			Median	11	4.3	0.8	350	17	1.0	140	70	0.3	99	0.4	4.9	38	1.5	180	0.4	0.5	0.1	5.6	87	0.2	0.3	0.2	7.9
			sd	12	6.6	0.9	380	99	3.4	210	98	2.8	220	0.1	7.5	300	39	150	0.0	2.2	1.2	12	220	2.1	5.5	3.0	13
			min	2.1	1.2	0.1	74	2.6	1.0	21	10	0.3	5.1	0.4	0.3	0.3	1.5	5.1	0.4	0.5	0.1	0.1	14	0.2	0.3	0.2	0.3
			max	92	54	5.2	2000	790	28	1600	570	12	1900	2.0	50	1700	340	790	0.4	13	8.6	91	1600	21	21	17	120
		PM10	Average	18	7.5	1.1	530	87	3.4	380	180	3.3	240	1.1	12	480	18	290	0.8	2.8	0.9	13	190	1.2	5.4	2.2	15
			Median	15	5.6	0.8	500	40	2.1	280.0	110	1.9	150	0.8	8.2	250	3.1	250	0.8	1.6	0.4	8.4	120	0.4	2.6	0.4	11
			sd	13	6.8	0.9	400	130	4.7	400	170	3.5	290	0.6	12	600	47	200	0.0	2.4	1.5	13	220	2.1	6.3	3.1	14
			min	2.5	1.5	0.1	100	3.5	2.1	38	18	0.6	10	0.8	0.6	1.8	3.1	10	0.8	1.0	0.2	0.2	20	0.4	0.6	0.4	0.6
			max	98	56	5.3	2100	970	43	2900	1200	20	2300	5.1	75	3200	340	1200	0.8	13	9.1	93	1700	21	33	19	120
	Outdoor	PM2.5	Average	13	3.0	1.2	540	69	1.7	200	190	3.1	190	0.5	6.9	160	19	240	0.4	2.4	0.8	9.7	140	0.9	4.2	2.5	13
			Median	11	2.2	0.8	430	14	1.0	100	120	0.3	69	0.4	3.6	22	1.5	200	0.4	0.5	0.1	6.7	72	0.2	0.3	1.2	8.8
			sd	12	2.3	1.2	390	140	4.1	240	220	3.8	350	0.5	10	320	62	180	0.0	2.4	1.4	9.7	150	1.4	6.2	3.3	14
			min	0.8	0.6	0.2	84	1.0	1.0	19	13	0.3	4.9	0.4	0.3	0.3	1.5	5.1	0.4	0.5	0.1	0.1	11	0.2	0.3	0.2	0.3
			max	140	17	6.1	2000	1050	37	2000	1500	18	2400	6.0	70	2000	470	900	0.4	13	8.1	58	820	6.9	26	19	100
		PM10	Average	22	3.8	1.3	640	130	8.4	560	460	7.1	320	2.1	16	1000	52	440	0.8	5.0	2.0	17	200	1.4	6.5	2.9	22
			Median	19	2.9	0.9	530	52	2.1	380	330	4.9	160	1.8	9.5	690	3.1	400	0.8	4.3	1.0	14	140	0.4	3.7	1.8	15
			sd	14	2.7	1.2	400	200	11	460	420	6.2	490	1.3	18	1000	85	250	0.0	3.9	2.2	14	162	1.8	7.4	3.7	20
			min	5.4	0.8	0.2	180	3.6	2.1	70	43	0.6	10	0.8	1.0	22	3.1	49	0.8	1.0	0.2	0.2	30	0.4	0.6	0.4	1.7
			max	150	20	6.3	2200	1500	77	3300	2100	32	3300	12	110	4600	470	1200	0.8	27	12	80	900	15	35	23	140
Schools	Indoor	PM2.5	Average	35	13	1.3	720	410	6.9	2500	400	8.9	1100	3.0	66	240	100	300	0.4	5.8	2.6	16	370	0.8	13	2.5	33
			Median	27	11	1.1	380	260	1.0	1300	210	5.4	590	0.4	42	120	1.5	260	0.4	0.5	2.5	3.0	190	0.2	0.3	0.2	27
			sd	25	9.6	0.8	740	670	23	2000	590	8.4	1600	4.0	57	320	310	200	0.0	19	2.3	20	440	1.6	16	4.1	21
			min	10	7.0	0.4	170	2.6	1.0	730	64	0.3	320	0.4	23	0.3	1.5	5.1	0.4	0.5	0.1	0.1	41	0.2	0.3	0.2	0.3
			max	110	57	3.2	2800	3400	100	7000	3100	22	8700	14	300	1400	1500	730	0.4	94	8.2	60	2200	5.6	46	15	90
		PM10	Average	65	21	1.7	810	660	17	5900	800	16	1600	10.8	140	670	120	450	0.8	7.1	5.1	19	500	1.5	18	2.7	60
			Median	53	18	1.8	490	380	2.1	5000	490	14	1000	8.5	100	450	3.1	410	0.8	1.0	4.8	12	380	0.4	16	0.4	49
			sd	39	11	0.9	750	790	29	4100	780	11	1900	9.5	86	730	320	320	0.0	19	3.0	22	490	1.6	17	4.1	30
			min	22	11	0.4	270	110	2.1	1600	150	0.6	510	0.8	50	91	3.1	10	0.8	1.0	0.8	0.2	42	0.4	0.6	0.4	14
			max	160	68	3.8	2900	4000	140	13000	4100	37	10000	31	400	3100	1500	1300	0.8	97	13	65	2500	5.8	55	15	130
	Outdoor	PM2.5	Average	21	5.1	1.3	550	170	15	720	270	5.7	480	0.8	45	230	21	240	0.4	2.5	0.7	14	300	0.6	11	2.1	30
			Median	18	4.6	1.0	370	130	1.0	380	240	0.3	340	0.4	15	30	1.5	150	0.4	0.5	0.1	8.6	170	0.2	11	0.2	22
			sd	15	2.6	0.8	430	220	51	1200	220	6.3	580	1.3	81	360	95	270	0.0	3.1	1.4	14	300	1.2	12	2.9	30
			min	1.9	2.7	0.3	140	2.6	1.0	78	73	0.3	5.1	0.4	0.3	0.3	1.5	5.1	0.4	0.5	0.1	0.1	63	0.2	0.3	0.2	0.3
			max	78	16	3.7	1700	1100	240	5900	980	18	3000	6.3	370	1500	480	870	0.4	9.9	4.9	43	1200	4.9	30	8	150
		PM10	Average	32	6.7	1.4	660	310	27	1500	600	9.8	780	3.0	77	1000	49	440	0.8	5.2	1.8	19	400	1.2	14	2.3	40
			Median	31	5.8	1.0	480	220	2.1	1200	550	7.1	580	2.1	34	570	3.1	310	0.8	4.3	1.1	14	300	0.4	12	0.4	35
			sd	15	3.2	0.9	440	320	78	1400	350	6.9	810	2.3	120	990	100	320	0.0	5.1	1.8	16	330	1.6	14	3.0	31
			min	9.9	3.6	0.3	250	48	2.1	330	160	0.6	82	0.8	2.8	31	3.1	10	0.8	1.0	0.2	0.2	100	0.4	0.6	0.4	4.5
			max	81	20	3.9	1900	1700	360	7500	1700	21	4400	9.2	540	4100	480	1000	0.8	24	6.9	55	1500	5.6	42	8.7	160

Table S5.3 - PM2.5 and PM10 daily exposure in each ME

	PM2.5 (ng/m^3.h)			PM10 (ng/m^3.h)		
Exposure	**House**	**School**	**Outdoor**	**House**	**School**	**Outdoor**
PM	190000	230000	51000	240000	420000	78000
OC	82000	81000	13000	100000	130000	17000
EC	14000	8700	3000	14000	11000	3500
S	6400	4600	600	7000	5200	1600
Al	750	2700	50	1200	4200	760
Ba	20	48	410	45	100	13
Ca	2700	16000	1200	5100	38000	3600
Fe	1400	2600	1300	2300	5200	1500
Mn	27	57	550	44	100	24
Si	2100	6800	740	3100	11000	1900
Sr	5.7	20	1800	15	70	7.3
Ti	96	420	110	160	880	190
Cl	2200	1500	5.0	6400	4300	2500
Mg	180	690	2.0	240	750	120
Na	2700	1900	14	4000	2900	1100
As	5.5	2.7	670	11	5.3	2.0
Br	26	37	1.0	37	46	13
Cr	7.2	17	34	12	33	4.4
Cu	130	100	73	170	123	46
K	2200	2400	1.0	2500	3200	990
Ni	13	5.0	6.0	15	9.5	2.9
Pb	49	82	2.0	71	110	35
V	26	16	3.0	29	18	5.7
Zn	160	210	28	200	390	99

Table S5.4 - PM2.5 and PM10 inhaled daily dose in each ME

	PM2.5 (ng)			PM10 (ng)		
Dose	**House**	**School**	**Outdoor**	**House**	**School**	**Outdoor**
PM	60000	96000	47000	75000	180000	71000
OC	25000	34000	11000	31000	57000	15000
EC	4200	3600	3000	4400	4700	3200
S	2000	1900	1200	2200	2200	1500
Al	230	1100	370	360	1800	690
Ba	6.3	20	2.3	14	42	12
Ca	840	6700	1600	1600	16000	3300
Fe	420	1100	600	720	2200	1300
Mn	8.2	24	13	14	44	22
Si	660	2800	1100	970	4400	1700
Sr	1.8	8.2	1.8	4.7	29	6.6
Ti	30	180	100	49	370	170
Cl	690	650	500	2000	1800	2200
Mg	5	290	46	75	310	110
Na	840	800	540	1200	1200	970
As	1.7	1.1	0.9	3.4	2.2	1.8
Br	8.0	16	5.6	12	19	12
Cr	2.2	7.0	1.6	3.8	14	4.0
Cu	42	42	31	53	52	42
K	670	1000	680	790	1400	900
Ni	3.9	2.1	1.3	4.8	4.0	2.6
Pb	15	34	25	22	48	31
V	8.1	6.8	4.6	9.0	7.4	5.2
Zn	49	88	67	63	160	90

Chapter 6

Chapter 6. Relationship between indoor and outdoor size-fractionated particulate matter in urban microenvironments: Levels, chemical composition and sources

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Published in: Environmental Research 183 (2020) DOI: 10.1016/j.envres.2020.109203

Accepted: 30 January 2020
Journal Impact Factor (2020): 6.28
Citations: 27

Abstract

Exposure to particulate matter has been associated with adverse health outcomes, particularly in susceptible population groups such as children. This study aims to characterise children's exposure to PM and its chemical constituents. Size-segregated aerosol samples (PM0.25, PM0.25–0.5, PM0.5–1.0, PM1.0–2.5 and PM2.5–10) were collected in the indoor and outdoor of homes and schools located in Lisbon (Portugal). Organic and elemental carbon were determined by a thermo-optical method, whereas major and trace elements were analysed by X-Ray Fluorescence. In school, the children were exposed to higher PM concentrations than in home, which might be associated not only to the elevated human occupancy but also to outdoor infiltration. The pattern of PM mass size distribution was dependent on the location (home vs. school and indoor vs. outdoor). The presence of EC in PM0.25 and OC in PM0.25–0.5 was linked to traffic exhaust emissions. OC and EC in PM2.5–10 may be explained by their adhesion to the surface of coarser particles. Generally, the concentrations of mineral and marine elements increased with increasing PM size, while for anthropogenic elements happened the opposite. In schools, the concentrations of mineral matter, anthropogenic elements and marine aerosol were higher than in homes. High mineral matter concentrations found in schools were related to the close proximity to busy roads and elevated human occupancy. Overall, the results suggest that exposure to PM is relevant and highlights the need for strategies that provide healthier indoor environments, principally in schools.

Keywords: Homes; Schools; Indoor/outdoor air; Size-segregated particles; Chemical elements; Children exposure.

6.1. Introduction

There is strong evidence that adverse health effects of particulate matter depend not only on the aerosol mass concentration, but also on many other properties including particle number concentration, size and its distribution, specific surface area and chemical composition (e.g. (Polichetti et al., 2009; Stafoggia et al., 2017; Valavanidis et al., 2008). Airborne particles span a wide range of diameters, from a few nanometers to hundreds of micrometers (Hinds, 1999). Particles of different sizes have different deposition patterns in lung regions, which might result in different health risks (Kim et al., 2015; Rajput et al., 2019). Fine particles, PM2.5 (particles with an aerodynamic diameter equal or smaller than 2.5 μm), can cause greater adverse health effects (Lepeule et al., 2012; Pope and Dockery, 2006) than coarser particles, PM2.5–10 (particles with aerodynamic diameter between 2.5 and 10 μm), due to their ability to reach the alveolar region of the respiratory tract and higher transition metal content (Janhäll et al., 2012; Rajput et al., 2019). Chemically, PM is composed of inorganic ions (e.g. ammonium, nitrates, sulphates, and soluble metals), insoluble metals, elemental carbon, organic compounds, biological components (allergens), microbial agents, and water (Kim et al., 2015; R. Zhang et al., 2015). Potentially toxic elements such as As, Cd, Cr, Pb, V and Zn are present predominantly in the fine fractions of size-segregated aerosols, while the crustal elements such as Al, Ca, Fe, Mg and Mn occur mainly in the coarse fractions (Clements et al., 2014).

Most of the human exposure to PM occurs indoors, where people spend the major fraction of their lives (Klepeis et al., 2001). Typically, indoor particles are a mix of ambient particles affected by outdoor ambient concentrations through natural and mechanical air exchange and infiltration, primary particles emitted indoors, and secondary particles formed indoors through reactions of gas-phase precursors (lai Chen et al., 2011; Morawska et al., 2017). Several studies have reported higher levels of airborne pollutants in indoor environments in comparison to outdoors (Hodas et al., 2016 and references therein). Ambient aerosol particles in urban environment are originated from several local sources, predominantly from fossil fuel burning, vehicular traffic, industrial emissions, and resuspension, but also from long-range transport (e.g. Belis et al., 2013; Karagulian et al., 2015). The natural sources account for a large fraction of aerosols in several regions and contribute mainly to coarser particles, whereas the anthropogenic sources are mostly responsible for the formation of primary and secondary fine, ultrafine, and nano-particles. Indoor sources of PM are associated to human activities (e.g. cooking, cleaning, and smoking), combustion processes (wood and fossil fuel burning), building materials (flooring, carpeting, paint, and plastics), use of various consumer products (aerosols, detergents, sprays, and cosmetics), secondary formation processes and dust resuspension (e.g. Abt et al., 2000a; Jones et al., 2000; Kim et al., 2015; Morawska et al., 2017; Oliveira et al., 2019; Urso et al., 2015; Wallace et al., 2006; Waring, 2014). The combustion processes and cleaning activities contribute

significantly to the emission of fine particles, while resuspension is principally associated to the coarse fractions of PM (Abt et al., 2000a; Fuoco et al., 2015; Nazaroff, 2004). In working environments, PM size distribution, concentrations, and chemical properties are more site-specific as these depend on the materials used, production methods, and working typologies (Bo et al., 2017). The characteristics of the particles depend on their originating sources and on the posterior processes involving the particles, hence the composition and toxicity of indoor particles is very complex, with similarities but also differences to outdoor particles (Hodas et al., 2016).

Children represent a highly vulnerable population group to air pollution because their respiratory and immune systems are still developing (e.g. Makri and Stilianakis, 2008; Sunyer, 2008). Due to their size, physiology and activity level, children inhalation rates are higher than adults resulting in larger specific doses (Bennett et al., 2008; Bennett and Zeman, 2004). They have a higher resting metabolic rate and oxygen consumption rate per unit of body weight than adults because of their rapid growth and relatively larger lung surface area per unit of body weight. Exposure to ambient air pollution at early age may affect children's growth and lung function (Chen et al., 2015; Tang et al., 2014; Urman et al., 2014; Zwozdziak et al., 2016a). Physiological immaturity is however only one explanatory factor of risk differences identified for children, and its intrinsic characteristic leaves few options for prevention. On the other hand, the influence of behaviours and activities at different developmental stages, quality of school and home environments, or commuting to and from school could also account for differential risks and create possibilities for intervention strategies to reduce exposure. Education is a crucial component of child's social development thus, schools are one of the main microenvironments where children spend their time. School-aged children spend around 23% of their daily time in school microenvironment and 61% in home (Pañella et al., 2017). Strategies for reducing health risk of children might include improvement of air quality in school and home microenvironments, child-focused information dissemination and behaviour change initiatives, or other measures specifically designed to reach children. Therefore, protection against potential health risks associated with exposure to PM requires the assessment of PM levels in the indoor air at both school and home microenvironments and in the outdoor air of the respective surrounding areas.

Most of the studies on indoor air quality in homes and schools have been focused on the assessment of mass concentration of airborne particles (Almeida et al., 2011; Jovanović et al., 2014; Morawska et al., 2017; Polednik, 2013; Rivas et al., 2014; Salthammer et al., 2016). To the authors' knowledge, information on their size distribution is very scarce in the literature. Moreover, few studies reported the size distribution of the chemical components. As aerosol size distributions can provide essential data about the emission sources, formation and growth mechanisms of aerosol particles (Hinds, 1999), knowledge of their size-fractionated chemical composition is important when studying their sources and impacts (Daher et al., 2013; Hitzenberger and Tohno, 2001; Huang et al., 2006; Karanasiou et al., 2007; M. Viana et al., 2014;

Zwozdziak et al., 2017). Thus, investigating the size-segregated aerosol particles is important to understand and manage the effects of aerosols on child health. With this in mind, the purpose of this study was to evaluate the relationship between the indoor and outdoor size distribution of particles and its chemical constituents affecting the child exposure. To this end, this characterization was carried out in the three microenvironments where schoolchildren spend most of their time, i.e. homes, schools and outdoor.

6.2. Methodology

6.2.1 Study area

This study was conducted in Lisbon, which is the capital and the largest city of Portugal. Lisbon is located in the western Iberian Peninsula on the Atlantic Ocean coast at the point where the river Tagus flows into the Atlantic (Figure 6.1). It has a Mediterranean climate. According to the 2011 census, the Lisbon metropolitan area that covers about 3015 km^2 has about 2.8 million inhabitants, representing approximately 27% of the country's population.

Lisbon is set on seven terraced hills, which together with the predominance of narrow streets and a dearth of green areas hinder the dispersion of pollutants. Lisbon was considered, in the annual report “Traffic Index 2018”, the most congested city in the Iberian Peninsula by the satellite navigation company TomTom. The dominant source of air pollutants in the city is road traffic emissions (Almeida et al., 2009b, 2009a). Moreover, it has a significant contribution of marine aerosol due to the geographic position and the dominant western wind regime (Almeida et al., 2013). In addition to the nearby airport with several continental and transatlantic flights, there is also an important port of call for cruises, receiving a high number of ships. These constitute additional sources of air pollutants that are transported across the city. The city is also frequently affected by North African air mass transport, which contributes significantly to the atmospheric mineral dust load (Almeida et al., 2008). Under adverse meteorological conditions, low dispersion conditions and thermal inversions, particularly in winter, high concentrations of air pollutants can be registered (Alves et al., 2010).

6.2.2 Sampling sites

The study was conducted in 8 sampling sites: 4 homes and 4 schools (referred to as H1–H4 and SA–SD, respectively), dispersed across Lisbon’s city centre. A map depicting the children's homes and schools location is given in Figure 6.1 The measurements were conducted between October 2017 and January 2018. According with the time-activity pattern survey developed by Faria et al. (2020), the schoolchildren in Lisbon spend around 56% in home and 27% in school during weekdays.

At each site, the sampling was performed concurrently in an indoor and an outdoor place. In the schools, a classroom and playground locations were chosen to conduct the measurements, which were assumed to give the best overall exposure from the indoor and the outdoor of the school, respectively. The selected schools are public and are not near any major pollution sources apart from traffic emissions. In the homes, the measurements were conducted in the living room and in the balcony.

Information on the general conditions in the classroom and inside home were manually recorded by the teachers and homes' inhabitants, respectively. The number of occupants per home ranged from 2 to 5, and in the classrooms the occupancy depended on the school hours, varying between 25 and 28 children. The schools have natural ventilation, which means that the air renewal occurs by opening doors and single glazing windows. All schools have traditional blackboards, with exception of school SA, which has whiteboards.

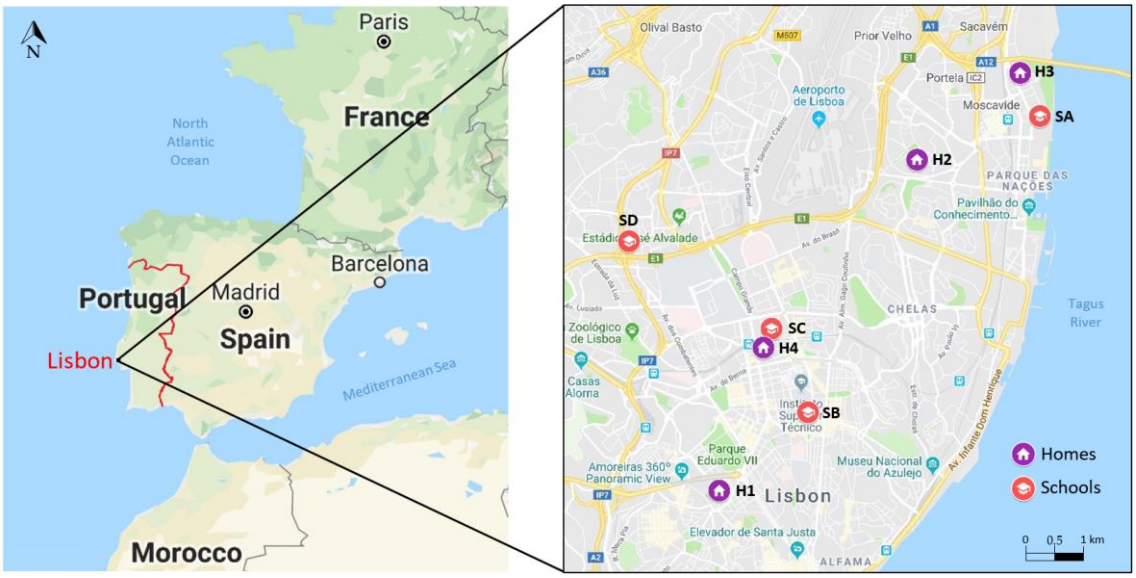

Figure 6.1 - Spatial distribution of the studied homes and schools in Lisbon, Portugal.

6.2.3 Instrumentation and measurements

The size distribution of the particles was obtained using a Personal Cascade Impactor Sampler (PCIS, SKC Inc.) connected to a SKC Leland Legacy pump, operating at 9.0 L/min. The PCIS is a miniaturised cascade impactor, consisting of four impaction stages followed by an after-filter. When sampling with the PCIS, the particles larger than the cut-off size of this stage cross the air streamlines and are collected upon the impaction plate. The finer particles with less inertia do not cross the streamlines and continue to the subsequent stage at which the nozzles are tighter, the air velocity through the nozzles is higher and finer particles are collected. This continues through the cascade impactor until the smallest particles are collected at the after-filter. According to the manufacturer specifications, particles are separated in the following aerodynamic particle

diameter ranges: <0.25; 0.25 to 0.5; 0.5 to 1.0; 1.0 to 2.5; and >2.5 μm. However, the accuracy of the <0.25 size fraction has been questioned (Fonseca et al., 2016) and this fraction probably includes a contribution from particles with Dp >0.25 μm. For the purpose of this study, and considering this limitation, the particle sizes reported in this work will be expressed throughout the manuscript as PM0.25, PM0.25–0.5, PM0.5–1.0 and PM1.0–2.5. Moreover, the data collected simultaneously by a Leckel sampler (MVS6, Sven Leckel), for the size range between 2.5 and 10 μm (PM2.5–10), was used to complement the results.

Two PCIS were placed indoors and one outdoors. Particles in the <0.25 μm stage were collected onto polytetrafluoroethylene filters (PTFE; SKC Inc.) of 37-mm diameter with 2.0 μm pore size. In the remaining stages, PTFE filters 25-mm diameter with 0.5 μm pore size were used. For the additional PCIS collecting indoors, quartz fibre filters (Whatman) were used. In order to facilitate the interpretation of the data, the lowest diameter of 0.03 μm was assumed for the last filter stage of particles with Dp <0.25 μm when representing the mass size distribution.

The flow rate (≈ 9.0 L/min) was checked at the beginning of each sample, with PCIS in calibration train with SKC pump, using a flowmeter (Bios Defender 510, MesaLabs). The flow was always set to within ±0.05 L/min of the desired flow rate.

The particle collection was performed during a week at each sampling place. In schools the samples were collected during school hours (about 8 h/day, depending on the school), from Monday to Friday. In homes the sampling period was 24 h during weekends (from 09:00 until 09:00 of the next day) and 15 h (18:00–9:00 h) during workdays, considered as the normal occupied period. A cumulative sampling was performed to guarantee the gravimetric representativeness of the sample. Thus, the samples were representative of weekly (5-day) occupied-hours concentrations.

The location of the aerosol instrumentation was chosen as a compromise between meeting conditions for undisturbed measurement and minimizing the annoyance to participants. The aerosol inlets were placed at roughly 1 m above the floor corresponding to breathing level of the children.

6.2.4 Sample analysis

Mass concentrations were gravimetrically determined by pre- and post-weighing the filter substrates on a microbalance (Sartorius R160P), after being stabilized for at least 24 h in a conditioned room (20°C and 50% relative humidity). PM mass concentrations were determined by dividing filter loads by the volume of air filtered. After weighing, the filters were temporarily stored in a freezer (± −15°C) until analysis.

The sampled PTFE filters were analysed by XRF for the determination of 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. Analysis was performed by the use of an ED-XRF Laboratory Instrument (Epsilon 5, PANalytical) (Manousakas et al., 2018). The elemental and organic carbon concentrations were determined by TOT method (Lab OC-EC Aerosol Analyzer, Sunset Laboratory Inc.) on the quartz filters. A detailed description of the analytical methodology is given by Popovicheva et al. (2019).

6.2.5 Statistical analysis

Statistical calculations using STATISTICA software were performed. Wilcoxon Matched pairs and Mann–Whitney U were used. These tests are non-parametric – hence they do not consider any assumptions related to the distribution – and basically are the same in that they compare between two medians to suggest whether both samples come from the same population or not. When both of the samples were not entirely independent of each other and had some factor in common, the Wilcoxon Matched pairs test was applied (differences between pairs of indoor and outdoor levels). When the samples were independent Mann–Whitney U test was applied (differences between homes and schools). Statistical significance refers to $p < 0.05$.

6.3. Results and Discussion

6.3.1 PM mass concentrations

The PM10 concentrations are given in Figure 6.2. The highest indoor PM10 levels were registered in the schools (33.0 – 97.2 μg/m^3) and the lowest values were measured in the homes (10.8 – 37.7 μg/m^3). The PM10 concentrations were usually lower inside the homes than outside, while in the schools the opposite was found. In schools, PM2.5-10 concentrations were considerably higher indoors (9.4 – 56.1 μg/m^3) than outdoors (8.6 – 15.8 μg/m^3), indicating that coarse particles measured in classrooms have major sources other than outdoor particles. These results are in line with findings of previous studies and are explained in detail in section 3.1.1.

For home H4, the indoor PM10 and PM2.5 concentrations were 2.2 and 2.5 times higher than outdoor, respectively, indicating an important contribution of fine particles. From the total PM2.5 mass, 74% was composed of particles with Dp <0.25 μm, as will be further explained. According to Diapouli et al. (2011) the high fine particle concentration indoors may be attributed to the presence of important indoor sources during measurements and/or to the higher penetration ratios of outdoor-generated fine particles indoors.

- Size distribution

The PM10 mass concentrations and percentage content in the five PM size fractions at both indoor and outdoor microenvironments of the homes and schools are shown in Figure 6.2. The indoor and outdoor particle size distributions are displayed in Figure 6.3.

In the homes, the largest mass fraction of PM indoors was observed for particles with Dp <0.25 µm, with contribution to PM10 varying between 30 and 71%, while outdoors the predominant size range was 2.5–10 µm, accounting from 19 to 62% of PM10 mass. For home H4, the indoor PM0.25 concentration was 3.5 times higher than outdoor, evidencing the important contribution from indoor sources in fine particle size range. The PM concentrations in the different size ranges in the homes are shown in Table S6.1 (supplementary material). Abt et al. (2000b) demonstrated that the highest effective penetration efficiency from outdoor into indoor was observed for particles ranging from 0.1 to 0.2 µm, for which the losses by impaction and diffusion are minimal. Chiang et al. (2012) studied the particle size distribution of the exhaust of light-duty diesel vehicles and revealed a higher contribution of the finest size grains to the particulate matter mass (66% in PM0.4 and 80% in PM1.0), evidencing that traffic-related particles may be present inside the homes. Several studies have demonstrated that the particles generated by indoor sources are associated mainly to human activities such as cooking, cleaning, smoking, burning candles and walking (Afshari et al., 2005; Diapouli et al., 2011; Ferro et al., 2004; Serfozo et al., 2014; Urso et al., 2015). These activities can generate new particles or promote the resuspension of particles that have settled previously. In homes, indoor combustion activities have been recognised as sources of fine particles, such as cooking food, smoking cigarettes and burning candles (Abt et al., 2000b; Afshari et al., 2005; Diapouli et al., 2011; Ferro et al., 2004; MacNeill et al., 2014a; Urso et al., 2015; Wallace, 2006). Liu et al. (2010) identified cooking as the main source of particles in the size fraction of <0.5 µm. Therefore, as the PM0.5 contribute the most to the total PM inside homes, it can be associated to generation of particles from cooking activities. The indoor PM mass concentrations in the coarse mode were lower than outdoor probably due to reduced penetration efficiency and faster settling times, as referred by Hussein et al. (2007). Moreover, as the sampling was conducted during the normal occupied period, the home samples comprised the sleeping hours when the occupant's activities are inexistent. The people's activities, through resuspension of particles previously settled and possible particles generation, influences the indoor particle concentration. This influence decreases with decreasing particle size, evidencing that the deposition rate varied by particle size (Viana et al., 2014). The coarse particle concentrations measured in homes have been associated to the movement of people and dusting or vacuuming (Abt et al., 2000b; Ferro et al., 2004; Urso et al., 2015).

For schools the coarser fraction encompassed the highest contribution to the total PM10 mass at both indoor (57%) and outdoor (43%) microenvironments, except in the indoor of school SA (28%; Figure 6.2) The indoor concentrations tended to be higher than those for the corresponding outdoor for the size range between 2.5 and 10 µm, reflecting the contribution of indoor sources. The PM concentrations in the different size ranges in the schools are shown in Table S6.2 (supplementary material). For schools SB, SC and SD the shape of indoor particle size

distributions showed a gradual increase of the PM concentration with increasing particle size (Figure 6.3). Several studies have linked the children's movements and physical activities to increased PM concentrations in school microenvironments (Braniš et al., 2005; Chithra and Nagendra, 2014; Kim et al., 2017; Joana Madureira et al., 2016b; Zwoździak et al., 2014). The particle resuspension (and emission) by the children's activity was identified as the most pronounced source for coarse particles. Fromme et al. (2007) suggested that the physical activity of students contributes to a constant process of resuspension of settled particles. Thus, the density of human occupancy also play an important role in worsening the indoor air quality in the schools. In school SA, the lower contribution of the coarser fraction to the total PM10 mass is mainly attributed to the use of whiteboards. This finding is explained by the low concentration of mineral matter, as detailed in section 3.2.2. Therefore, in school SA the PM size distributions among the size ranges (0.03–0.25, 0.25–0.5, 0.5–1.0, 1.0–2.5 and 2.5–10 μm) are not considerably different and there is no increased contribution of coarser particles (Figure 6.3).

Generally, in the outdoor of both homes and schools the highest mass concentrations of PM were found in the coarse fraction. This might be influenced by the high mineral and marine aerosol contributions in the study area, as described in section 3.2.2.

Apart from the highest contribution of particles with Dp <0.25 μm to the total PM10 mass in the indoor of the homes, this size range also constituted a high portion of the aerosol mass in the respective outdoor (21–43% of total PM10 mass) and in the indoor and outdoor of the schools (Figure 6.2); the values ranged from 7 to 29% and from 16 to 34% of the PM10 mass, respectively. A high contribution of the finest fractions to the outdoor PM mass may be either of primary origin (mainly emitted during combustion processes, such as traffic exhaust emissions) or of secondary origin, resulting from photochemical reactions (e.g. Berghmans et al., 2009; Chiang et al., 2012; Dall'Osto et al., 2012). Moreover, since the finer particles can easily penetrate deeply into the lungs (Rajput et al., 2019) and the people tend to spend more time indoors (Klepeis et al., 2001), the higher concentration of the finer particle size range content in the indoor aerosol may be important when considering the impact on human health.

The percentage content of PM0.25–0.5, PM0.5–1.0 and PM1.0–2.5 to the total PM10 mass varied both among locations and between indoor and outdoor microenvironments (Figure 6.2). The pattern of the particle mass size distribution was found to be heterogeneous not only among homes but also between indoor and outdoor microenvironments (Figure 6.3). Previous studies have stated that the particle mass size distributions change not only among sampling locations, but also over time and season (Fonseca et al., 2016; Pant et al., 2016). The PM mass size distribution obtained in this study provides essential data for determining particle dose in children, as demonstrated in Chalvatzaki et al. (2020).

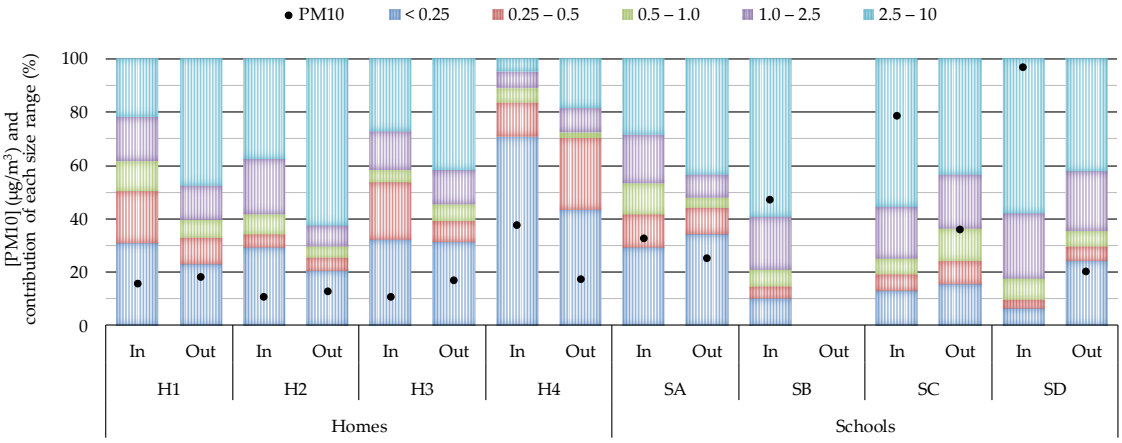

Figure 6.2 - PM10 concentrations and contribution of each size-fractionated PM (PM0.25, PM0.25–0.5, PM0.5–1.0, PM1.0–2.5, PM2.5–10) in the homes and schools. In – Indoor; Out – Outdoor.

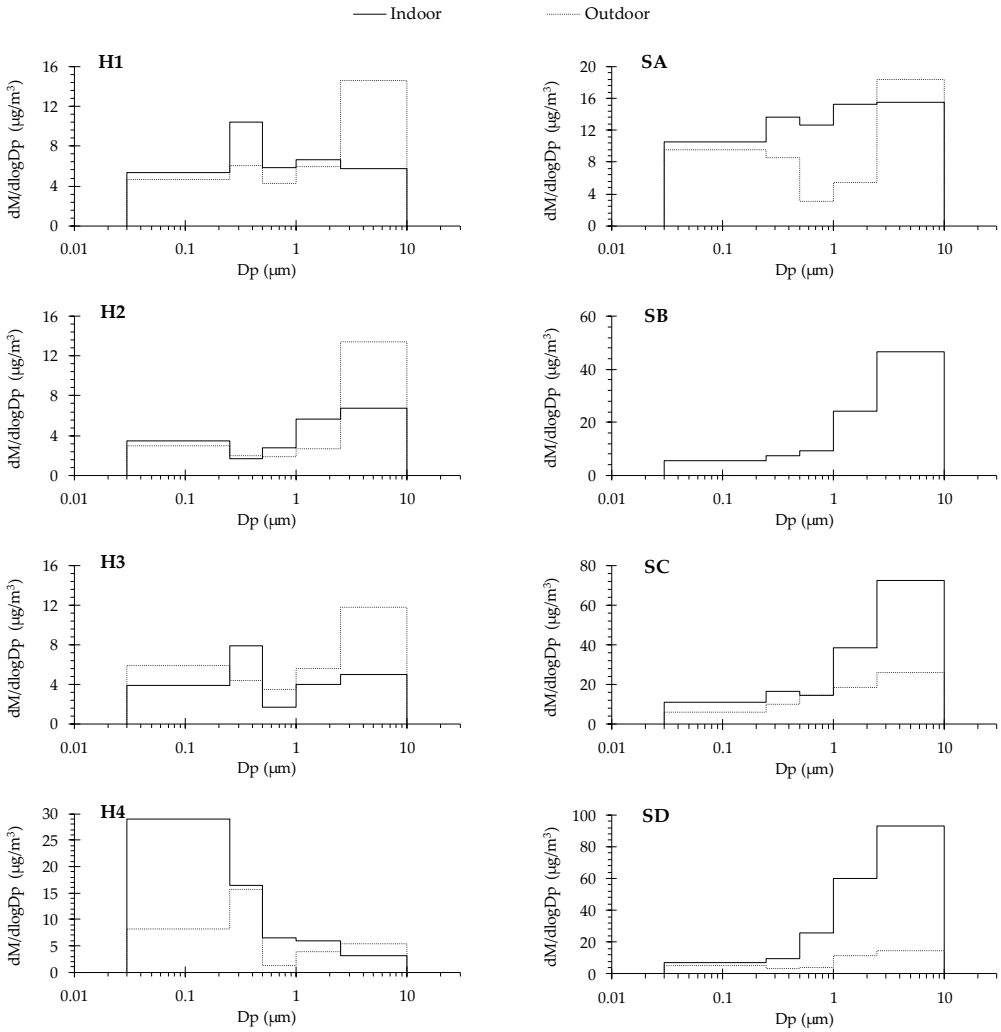

Figure 6.3 - PM mass size distribution in the homes and schools. Note that the scales are different.

3.1.2 Indoor–outdoor interplay

The I/O ratio has been shown to be an effective indicator to evaluate the relationship between the indoor PM concentrations and the corresponding outdoor concentrations. In the present study, this analysis was performed for each of the size ranges (Table S6.3, supplementary material). In general, the I/O ratio was larger than 1 for all size ranges in both homes and schools, with exception of PM2.5–10 for homes. I/O ratio above 1, in the size ranges for particles with Dp <2.5 µm, was probably attributed not only to their higher penetration efficiency, but also to the existence of considerable indoor sources of fine particles associated with the human activities. Even though most of the sampling time in homes was conducted during the sleeping hours, the high fine particle concentrations were considerably influenced by their lower deposition velocity. In homes the I/O ratio for PM2.5–10 varied between 0.4 and 0.6, evidencing not only the absence of indoor activities during the seeping hours, but also the protection of the building envelopes against the coarser particles coming from outdoors. The highest I/O ratios were observed in the schools. This may be associated with the elevated indoor human activities inside the classrooms that induce the generation and resuspension of particles. Reduction of indoor particle concentrations may be achieved by improving the ventilation conditions (Park et al., 2014).

6.3.2 PM chemical composition

The size-segregated chemical composition of the PM samples collected in the indoor and outdoor of both homes and schools is shown in Table 6.1. OC and EC were only analysed in the indoor samples.

Figure 6.4 depicts the average mass closure for the size-segregated PM (in %) in the indoor and outdoor of the homes and schools. The PM chemical components were grouped into five different categories, based on their chemical composition and source origin: marine aerosol (MA; sum of Na and Cl), mineral matter (MM; calculated as the sum of Mg, Al, Si, K, Ca and Fe), OC, EC and anthropogenic elements (AE; sum of S, Ti, V, Cr, Mn, Ni, Cu, Zn, As, Br, Sr, Ba and Pb). The mass size distributions of PM chemical components for home H1 and school SC are shown as example in Figure 6.5 and Figure 6.6, respectively. Using the mass size distribution of the chemical components, the geometric mean diameter (GMD) and the geometric standard deviation (GSD) for the homes and schools were calculated (Table 6.1).

In indoors, the undetermined fraction for the total PM10 mass varied between 46 and 80% in the homes and between 40 and 58% in the schools (Figure 6.4). These undetermined fractions can be explained by the presence of oxide species, heteroatoms from the carbonaceous compounds, water molecules (moisture, formation and crystallization water) and mineral components such as carbonates that have not been determined.

- Carbonaceous constituents

Carbonaceous aerosol is commonly divided into an OC and an EC fraction. OC represented the major contributor to PM in the indoor of the homes and schools for all size ranges (Figure 6.4) accounting on average for 14–69% of the total PM10 mass, except for the range 1.0–2.5 μm in schools where the Ca was generally the most abundant component (16%), closely followed by OC. These results are in agreement with the high levels of OC reported in other indoor microenvironments (Almeida-Silva et al., 2015; Alves et al., 2014; Jones et al., 2000; M. Viana et al., 2014). In general, the OC concentrations in the schools were significantly higher than in the homes ($p<0.05$) (Table 6.1). Exceptionally, for home H4 the concentrations of OC in PM0.25 and PM0.25–0.5 were considerably elevated, with values 7.4 and 6.3 times higher than those found in the remaining homes, respectively. For particles with Dp <0.25 μm, the EC represented the second largest PM component for both homes and schools (Table 6.1).

Studies have shown that the sources of carbonaceous aerosol can be distinguished by analysing the correlation between the OC and EC (Kumar et al., 2016; Wang et al., 2019; Wei et al., 2019). The linear regression analysis between OC and EC in the different particle size ranges is shown in Figure S6.1 of the supplementary material. A significant correlation was observed for PM2.5–10 (R=0.89), PM1.0–2.5 (R=0.83) and PM0.5–1.0 (R=0.77), indicating that they came from related sources or were transported to the measurement site simultaneously. The OC/EC ratio has been usually analysed for determining the type and source of the carbonaceous aerosols (Kumar et al., 2016; Novakov et al., 2005; Wei et al., 2019). The highest OC/EC ratios were observed for the PM0.25–0.5 and the lowest ratios were found in the finest fraction (PM0.25), in both homes and schools (Table S6.4, supplementary material). It has been referred in the study of Kumar et al. (2016) that the low OC/EC ratios (typically <2–3) are mainly associated with fossil fuel and vehicular emissions, which generate elevated EC and lower OC concentrations. Conversely, high OC/EC ratios represent the dominant contribution of biomass burning emissions. Moreover, the high OC/EC ratios may also be associated not only to the existence of indoor sources of organic compounds (such as skin debris, clothing fibres, cleaning products and waxes) (Almeida-Silva et al., 2015; Alves et al., 2014) but also to the formation of secondary organic carbon (Aoki and Tanabe, 2007; Jathar et al., 2013; Liu et al., 2015).

Size distributions of EC and OC may provide important information about the emission sources, formation, and growth mechanism of aerosol particles (Guo, 2015). Generally, OC size distributions showed a bimodal distribution, peaking in the size of 0.25–0.5 and 2.5–10 μm (Figure 6.5 and Figure 6.6). In homes the highest peak occurred for PM0.25–0.5, while in schools it was more evident in the coarser size range. EC size distributions revealed the highest peak at the lowest size range (PM0.25), both in the homes (Figure 6.5) and schools (Figure 6.6). This

result is in accordance with the findings of Hitzenberger and Tohno (2001) in Europe and of Wu et al. (2017) in China, which showed that the EC mass in urban environment mostly occurred in the fine fraction, peaking at the sizes of 0.15 and 0.2 μm, respectively. Additionally, in schools a secondary EC peak was observed in the coarser size range, although with a low mass fraction.

OC and EC in the fine mode are emitted directly into the atmosphere predominantly during incomplete combustion emissions, such as vehicular exhaust, coal combustion, and biomass burning (Guo, 2015; Salma et al., 2017). According to Chen et al. (2013), fossil source may be relatively more important for urban areas and biomass burning may have great influence on rural areas. EC is considered a good indicator of primary anthropogenic sources since it has limited chemical transformations (Pio et al., 2011). Guo (2015) analysed OC and EC data collected over urban and rural areas of northern China and also verified that the mass median aerodynamic diameter (MMAD) in the fine particles for OC was higher than that for EC. Alves et al. (2015) have determined specifically the size-segregated PM emissions from motor vehicles and verified that the MMAD for EC and OC were 0.17 and 0.32 μm, respectively. These results may suggest that EC and OC present in the fine particle fractions (PM0.25 and PM0.25–0.5, respectively) are related to traffic exhaust emissions that penetrate inside of both homes and schools. This association can be confirmed with the strong linear correlation (R=0.96) between the values of EC in PM0.25 and the OC in PM0.25–0.5 (Figure S6.2, supplementary material).

The OC and EC showed high correlation with mineral matter for PM2.5–10 (R=0.96 for OC and 0.95 for EC; Figure S6.3, supplementary material). Rivas et al. (2014b) have linked this behaviour to dry and wet deposition of OC on the floor and to their possible retention by adsorption on mineral elements. Therefore, OC is jointly resuspended with the mineral matter. Moreover, Glaser et al. (2005) found that road dust samples had a significant contribution of tire abrasion and exhaust emissions to BC and evidenced that this contribution varied with distance to the highway (BC concentrations decreased with increasing distance to the highway). Thus, in the present study the peaks of OC and EC in the coarse mode may be explained by their aggregation to the coarser particles deposited on the surfaces, which are resuspended with people's movement. In the schools, the OC was more enriched in the coarse mode probably due to the higher occupancy and consequent elevated children's activity in the classroom.

- Major and trace elements

Inorganic elements (IE) including Na, Mg, Al, Si, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Br, Sr, Ba and Pb in the indoor and outdoor size-segregated particles collected both in the homes and schools were analysed (Table 6.1). On average, the concentration of inorganic elements in the homes were 2.4 and 3.1 μg/m^3 and in the schools were 12.0 and 6.1 μg/m^3, for the indoor and outdoor microenvironments, respectively. The IE concentrations in the schools

were significantly higher than in the homes ($p<0.05$), for both indoor and outdoor microenvironments.

Generally, the concentrations of IE increased with increasing particle aerodynamic diameter in the indoor and outdoor microenvironments of both homes and schools. Moreover, usually the coarse particles contained higher percentages of crustal elements while fine particles had higher percentages of anthropogenic elements.

- Mineral matter

Mineral elements (sum of Al, Si, K, Ca, Fe and Mg) were the main inorganic elements in the indoors and outdoors of both sampling sites. Numerous studies have reported that the presence of mineral elements in PM is mainly associated to soil and city dust resuspension processes and Saharan dust intrusions (Pey et al., 2009). Some part of the crustal material can also be related to construction and demolition activities and road dust (Balasubramanian et al., 2003). Artíñano et al. (2001) indicated that in the Iberian Peninsula there are factors that favour the resuspension of dust, such as the dryness and semi-arid soil associated with the high convective atmospheric dynamics. Thus, high levels of crustal material may be associated with both local and regional origin due to high convective dynamics and low rainfall. The chemical and mineralogical composition of these particles varies from one region to another, depending on the characteristics and the constitution of the soil (Calvo et al., 2013).

The contribution of mineral matter (MM) to IE usually increased with increasing PM size. In fact, in indoor of the homes (excluding the home H4; details further below) the MM accounted for about 32–38% of the mass of the IE in PM0.25, 48–61% of the mass of the IE in PM0.25–0.5, 52–75% of the mass of the IE in PM0.5–1.0, 58–83% of the mass of the IE in PM1.0–2.5 and 36–62% of the mass of the IE in PM2.5–10; in indoor of the schools the percentage of mass of the IE ranged from 48 to 71, 63 to 85, 70 to 93, 78 to 92 and 81 to 94 % in PM0.25, PM0.25–0.5, PM0.5–1.0, PM1.0–2.5, and PM2.5–10, respectively. This study evidenced that generally the coarser the PM size the higher the percentage of mineral elements, as observed by Hassanvand et al. (2015). On the contrary, in the indoor of home H4 the highest contribution of MM for the total PM10 mass was observed for the finest size range <0.25 (39.8%). This finding revealed that indoor sources may be major contributors to typically mineral elements such as K, Al, Si, Ca and Fe in particles with Dp <0.25 μm, and thus the sources of these elements in ultrafine particles should be further explored. The mass size distribution of mineral elements were dominated by super-micron particles (Dp >1.0 μm; Figure 6.5 and Figure 6.6). Moreover, in indoors the peak occurred generally with more consistently in the range 1.0–2.5 μm for homes, while it is more evident in the coarser fraction for schools. In outdoors the peak is mostly present also in the coarser fraction.

Concentrations of MM in the homes and schools are given in Table S6.1 and Table S6.2 (supplementary material), respectively. In indoors, the concentrations of MM in the homes were significantly lower than those found in the schools ($p<0.05$). The MM concentrations were from 1.1 (for PM0.25) up to 14 (for PM2.5–10) times higher in the schools than in the homes. The highest difference between the levels of MM for PM2.5–10, accounted for 0.4 μg/m^3 in home and 5.6 μg/m^3 in school, evidencing that the high MM contents may enter from playground or road dust. In outdoors, the concentrations of MM were also higher in the schools than in the homes for all size ranges, but with much lower significance (on average 2.4 times higher). Besides the home samples comprised a considerable amount of time (sleeping hours) with no people's activities, these differences may also be associated to the close proximity of the schools to the busy roads and to the elevated human occupancy, which promotes particle resuspension. Faria et al. (2020) determined the time-activity pattern of schoolchildren from Lisbon and found that most children go to school by private car; favouring the congestion on the roads near the schools. Apart from playground and road dust resuspension and entrainment towards the classroom by children, one additional source of MM is suggested in indoor air by the slightly higher ratio of Ca/Al (12.5) obtained in comparison to outdoor (3.6). This might suggest the presence of an additional source of Ca in indoor air, which could be related to the use of chalk on blackboards, as also identified by Viana et al. (2014) in Spanish schools. In the school SA the concentration of Ca was between 58 and 85% lower than in the remaining schools, coinciding with the use of markers on whiteboards.

Particularly, despite its usually large grain size distribution, K also showed a relevant peak across the fine range between 0.25 and 0.5 μm (Figure 6.5 and Figure 6.6). The presence of K in fine particles could be explained by the contribution of different combustion sources, including traffic engine emissions, given that this element is also ingredient of lubricant oil additives, and biomass burning emissions (Eleftheriadis et al., 2014; A. L. Miller et al., 2007; Yamasoe et al., 2000; Zwozdziak et al., 2017).

- Anthropogenic elements

In indoor of the homes the anthropogenic elements (sum of S, Ti, V, Cr, Mn, Ni, Cu, Zn, As, Br, Sr, Ba and Pb) contributed 6.6–11% to the mass of the IE in PM2.5–10, 8.5–12% to the mass of the IE in PM1.0–2.5, 9.9–18% to the mass of the IE in PM0.5–1.0, 16–50% to the mass of the IE in PM0.25–0.5 and 18–67% to the mass of the IE in PM0.25; in indoor of the schools the percentage of mass of the IE ranged from 2.9 to 5.4, 2.8 to 7.6, 3.0 to 12, 9.1 to 33 and 28 to 51 % in PM2.5–10, PM1.0–2.5, PM0.5–1.0, PM0.25–0.5, and PM0.25, respectively. This study evidenced that the finer the PM size the higher the percentage of anthropogenic elements. Concentrations of anthropogenic elements in the homes and schools are given in Table S6.1 and

Table S6.2 (supplementary material), respectively. Generally, the concentrations of anthropogenic elements in the school microenvironment were significantly higher than in homes, especially for the coarse particles (PM2.5–10), with concentrations on average 4 times higher. In outdoor air, the concentrations of anthropogenic elements were also higher in the schools than in the homes for all size ranges. These differences may be due to the close proximity of the schools to busy roads and to the elevated human occupancy that promotes the generation of particles. Moreover, it should be noted that the sampling was carried out during the occupied period; in the schools during the school hours (daytime) and in homes majority in the night-time, as described in section 2.3. This approach surely affected both the outdoor and the indoor measured concentrations.

Distinct size distribution patterns were observed for the anthropogenic elements, with no element showing a prevalence in PM0.25 and the majority being distributed above 1.0 µm. The collected mass load for the majority of the finer size ranges (<0.25, 0.25–0.5 and 0.5–1.0) was not enough to be detected by XRF analysis (as shown in Table 6.1). Thus, no clear size distribution patterns could be drawn. Nevertheless, this indicates that the concentrations of anthropogenic elements in the fine fractions are low, and unlikely to pose a health risk. To obtain further insight of anthropogenic elements in size segregated particles, the analysis should employ a more sensitive method, or the sampled volume should be increased, although the time resolution would be limited.

- Marine aerosol

The marine aerosol contribution was relatively small for particles <0.5 µm, accounting for 0.11–0.79% of the total PM0.5 mass indoors, and consisting mainly of Cl. An indoor source of fine Cl particles such as cleaning products may influence this contribution. Inside the home H4 the concentrations of Cl in PM0.25 were between 41 and 77 times higher than in the other homes.

A contribution of marine aerosol between 1 and 13% was evident for particles with Dp >0.5 µm by the linear correlation of Na and Cl (R=0.94; Figure S6.4, supplementary material), probably associated to the close proximity to the Atlantic coast. This result may be intensified due to the dominant western wind regime, influenced by the presence of the semi-permanent Azores high-pressure and the Icelandic low-pressure systems over the North Atlantic Ocean. The results confirm that the marine aerosol is dominantly in the coarse mode, as demonstrated by Almeida et al. (2006).

6.3.3 Indoor–outdoor interplay

Remarkably different behaviours were observed when the concentrations of indoor inorganic elements were compared with concentrations of outdoor inorganic elements. Correlation

coefficients (R) of the inorganic elements measured in both sampling sites are presented in Table S5 (supplementary material). The indoor concentrations of mineral and marine elements were considerably correlated with outdoor levels ($0.78<R<0.91$), with exception of the Na ($R=0.69$) and Ca ($R=0.62$). The correlation coefficient between Ca concentrations outdoors and in living rooms of the homes ($R=0.77$) were rather stronger than the correlation in the schools between concentrations outdoors and those of the classrooms ($R=0.60$). This result suggests that the correlation coefficients depend on the presence of major indoor particulate sources since the contributions from indoor Ca sources dominate in classrooms due to the use of chalk on blackboards, as previously described. The elements most poorly correlated were Cu ($R=0.22$), Ba ($R=0.17$), Ni ($R=0.12$) and Br ($R=0.01$), evidencing that they have different origins in the indoor and outdoor environments.

In terms of I/O ratio, the anthropogenic elements presented values slightly higher than 1 for all size ranges, excepting for PM2.5–10 in homes, where the concentrations indoors were half of those outdoors (Table S6.3, supplementary material). These results may suggest that outdoor air infiltration and primary particles emitted indoors were the main sources of anthropogenic elements found indoors. Anthropogenic elements such as S, Sr, Cu, Ba, Cr, Ni, Zn, Mn and Pb, may have been emitted from road traffic in the form of exhaust emissions, as well as through releases associated to the wear of automotive components such as brakes, tyres and catalytic converters (Hjortenkrans et al., 2007; Lough et al., 2005; Prichard and Fisher, 2012; Sternbeck et al., 2002; Thorpe and Harrison, 2008; Wiseman et al., 2013). Moreover, although the marketing of leaded gasoline was banned in the EU as of January 2000, Pacyna et al. (2007) indicated that there is still lead content as an impurity in the so-called unleaded gasoline due to the lead content of crude oil. Thus, the combustion of gasoline is still considered an important source of lead due to the huge amount of fuel consumed. In addition, other studies have also demonstrated that resuspension of soil previously contaminated with Pb, associated to use of leaded fuel, is a significant source of Pb in several urban areas (Lough et al., 2005; Young et al., 2002). V and Ni are also released in the fuel oil combustion in several industrial processes, as well as shipping (Jang et al., 2007; Querol et al., 2009). Nowadays, as Lisbon is becoming an important port of call for cruises, shipping may be a significant emission source of these elements. Moreover, aircraft engines are also associated to the emission of metal particles, such as Al, Ti, Cr, Fe, Ni, and Ba (Fordyce and Sheibley, 1975).

Table 6.1 - Elemental concentration (arithmetic mean ± standard deviation; in ng/m^3) in the size-segregated PM and respective geometric mean diameter and standard deviation (GMD ± GSD; in µm), in the homes and schools.

		Homes						Schools					
		< 0.25	0.25 – 0.5	0.5 – 1.0	1.0 – 2.5	2.5 – 10	GMD ± GSD	< 0.25	0.25 – 0.5	0.5 – 1.0	1.0 – 2.5	2.5 – 10	GMD ± GSD
Na	I	<LoD	17.0 ± –	31.2 ± 23.7	39.2 ± 12.6	80.6 ± 41.5	2.6 ± 2.2	<LoD	<LoD	50.1 ± 4.7	114.4 ± 69.8	158.4 ± 124.6	2.7 ± 1.9
	O	<LoD	15.0 ± –	16.5 ± 0.5	29.7 ± 12.9	180.2 ± 81.0	4.0 ± 1.6	<LoD	39.3 ± 25.2	75.7 ± 42.6	136.5 ± 26.7	161.2 ± 57.1	3.0 ± 1.9
Mg	I	<LoD	<LoD	<LoD	<LoD	2.6 ± 2.0	5.0 ± 1.0	<LoD	<LoD	<LoD	<LoD	10.1 ± 17.1	5.0 ± 1.0
	O	<LoD	<LoD	<LoD	21.3 ± 15.9	18.8 ± 7.9	3.5 ± 1.6	<LoD	<LoD	<LoD	56.1 ± 2.3	23.7 ± 27.7	3.3 ± 1.5
Al	I	32.9 ± 5.1	13.0 ± 13.9	30.0 ± 40.9	38.8 ± 34.6	25.9 ± 26.8	1.4 ± 2.8	61.8 ± 18.7	20.8 ± 18.7	59.9 ± 51.4	146.8 ± 122.5	284.6 ± 182.5	2.1 ± 3.3
	O	17.3 ± 12.8	31.0 ± –	5.5 ± 0.4	34.1 ± 48.6	42.8 ± 35.2	1.9 ± 3.4	78.7 ± 35.6	15.3 ± –	37.1 ± 23.4	111.2 ± 36.9	157.2 ± 72.9	1.9 ± 3.4
Si	I	62.0 ± 17.7	24.8 ± 19.7	70.1 ± 72.4	94.0 ± 66.4	89.0 ± 60.1	1.5 ± 3.1	29.3 ± 18.7	53.0 ± 57.8	135.5 ± 104.8	296.5 ± 242.4	669.9 ± 452.7	2.6 ± 2.4
	O	10.5 ± –	39.5 ± 37.5	16.3 ± 7.8	78.7 ± 96.3	134.2 ± 93.1	2.7 ± 2.3	89.8 ± –	93.7 ± –	82.8 ± 45.7	238.5 ± 76.3	333.6 ± 210.7	2.3 ± 2.4
S	I	196.5 ± 116.1	66.6 ± 64.3	23.8 ± 10.4	38.9 ± 10.6	42.7 ± 15.2	0.3 ± 4.4	170.2 ± 110.1	72.1 ± 30.4	29.9 ± 7.4	52.5 ± 20.4	88.3 ± 29.8	0.6 ± 4.7
	O	168.4 ± 83.5	46.2 ± 21.3	16.0 ± 11.0	31.6 ± 5.9	79.9 ± 17.3	0.4 ± 5.3	184.9 ± 94.0	71.9 ± 39.6	28.6 ± 21.5	56.8 ± 37.6	99.4 ± 50.3	0.6 ± 4.7
Cl	I	36.3 ± 67.9	16.0 ± 17.1	36.9 ± 16.0	93.5 ± 37.0	252.2 ± 158.6	2.4 ± 2.8	7.0 ± 1.6	29.5 ± 21.6	92.5 ± 47.3	189.0 ± 81.5	466.0 ± 343.9	2.5 ± 2.4
	O	4.1 ± 2.3	12.5 ± 7.0	30.0 ± 22.5	103.3 ± 54.1	674.7 ± 443.7	3.6 ± 2.0	8.4 ± 5.2	14.5 ± 20.0	129.4 ± 124.7	246.3 ± 211.6	770.6 ± 563.4	3.2 ± 2.2
K	I	164.5 ± 190.3	55.5 ± 28.1	18.5 ± 10.3	25.1 ± 8.1	25.5 ± 12.3	0.4 ± 3.9	113.7 ± 97.4	84.6 ± 88.5	32.6 ± 24.0	52.7 ± 32.6	126.6 ± 111.0	0.8 ± 4.6
	O	91.7 ± 57.0	59.1 ± 44.8	14.5 ± 6.6	25.6 ± 12.6	54.7 ± 10.4	0.6 ± 4.8	137.0 ± 100.1	82.4 ± 12.4	29.4 ± 4.6	59.3 ± 16.0	105.9 ± 46.3	0.7 ± 4.6
Ca	I	14.9 ± 11.2	16.8 ± 2.8	56.8 ± 20.0	161.5 ± 37.4	185.0 ± 85.5	2.0 ± 2.6	66.6 ± 38.5	202.0 ± 229.9	723.3 ± 859.6	2166.7 ± 2561.8	4035.3 ± 2205.4	2.8 ± 2.2
	O	5.9 ± 2.8	10.0 ± 3.0	30.4 ± 6.3	117.0 ± 35.1	375.7 ± 76.2	3.2 ± 2.2	36.6 ± 28.0	44.0 ± 29.2	108.6 ± 53.5	402.7 ± 142.3	862.0 ± 361.9	2.7 ± 2.4
Ti	I	2.0 ± –	1.6 ± 1.1	2.7 ± 2.9	5.4 ± 3.2	4.6 ± 2.8	1.7 ± 2.5	7.4 ± –	6.8 ± 3.8	13.5 ± 10.9	40.0 ± 36.7	80.3 ± 38.5	2.7 ± 2.3
	O	<LoD	1.6 ± 1.8	2.2 ± 1.1	5.6 ± 3.9	8.5 ± 3.6	2.3 ± 2.4	4.6 ± 3.0	3.0 ± 1.4	5.8 ± 4.3	23.5 ± 16.4	42.5 ± 33.2	2.5 ± 2.5
V	I	3.2 ± –	1.1 ± –	<LoD	<LoD	0.3 ± 0.1	3.8 ± 1.6	<LoD	1.0 ± –	<LoD	<LoD	0.2 ± 0.0	3.9 ± 1.4
	O	1.8 ± –	0.8 ± 0.7	1.2 ± –	1.0 ± 0.8	0.8 ± 0.6	2.9 ± 2.7	<LoD	0.6 ± –	<LoD	<LoD	0.2 ± 0.1	3.6 ± 1.7
Cr	I	1.5 ± –	0.6 ± 0.1	0.4 ± –	0.7 ± 0.1	0.3 ± 0.1	1.1 ± 2.9	4.5 ± –	0.6 ± –	0.5 ± –	1.4 ± 1.2	2.6 ± 0.9	2.4 ± 3.0
	O	1.3 ± 0.3	0.5 ± 0.1	0.4 ± 0.2	0.7 ± 0.2	1.2 ± 0.4	1.2 ± 4.2	5.4 ± –	<LoD	0.9 ± 0.3	1.5 ± 1.0	1.3 ± 0.5	1.9 ± 3.0
Mn	I	2.3 ± 0.2	1.9 ± –	1.7 ± 0.5	1.1 ± 0.3	1.4 ± 0.8	2.3 ± 2.9	5.4 ± –	2.2 ± –	3.0 ± 1.5	9.9 ± 8.5	8.3 ± 5.6	3.2 ± 2.1
	O	3.2 ± –	<LoD	1.1 ± 0.4	1.7 ± 0.6	4.2 ± 1.6	2.8 ± 2.7	7.4 ± –	<LoD	2.2 ± –	6.1 ± –	4.7 ± 1.7	2.8 ± 2.9
Fe	I	14.6 ± 8.1	24.2 ± 17.1	48.6 ± 29.3	95.0 ± 40.8	67.9 ± 39.0	1.4 ± 2.9	18.4 ± 2.2	41.8 ± 22.6	97.6 ± 77.6	268.7 ± 244.7	468.5 ± 257.0	2.4 ± 2.5
	O	7.8 ± 4.2	31.4 ± 16.9	53.3 ± 15.1	129.3 ± 44.9	245.6 ± 66.1	2.3 ± 2.6	27.2 ± 30.5	53.7 ± 42.0	105.5 ± 86.9	309.6 ± 234.8	395.2 ± 63.5	2.2 ± 2.6
Ni	I	1.8 ± –	0.4 ± –	<LoD	<LoD	0.2 ± 0.0	3.8 ± 1.6	<LoD	<LoD	<LoD	1.7 ± –	0.8 ± 0.7	4.5 ± 1.2
	O	1.3 ± –	<LoD	<LoD	<LoD	0.6 ± 0.3	3.9 ± 2.6	<LoD	<LoD	<LoD	<LoD	0.4 ± 0.2	5.0 ± 1.0
Cu	I	8.0 ± 4.7	3.6 ± 3.2	4.5 ± 2.0	4.1 ± 1.7	2.1 ± 1.1	0.7 ± 3.5	18.1 ± –	7.3 ± 5.4	6.3 ± 7.4	5.9 ± 7.1	2.9 ± 4.5	1.5 ± 2.1
	O	5.9 ± 4.8	3.0 ± 2.0	4.6 ± 2.2	5.8 ± 2.7	7.7 ± 2.8	1.5 ± 3.2	32.8 ± –	3.7 ± 2.8	5.8 ± 5.2	7.3 ± 6.1	5.5 ± 0.9	1.2 ± 3.1
Zn	I	4.5 ± 1.5	5.3 ± 2.6	3.2 ± 1.0	3.9 ± 1.1	3.3 ± 1.9	0.6 ± 3.8	9.3 ± 6.8	9.3 ± 2.3	7.3 ± 1.6	15.6 ± 5.1	28.7 ± 22.5	1.3 ± 3.9
	O	3.9 ± 1.0	5.2 ± 1.7	3.0 ± 1.0	3.7 ± 0.9	9.3 ± 3.6	1.0 ± 4.3	8.0 ± 3.3	8.7 ± 4.7	5.0 ± 1.8	8.6 ± 3.5	12.4 ± 4.1	1.0 ± 4.2
As	I	<LoD	<LoD	<LoD	<LoD	0.4 ± 0.0	5.0 ± 1.0	<LoD	<LoD	<LoD	<LoD	0.4 ± 0.0	5.0 ± 1.0
	O	<LoD	<LoD	<LoD	<LoD	0.4 ± 0.0	5.0 ± 1.0	<LoD	<LoD	<LoD	<LoD	0.4 ± 0.0	5.0 ± 1.0
Br	I	3.1 ± 1.8	1.1 ± 0.3	<LoD	<LoD	0.9 ± 0.3	1.6 ± 3.5	7.1 ± 3.4	1.7 ± 0.4	<LoD	<LoD	1.5 ± 0.9	2.6 ± 2.6
	O	1.7 ± 0.2	1.3 ± 0.5	<LoD	<LoD	2.3 ± 1.2	2.0 ± 4.4	3.0 ± –	<LoD	<LoD	<LoD	3.6 ± 2.6	3.4 ± 2.5
Sr	I	<LoD	<LoD	<LoD	0.5 ± –	0.6 ± 0.2	4.5 ± 1.2	<LoD	<LoD	2.9 ± –	5.5 ± 6.7	9.2 ± 6.2	4.0 ± 1.5
	O	<LoD	0.7 ± –	<LoD	0.9 ± –	1.2 ± 0.4	3.6 ± 1.9	<LoD	<LoD	<LoD	1.1 ± –	2.4 ± 1.1	4.6 ± 1.2
Ba	I	<LoD	<LoD	<LoD	8.1 ± –	1.7 ± 1.3	4.2 ± 1.1	<LoD	<LoD	<LoD	11.7 ± –	12.3 ± 10.4	4.6 ± 1.2
	O	<LoD	<LoD	5.3 ± –	5.6 ± –	6.2 ± 1.6	3.7 ± 1.6	<LoD	<LoD	<LoD	12.1 ± –	19.3 ± 19.7	3.9 ± 1.1
Pb	I	8.2 ± 0.2	3.4 ± 2.1	3.2 ± 0.4	3.2 ± –	1.6 ± 1.1	1.8 ± 2.5	15.4 ± –	8.5 ± –	6.8 ± –	8.5 ± –	5.1 ± 9.5	3.8 ± 1.6
	O	7.5 ± –	2.2 ± 1.0	3.4 ± 0.8	3.1 ± 0.5	3.8 ± 1.2	1.5 ± 3.3	26.1 ± –	<LoD	5.2 ± –	<LoD	2.9 ± 4.5	2.0 ± 1.4
OC	I	4027.9 ± 4748.9	1883.8 ± 2095.3	435.8 ± 320.9	462.0 ± 222.4	848.0 ± 277.1	0.4 ± 4.4	3799.5 ± 947.5	1510.4 ± 345.5	903.2 ± 228.8	1914.5 ± 978.0	9171.6 ± 3005.8	1.3 ± 5.2
	O	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
EC	I	661.0 ± 300.4	26.0 ± 22.7	18.2 ± 12.4	20.5 ± 12.3	37.5 ± 18.5	0.1 ± 2.8	822.8 ± 102.5	59.3 ± 42.9	77.4 ± 46.8	87.4 ± 41.0	453.6 ± 215.7	0.4 ± 6.0
	O	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA

I Indoor; O Outdoor; <LoD Below limit of detection; NA Not analysed;

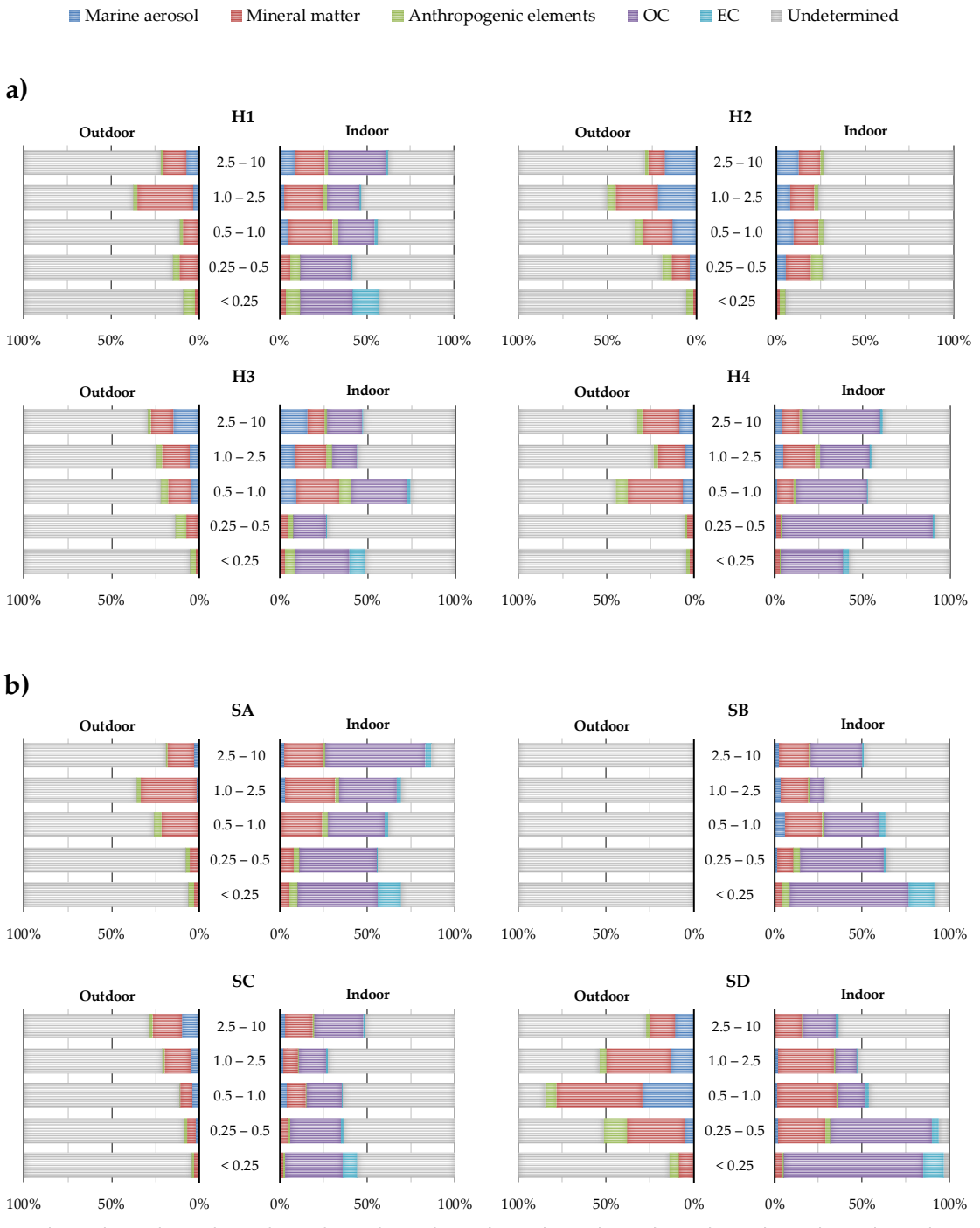

Figure 6.4 - Average mass closure of PM (in %) in 5 aerodynamic diameter ranges (<0.25; 0.25 to 0.5; 0.5 to 1.0; 1.0 to 2.5; and 2.5 to 10 µm) in the indoor and outdoor of the **a)** homes and **b)** schools. OC and EC data only available for indoors. Unavailable data for outdoor of school SB and for OC and EC in home H2.

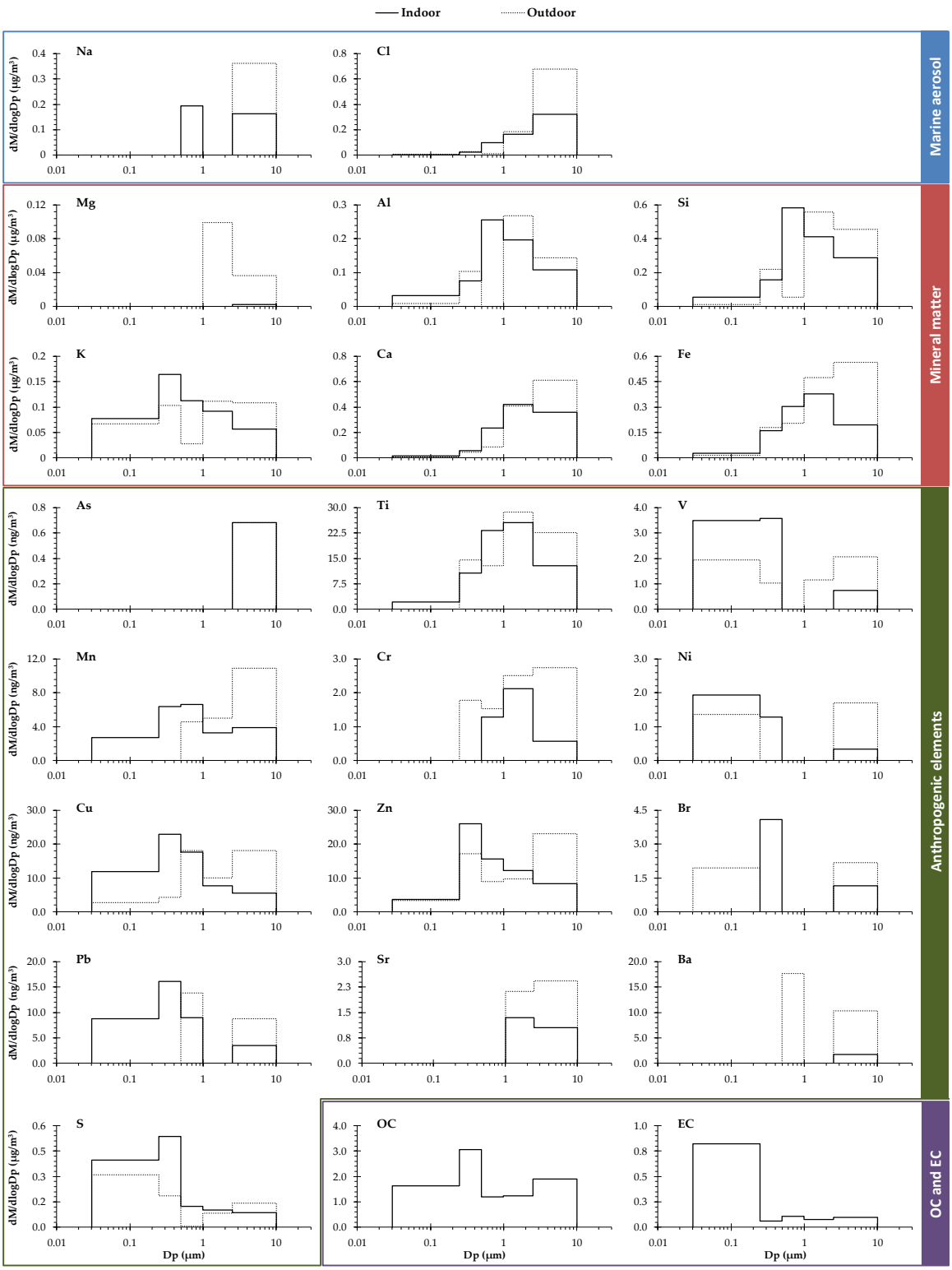

Figure 6.5 - Mass size distribution of PM chemical components in the home H1. Note that the scales and units are different. OC and EC data only available for indoor

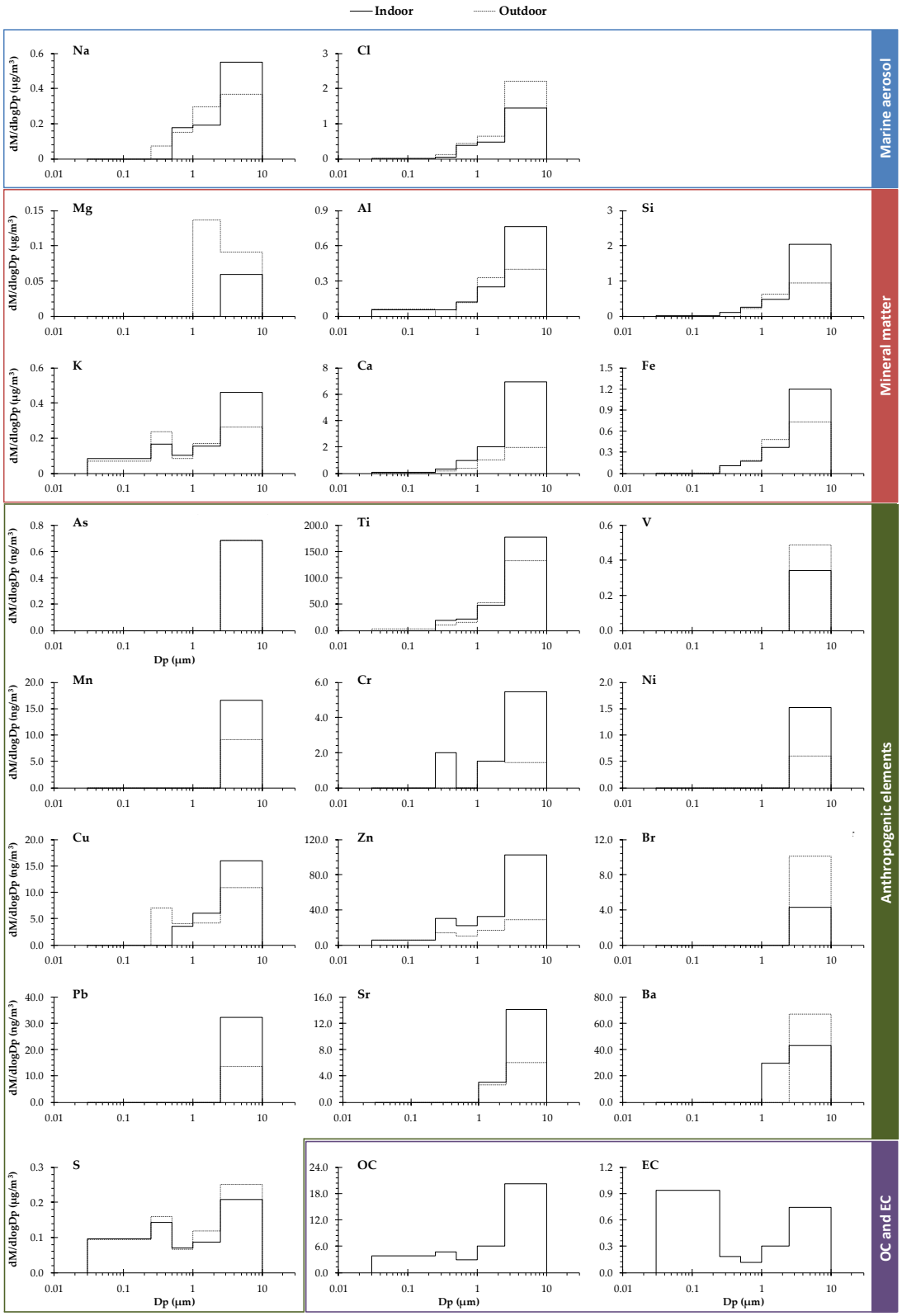

Figure 6.6 - Mass size distribution of PM chemical components in the school SC. Note that the scales and units are different. OC and EC data only available for indoor.

6.4 Conclusions

The mass concentration and chemical composition of size-segregated particles (PM0.25, PM0.25–0.5, PM0.5–1.0, PM1.0–2.5 and PM2.5–10) were determined in indoor and outdoor of homes and schools in Lisbon (Portugal). The main findings from this work may be summarised as follows:

- Typically, the children were exposed to significantly higher PM concentrations in school than in home, with organic carbon and mineral matter as main contributors (OC = 27% and 36% of the total PM10 mass inside schools and homes, respectively; MM = 16% and 7% inside schools and homes, respectively). The highest contributions of MM observed in schools were associated not only to the elevated particle resuspension but also to the indoor source of Ca related to the use of chalk on blackboards.
- The high PM0.25 content measured inside homes (30–71% of the total PM10 mass) may be important when considering the impact on human health. In schools, the coarser size ranges accounted for the largest mass fraction of PM10 (28–59%).
- The indoor PM concentrations were frequently higher than those outdoors for all size ranges, except for PM2.5–10 in homes. Human activity and outdoor infiltration are the main sources associated to indoor PM.
- The pattern of the particle mass size distribution was dependent on the location, not only between home and school, but also comparing indoor and outdoor microenvironments.
- A bimodal distribution of OC and EC was observed inside the schools. The presence of these carbonaceous compounds in the fine fraction was linked to primary sources (e.g. traffic exhaust emissions) while in the coarse fraction they showed good correlations with mineral matter, suggesting their resuspension by human activity. EC in homes only showed a unimodal distribution.
- The strong impact of EC in particles with Dp <0.25 μm was very relevant (10% in terms of total PM0.25 mass).
- Generally, the concentrations of mineral and marine elements increased with increasing PM size, while for anthropogenic elements happened the opposite.
- In the schools the concentrations of mineral matter, anthropogenic elements and marine aerosol were higher than in the homes, for both indoor and outdoor microenvironments.
- A unimodal distribution was detected for mineral elements and marine aerosol. Different size distributions were observed for certain species (e.g. K and Cl partition in a fine mode).
- Toxic and carcinogenic species (such as As, Cr, Pb, V and Ni) showed consistently very low concentrations for the size ranges with Dp <2.5 μm. This might be of particular relevance for epidemiological studies.

Besides characterising the particles and identifying possible sources, the results reported may be useful to establish practical air pollution mitigation strategies in indoor spaces. Moreover, the PM mass size distribution provides essential data for determining particle dose in children.

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Supplementary material

Table S6.1- Concentrations of PMx and its chemical compounds in the indoor and outdoor of the homes.

		Particle size (µm)	PMx (µg/m3)	MA (ng/m3)	MM (ng/m3)	AE (ng/m3)	OC (ng/m3)	EC (ng/m3)
H1	Indoor	< 0.25	5.0	1.8	190.8	396.8	1493.0	755.5
		0.25-0.5	3.1	7.5	184.1	189.1	917.4	17.9
		0.5-1	1.8	88.3	448.6	59.1	361.8	32.0
		1-2.5	2.6	64.6	595.7	61.4	491.5	30.8
		2.5-10	3.5	292.4	605.7	76.3	1141.8	58.0
		< 10	16.0	454.5	2024.9	782.8	4405.5	894.1
	Outdoor	< 0.25	4.3	6.1	100.9	296.2	NA	NA
		0.25-0.5	1.8	7.8	195.3	67.2	NA	NA
		0.5-1	1.3	3.8	111.7	24.8	NA	NA
		1-2.5	2.4	72.9	763.8	56.7	NA	NA
		2.5-10	8.8	625.9	1156.9	149.6	NA	NA
		< 10	18.5	716.4	2328.6	594.5	NA	NA
H2	Indoor	< 0.25	3.2	2.0	65.0	104.0	NA	NA
		0.25-0.5	0.5	27.1	69.7	33.4	NA	NA
		0.5-1	0.8	81.2	113.9	24.8	NA	NA
		1-2.5	2.3	177.6	307.9	47.7	NA	NA
		2.5-10	4.0	503.1	501.1	80.0	NA	NA
		< 10	10.8	791.0	1057.8	290.0	NA	NA
	Outdoor	< 0.25	2.7	1.6	52.3	100.1	NA	NA
		0.25-0.5	0.6	22.2	63.3	31.0	NA	NA
		0.5-1	0.6	74.7	90.3	26.7	NA	NA
		1-2.5	1.0	225.4	251.3	49.4	NA	NA
		2.5-10	8.1	1439.5	760.0	131.8	NA	NA
		< 10	13.0	1763.5	1217.1	338.9	NA	NA
H3	Indoor	< 0.25	3.5	3.4	104.0	200.0	1084.4	324.7
		0.25-0.5	2.4	5.1	109.3	64.0	446.1	8.4
		0.5-1	0.5	45.7	120.7	36.1	158.3	8.0
		1-2.5	1.6	135.4	283.6	55.6	226.3	6.9
		2.5-10	3.0	462.5	295.2	53.3	591.3	22.0
		< 10	11.0	652.1	912.7	409.0	2506.4	370.1
	Outdoor	< 0.25	5.4	2.7	103.3	193.3	NA	NA
		0.25-0.5	1.3	12.8	84.2	83.9	NA	NA
		0.5-1	1.0	48.8	139.5	45.3	NA	NA
		1-2.5	2.2	122.6	348.4	68.8	NA	NA
		2.5-10	7.1	1072.7	897.3	129.4	NA	NA
		< 10	17.1	1259.5	1572.7	520.7	NA	NA
H4	Indoor	< 0.25	26.6	138.2	605.8	162.8	9506.4	902.8
		0.25-0.5	5.0	41.4	123.3	32.0	4287.9	51.5
		0.5-1	1.9	26.0	182.4	29.7	787.2	14.5
		1-2.5	2.3	113.9	430.8	61.8	668.1	23.8
		2.5-10	1.8	73.1	181.1	30.6	811.0	32.6
		< 10	37.7	392.6	1523.4	316.9	16060.6	1025.2
	Outdoor	< 0.25	7.5	5.9	210.1	131.0	NA	NA
		0.25-0.5	4.7	22.3	169.3	54.5	NA	NA
		0.5-1	0.4	25.6	127.3	26.6	NA	NA
		1-2.5	1.5	81.2	238.9	36.2	NA	NA
		2.5-10	3.2	281.3	673.0	93.1	NA	NA
		< 10	17.4	416.3	1418.6	341.4	NA	NA

MA Marine aerosol; MM Mineral matter; AE Anthropogenic elements; NA Not analysed;

Table S6.2 - Concentrations of PMx and its chemical compounds in the indoor and outdoor of the schools.

		Particle size (µm)	PMx (µg/m3)	MA (ng/m3)	MM (ng/m3)	AE (ng/m3)	OC (ng/m3)	EC (ng/m3)
SA	Indoor	< 0.25	9.7	8.4	349.1	372.9	3141.5	947.2
		0.25-0.5	4.1	10.2	305.8	154.7	1832.3	30.9
		0.5-1	3.8	21.6	470.3	68.0	658.4	45.8
		1-2.5	6.1	143.2	1283.4	116.6	1477.8	111.1
		2.5-10	9.4	235.3	2090.9	132.1	5374.9	313.7
		< 10	33.0	418.7	4499.4	844.3	12484.8	1448.7
	Outdoor	< 0.25	8.7	7.4	270.7	285.8	NA	NA
		0.25-0.5	2.6	3.0	134.4	61.7	NA	NA
		0.5-1	0.9	3.5	196.9	40.1	NA	NA
		1-2.5	2.2	30.6	686.5	59.7	NA	NA
		2.5-10	11.1	313.3	1729.4	96.1	NA	NA
		< 10	25.5	357.7	3017.9	543.3	NA	NA
SB	Indoor	< 0.25	5.0	7.3	217.4	216.7	3370.7	716.1
		0.25-0.5	2.2	34.1	203.7	84.7	1055.5	30.3
		0.5-1	2.8	161.4	589.1	43.0	863.0	90.7
		1-2.5	9.6	338.9	1522.2	82.4	776.8	29.6
		2.5-10	28.0	792.5	4778.5	193.1	8285.6	292.1
		< 10	47.5	1334.3	7311.0	620.0	14351.6	1158.7
	Outdoor	< 0.25	–	–	–	–	–	–
		0.25-0.5	–	–	–	–	–	–
		0.5-1	–	–	–	–	–	–
		1-2.5	–	–	–	–	–	–
		2.5-10	–	–	–	–	–	–
		< 10	–	–	–	–	–	–
SC	Indoor	< 0.25	10.5	7.7	198.2	94.0	3480.8	861.6
		0.25-0.5	5.0	15.6	229.7	58.4	1437.7	54.7
		0.5-1	4.4	169.2	479.1	35.5	880.1	35.5
		1-2.5	15.3	266.1	1291.3	82.1	2433.1	121.4
		2.5-10	43.6	1205.9	6920.3	375.5	12198.5	448.6
		< 10	78.8	1664.6	9118.7	645.5	20430.2	1521.8
	Outdoor	< 0.25	5.7	3.8	162.2	94.7	NA	NA
		0.25-0.5	3.1	59.1	155.9	57.6	NA	NA
		0.5-1	4.4	177.5	298.5	28.9	NA	NA
		1-2.5	7.4	372.3	1094.1	78.2	NA	NA
		2.5-10	15.8	1553.1	2645.4	320.5	NA	NA
		< 10	36.4	2165.9	4356.1	580.0	NA	NA
SD	Indoor	< 0.25	6.5	4.7	255.9	99.2	5204.9	766.4
		0.25-0.5	3.0	58.0	795.5	85.1	1715.9	121.3
		0.5-1	7.8	117.9	2657.0	84.8	1211.4	137.7
		1-2.5	23.8	465.4	7628.7	233.0	2970.5	87.7
		2.5-10	56.1	263.8	8590.2	261.7	10827.5	760.1
		< 10	97.2	909.7	19927.4	763.6	21930.1	1873.2
	Outdoor	< 0.25	5.0	14.1	416.7	282.1	NA	NA
		0.25-0.5	1.1	60.0	359.0	143.0	NA	NA
		0.5-1	1.2	358.7	594.5	76.1	NA	NA
		1-2.5	4.6	609.0	1695.4	174.4	NA	NA
		2.5-10	8.6	928.9	1257.9	168.9	NA	NA
		< 10	20.5	1970.6	4323.5	844.5	NA	NA

MA Marine aerosol; MM Mineral matter; AE Anthropogenic elements; NA Not analysed;
Unavailable data for outdoor of school SB

Table S6.3 - I/O ratios of PMx and its chemical compounds in the homes and schools.

		Particle size (µm)	PMx	MA	MM	AE
Homes	H1	< 0.25	1.2	0.3	1.9	1.3
		0.25-0.5	1.7	1.0	0.9	2.8
		0.5-1	1.4	23.4	4.0	2.4
		1-2.5	1.1	0.9	0.8	1.1
		2.5-10	0.4	0.5	0.5	0.5
		< 10	0.9	0.6	0.9	1.3
	H2	< 0.25	1.2	1.2	1.2	1.0
		0.25-0.5	0.8	1.2	1.1	1.1
		0.5-1	1.5	1.1	1.3	0.9
		1-2.5	2.2	0.8	1.2	1.0
		2.5-10	0.5	0.3	0.7	0.6
		< 10	0.8	0.4	0.9	0.9
	H3	< 0.25	0.7	1.3	1.0	1.0
		0.25-0.5	1.8	0.4	1.3	0.8
		0.5-1	0.5	0.9	0.9	0.8
		1-2.5	0.7	1.1	0.8	0.8
		2.5-10	0.4	0.4	0.3	0.4
		< 10	0.6	0.5	0.6	0.8
	H4	< 0.25	3.5	23.6	2.9	1.2
		0.25-0.5	1.1	1.9	0.7	0.6
		0.5-1	4.8	1.0	1.4	1.1
		1-2.5	1.5	1.4	1.8	1.7
		2.5-10	0.6	0.3	0.3	0.3
		< 10	2.2	0.9	1.1	0.9
Schools	SA	< 0.25	1.1	1.1	1.3	1.3
		0.25-0.5	1.6	3.4	2.3	2.5
		0.5-1	4.1	6.3	2.4	1.7
		1-2.5	2.8	4.7	1.9	2.0
		2.5-10	0.8	0.8	1.2	1.4
		< 10	1.3	1.2	1.5	1.6
	SB	< 0.25	–	–	–	–
		0.25-0.5	–	–	–	–
		0.5-1	–	–	–	–
		1-2.5	–	–	–	–
		2.5-10	–	–	–	–
		< 10	–	–	–	–
	SC	< 0.25	1.8	2.0	1.2	1.0
		0.25-0.5	1.6	0.3	1.5	1.0
		0.5-1	1.0	1.0	1.6	1.2
		1-2.5	2.1	0.7	1.2	1.1
		2.5-10	2.8	0.8	2.6	1.2
		< 10	2.2	0.8	2.1	1.1
	SD	< 0.25	1.3	0.3	0.6	0.4
		0.25-0.5	2.7	1.0	2.2	0.6
		0.5-1	6.4	0.3	4.5	1.1
		1-2.5	5.2	0.8	4.5	1.3
		2.5-10	6.5	0.3	6.8	1.5
		< 10	4.7	0.5	4.6	0.9

MA Marine aerosol; MM Mineral matter; AE Anthropogenic elements;
Unavailable data for outdoor of school SB

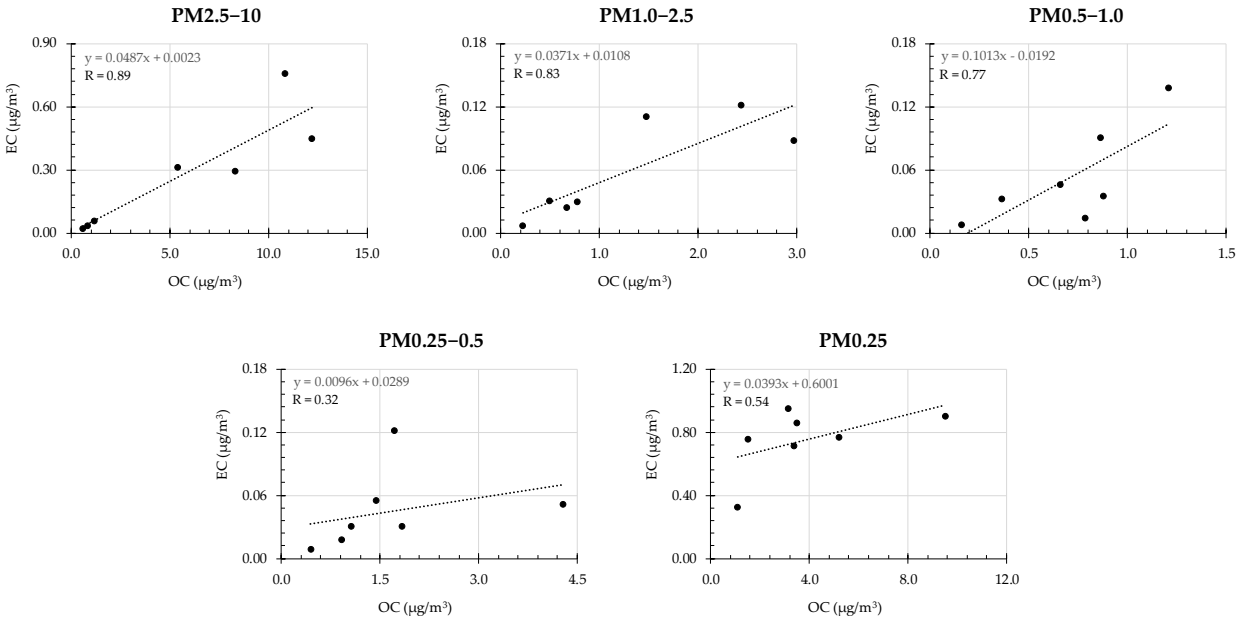


Figure S6.1 - Linear regression plots between the EC and OC concentrations in the different particle size ranges. EC and OC data of both homes and schools.

Table S6.4 - OC/EC ratios for the different particle size ranges in the indoor of the homes and schools.

Particle size (µm)	Homes				Schools			
	H1	H2	H3	H4	SA	SB	SC	SD
< 0.25	2.0	–	3.3	10.5	3.3	4.7	4.0	6.8
0.25 – 0.5	51.3	–	52.9	83.2	59.3	34.8	26.3	14.1
0.5 – 1.0	11.3	–	19.7	54.3	14.4	9.5	24.8	8.8
1.0 – 2.5	16.0	–	32.7	28.1	13.3	26.2	20.0	33.9
2.5 – 10	19.7	–	26.8	24.9	17.1	28.4	27.2	14.2

Unavailable data for OC and EC in home H2

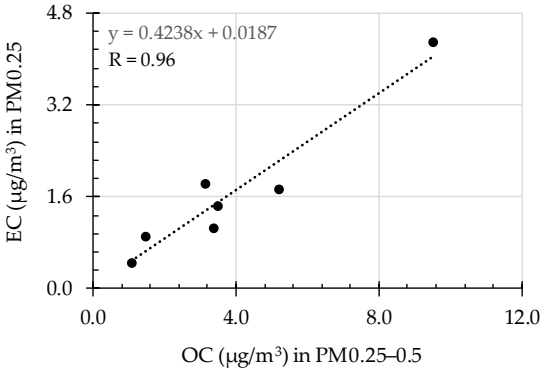


Figure S6.2 - EC and OC data of both homes and schools.

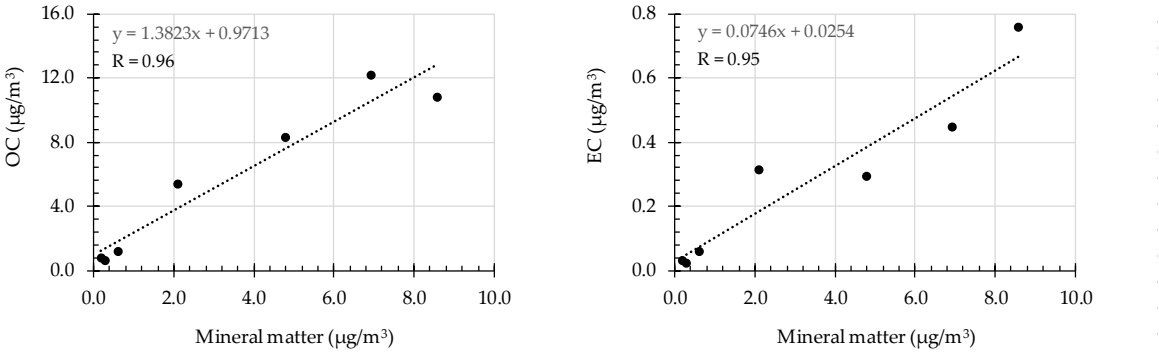


Figure S6.3 - Relationship of OC and EC with mineral matter for PM2.5–10.

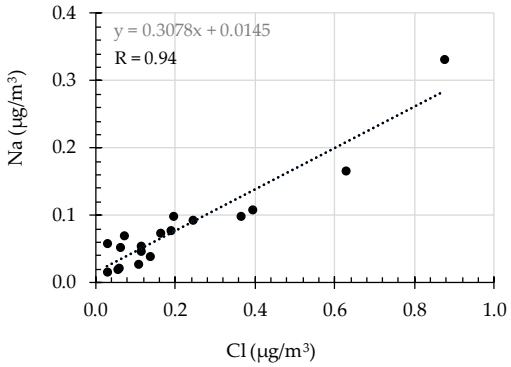
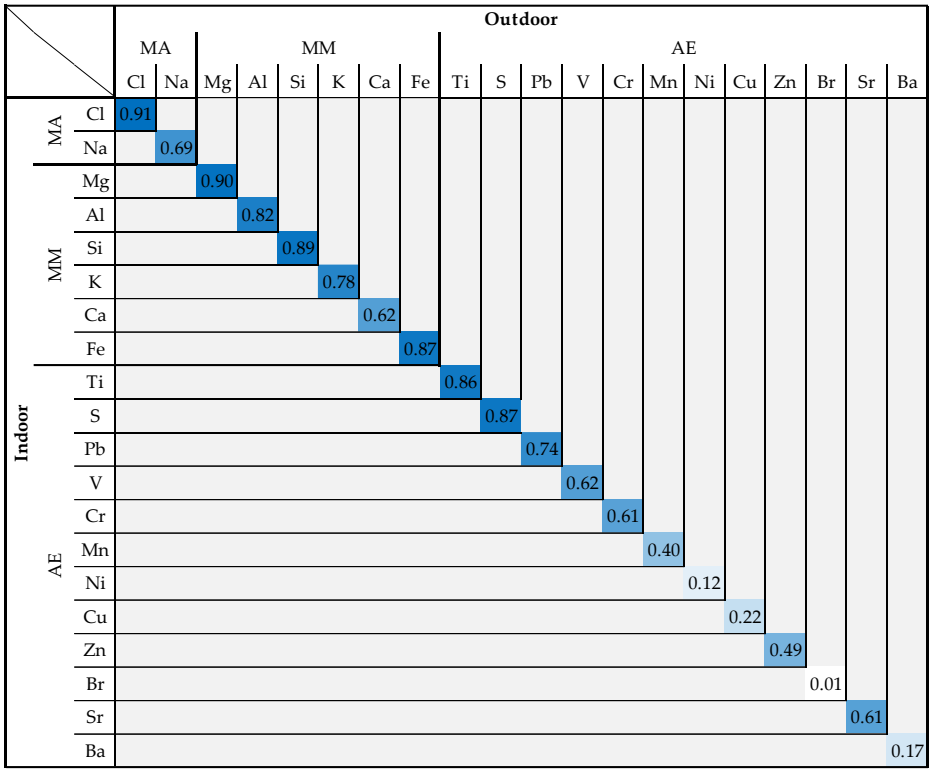


Figure S6.4 - Scatter plot of the concentration of Na vs. Cl in particles with Dp >0.5 µm.

Figure S6.5 - Correlation coefficient (R) of the linear regression of the indoor and outdoor inorganic element concentrations. Merged data of homes and schools for all size fractions.



MA Marine aerosol; MM Mineral matter; AE Anthropogenic elements

Chapter 7

Chapter 7. Assessment of children's potential exposure to bioburden in indoor environments

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Published in: Atmosphere 2020, 11, 993; doi:10.3390/atmos11090993

Accepted: 15 September 2020

Journal Impact Factor (2020): 2.686

Citations: 5

Abstract

The exposure to particles and bioaerosols has been associated with the increase in health effects in children. The objective of this study was to assess the indoor exposure to bioburden in the indoor microenvironments more frequented by children. Air particulate matter and settled dust were sampled in 33 dwellings and four schools with a medium volume sampler and with a passive method using electrostatic dust collectors (EDC), respectively. Settled dust collected by EDC was analyzed by culture-based methods (including azole resistance profile) and using qPCR. Results showed that the PM2.5 and PM10 concentrations in classrooms (31.15 μg/m^3 and 57.83 μg/m^3, respectively) were higher than in homes (15.26 μg/m^3 and 18.95 μg/m^3, respectively) and highly exceeded the limit values established by the Portuguese legislation for indoor air quality. The fungal species most commonly found in bedrooms was *Penicillium* sp. (91.79%), whereas, in living rooms, it was *Rhizopus* sp. (37.95%). Aspergillus sections with toxigenic potential were found in bedrooms and living rooms and were able to grow on VOR. Although not correlated with PM, EDC provided information regarding the bioburden. Future studies, applying EDC coupled with PM assessment, should be implemented to allow for a long-term integrated sample of organic dust.

Keywords: Indoor air quality; Microenvironments; Schools; Dwellings; Bioburden; Electrostatic dust collector

7.1. Introduction

Children are more susceptible to air pollutants compared to adults since they breathe more air relative to their body weight, their immune system is still in development and they have a lower ability to deal with the toxicity due to their undeveloped airways (Selgrade et al., 2008; WHO, 2005). Children spend more than 85% of their time in indoor environments, mainly at home and school (Faria et al., 2020) and therefore it is essential to assess the indoor air quality (IAQ) in these microenvironments to estimate their integrated exposure to air pollutants.

Pollutants such as particulate matter are linked to an increase in morbidity and mortality (Douwes et al., 2003; Martinelli et al., 2013). PM is a complex mixture of small-diameter particles with different physical and chemical characteristics. PM is classified according to their diameter (e.g., PM2.5 and PM10, which are particles with an aerodynamic diameter smaller than 2.5 and 10 μm, respectively), because this physical characteristic highly affects the penetration into the respiratory tract (Calvo et al., 2013; Seinfeld and Pandis, 1998). PM2.5 or fine particles reach the lower respiratory tract, while the PM2.5–10 or coarse particles can reach the upper respiratory tract. In addition, the health impact of the PM depends on its composition, which is highly determined by the emission sources.

Bioaerosols are usually defined as PM with biological origins such as microorganisms, pollen and plant fibers. The exposure to biological agents can lead to a wide range of adverse health effects, including allergies, infection diseases, breathing problems and cancer (Douwes et al., 2003).

Previous studies reported a wide range of environmental factors that influence bioburden (covering bacteria and fungi) indoors, such as the occupancy of the spaces (Ekhaise and Ogboghodo, 2011; Sudharsanam et al., 2012), building layout, ventilation (Ekhaise et al., 2010) and cleaning procedures including the type of products applied (Douwes et al., 2003). Furthermore, poor maintenance of heating, ventilation and air conditioning systems can also enhance the hazardous effects of many biological and nonbiological pollutants (Salama and Berekaa, 2016). Due to the influence of these multiple environmental variables, sampling bioburden should be performed by passive methods, together with more conventional air sampling (Cabo Verde et al., 2015; Klánová and Hollerová, 2003; Park et al., 2013; Tang and Wan, 2013). Indeed, passive methods allow defining the contamination of a larger period of time (ranging from weeks to several months), whereas air samples can only replicate the load from a shorter period of time (mostly minutes) (Viegas et al., 2018a).

The electrostatic dust collector (EDC) is a passive collection device easy-to-use that comprises an electrostatic polypropylene cloth (ACGIH, 2009). The use of this device is gradually increasing since it is low-cost and effective for the collection of dust (Kilburg-Basnyat et al., 2016; Viegas et al., 2019, 2018a), and it has already been applied for the bioburden assessment in several indoor environments (Cozen et al.,

2008; Dorado-García et al., 2013; Feld et al., 2018; Kilburg-Basnyat et al., 2015; Madsen et al., 2012; Normand et al., 2009; Viegas et al., 2020, 2019, 2018a, 2018b).

The emergence worldwide of drug-resistant human pathogenic fungal species, such as *Candida* sp. and *Aspergillus fumigatus*, and the increasing reports of therapeutic failure against fungal infections caused by environmental resistant strains (Fisher et al., 2018; Snelders et al., 2011; Verweij et al., 2016), has revealed the need of surveillance of fungal resistance in the indoor and outdoor environments, which is mostly described for *Aspergillus* section *Fumigati* (Ahmad et al., 2014; Chen et al., 2019; Cho et al., 2019; Loeffert et al., 2018; Monteiro et al., 2019; Snelders et al., 2009).

In this study, the exposure to PM and bioburden in the indoor microenvironments frequented by children was assessed by particle measurement and by the use of EDCs. This work also explored the suitability of EDCs for identifying critical control points of indoor exposure to PM, and for characterizing the bioburden present indoors. The fungal burden was also characterized through molecular detection of the species with toxigenic potential and also via analysis of antifungal resistance profile.

7.2. Materials and Methods

7.2.1. Location of the Studied Schools and Dwellings

This work was developed in the framework of the LIFE Index Air. Available online: http://www.lifeindexair.net/) (accessed on 14-09-2020) and was conducted in 33 dwellings (D1–D33) and 4 schools (S1–S4) located in the city of Lisbon, Portugal from September 2017 to October 2018. Figure 7.1 shows the location of the studied schools and homes.

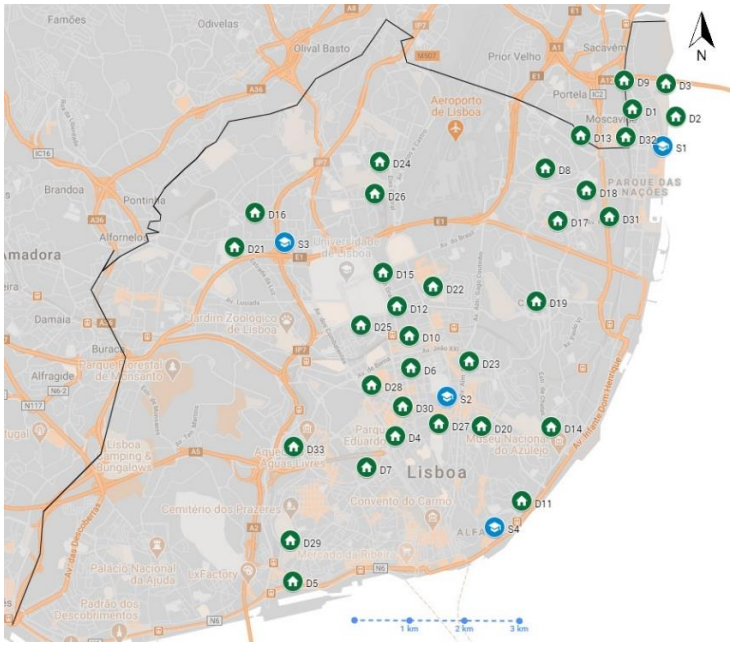

Figure 7.1 - Location of the studied schools (blue) and dwellings (green) in Lisbon, Portugal.

7.2.2. Air Particulate Matter and Settled Dust Sampling

PM2.5 and PM2.5–10 was sampled with a medium volume sampler (MVS6, Leckel, Sven Leckel, Germany), which was installed in the living room of the dwellings and in a classroom of the schools, as described by Faria et al. (2020). Filters were analyzed by gravimetry before and after sampling with a microbalance (Sartorius R160P, Greifensee, Switzerland) and PM mass concentration was determined by dividing the filter loads by the volume of filtered air. All microenvironments were monitored for 5 days during the occupied period, summing a total of 330 sampled filters.

Dust was collected through a passive method using an electrostatic dust collector (EDC), which comprises an electrostatic polypropylene cloth (ACGIH, 2009). Dust was collected from 30 to 44 days in an EDC with a surface exposure area of 0.00636 m^2. In the dwellings, the EDCs were exposed in the living room (a total of 33) and in the children's bedroom (a total of 31) and in schools, the EDCs were placed in the classrooms (a total of 4). The EDC was then used for the bioburden assessment.

7.2.3. Electrostatic Dust Cloth Extraction and Bioburden Characterization

In order to determine the mass of the collected dust, each EDC was weighted after sampling and subtracted to the mean of 10 EDCs weighted before sampling. Settled dust collected by the EDC was analyzed by culture-based methods and using real-time PCR (qPCR), targeting 4 different *Aspergillus* sections (*Flavi*, *Fumigati*, *Circumdati* and *Nidulantes*). The target fungi were selected based on the classification as indicators of harmful fungal contamination (Dillon et al., 1996).

EDC samples were subject to extraction and bioburden characterized by culture-based methods as previously described (Madsen et al., 2012; Viegas et al., 2020, 2019, 2018a, 2018b). EDC were washed and 0.15 mL seeded onto 2% malt extract agar (MEA) with 0.05 g/L chloramphenicol media; dichloran glycerol (DG18) agar-based media; tryptic soy agar (TSA) with 0.2% nystatin for total bacteria assessment; violet red bile agar (VRBA) for Gram-negative bacteria.

Samples were also spread (0.15 mL) onto Sabouraud dextrose agar (SDA) media supplemented with 4 mg/L itraconazole (ITR), 1 mg/L voriconazole (VOR) or 0.5 mg/L posaconazole (POS, protocol adapted from the EUCAST 2017 guidelines) (Arendrup et al., 2011) for the screening of antifungal resistance (Viegas et al., 2019). Incubation of MEA, DG18 and azole screening plates at 27 °C for 5 to 7 days and TSA and VRBA plates at 30 and 35 °C for 7 days, respectively, was performed.

Molecular identification of the different fungal species/strains was achieved by qPCR using the CFX-Connect PCR System (Bio-Rad) on EDC collected (bedrooms n = 31; living rooms n = 33; classrooms = 4). Reactions included 1× iQ Supermix (Bio-Rad), 0.5 μM of each primer (Table 7.1), and 0.375 μM of TaqMan probe in a total volume of 20 μL. Amplification followed a three-step PCR: 50 cycles with

denaturation at 95 °C for 30 s, annealing at 52 °C for 30 s and extension at 72 °C for 30 s (Table 7.1). Nontemplate control was used in every PCR reaction. For each gene that was amplified, a nontemplate control and positive control were used, consisting of DNA obtained from a reference that belonged to the culture collection of the Reference Unit for Parasitic and Fungal Infections, Department of Infectious Diseases of the National Institute of Health, from Dr. Ricardo Jorge. These strains have been sequenced for ITS B-tubulin and Calmodulin.

Table 7.1 - Sequence of primers and TaqMan probes used for real-time PCR.

***Aspergillus* Sections Targeted**	**Sequences**	**Reference**
Flavi (Strains with toxigenic potential)		(Arendrup et al., 2011)
Forward Primer	5'-GTCCAAGCAACAGGCCAAGT-3'	
Reverse Primer	5'-TCGTGCATGTTGGTGATGGT-3'	
Probe	5'-TGTCTTGATCGGCGCCCG-3'	
Fumigati		
Forward Primer	5'-CGCGTCCGGTCCTCG-3'	(Cruz-Perez et al., 2001)
Reverse Primer	5'-TTAGAAAAATAAAGTTGGGTGTCGG -3'	
Probe	5'-TGTCACCTGCTCTGTAGGCCCG -3'	
Circumdati		
Forward Primer	5'-CGGGTCTAATGCAGCTCCAA-3'	(Viegas et al., 2017a)
Reverse Primer	5'-CGGGCACCAATCCTTTCA-3'	
Probe	5'-CGTCAATAAGCGCTTTT-3'	
Nidulantes		
Forward Primer	5' – CGGCGGGGAGCCCT-3'	(US-EPA, 2017)
Reverse Primer	5' – CCATTGTTGAAAGTTTTGACTGATcTTA-3'	
Probe	5' – AGACTGCATCACTCTCAGGCATGAAGTTCAG-3'	

7.2.4. Statistical Analysis

The statistical software SPSS V24.0 for Windows® was used for data analysis. The results were considered significant at a 5% significance level. The frequency analysis (n, %) was applied for the qualitative data, and the minimum, maximum, median and interquartile range were calculated for the quantitative data. The median and the interquartile range were used, since outliers were detected and the mean and standard deviation were influenced by these values. The Shapiro-Wilk test was applied to test data normality, and Spearman's correlation coefficient to study the relationship between two quantitative variables. Kruskal–Wallis test was used to compare EDC weight, fungal counts on MEA and DG18 and bacteria counts on TSA and VRB among the different sampling locations, since the assumption of normality was not verified. When statistically significant differences were detected, the Kruskal–Wallis multiple comparisons test was the analyses selected. For the comparison of the concentration of the particles between the two sampling locations (classroom and living room) the Mann–Whitney test was used, since the assumption of normality was not verified.

7.3. Results

7.3.1. Particulate Matter Assessment

The PM2.5 and PM10 average concentrations in the classrooms were 31.15 and 57.83 μg/m^3, respectively, with a range between 19.47 and 52.91 μg/m^3 for PM2.5 and between 32.72 and 109.02 μg/m^3 for PM10. Table 7.2 shows that in dwellings, the concentrations ranged between 6.05 and 67.96 μg/m^3 for PM2.5 and between 9.14 and 72.95 μg/m^3 for PM10, with an average concentration of 15.26 μg/m^3 and 18.95 μg/m^3, respectively. The PM2.5 concentrations exceeded the 8-hr limit value established by the Portuguese legislation for indoor air quality (Portaria 353-A/2013, 25 μg/m^3) in 50% of the schools and in 12% of the dwellings and the PM10 limit value (50 μg/m^3) was exceeded in 50% of the schools and in 3% of the dwellings.

Regarding the settled dust collected by the EDC, the schools presented an average level of 1.42 g/m^2/d with a range between 1.28 and 1.57 g/m^2/d and the dwellings registered an average of 3.36 g/m^2/d with a range between 1.27 and 11.16 g/m^2/d. In dwellings, the living room presented an average amount of 3.6 g/m^2/d and the bedroom of 3.11 g/m^2/d (Table 7.2).

Table 7.2 - Settled dust (g/m^2/d) and PM2.5 and PM10 concentrations (μg/m^3) measured in dwellings and schools.

		Settled Dust (g/m^2/d)	**PM2.5 (μg/m^3)**	**PM10 (μg/m^3)**
Schools	Average	1.42	31.15	57.83
	Range (min–max)	1.28–1.57	19.47–52.91	32.72–109.02
Dwellings	Average	3.36	-	-
	Range (min–max)	1.27–11.16	-	-
Living Rooms	Average	3.60	15.26	18.95
	Range (min–max)	1.28–11.16	6.05–67.96	9.14–72.95
Bedrooms	Average	3.11	-	-
	Range (min–max)	1.27–10.74	-	-

7.3.2. Bacterial Contamination Assessment

From the 31 samples collected in the bedrooms, the total bacteria contamination ranged from below the detection limit to 1.42 × 10^3 CFU/m^2/d, with the Gram-negative bacteria contamination, ranging from below the detection limit to 3.15 × 10^1 CFU/m^2/d.

Total bacteria contamination in the 33 EDC collected in living rooms ranged from below the detection limit to 3.42 × 10^3 CFU/m^2/d, with the Gram-negative bacteria contamination, ranging from below the detection limit to 4.60 × 10^1 CFU/m^2/d.

In the 4 EDC samples collected in the classrooms, the total bacteria contamination ranged from below the detection limit to 6.2 × 10^1 CFU/m^2/d, while there was no contamination by Gram-negative bacteria (Table 7.3).

Table 7.3 - Bacteria contamination (CFU/m^2/d) in each studied location.

Location			**Total Bacteria**	**Gram-Negative Bacteria**
	Average	N	CFU/m²/d	CFU/m²/d
Bedrooms	Range (min–max)	31	*−1.42x10³	*−3.15x10¹
Living Rooms	Range (min–max)	33	*−3.42x103	*−4.60x10¹
Classrooms	Range (min–max)	4	*−6.2x10¹	-

N—Number of samples collected. *−Below the detection limit.

7.3.3. Fungal Contamination Assessment

A total of 31 EDC were collected from bedrooms. The fungal contamination in these samples ranged from lower the detection limit to 2.00 × 10^3 CFU/m^2/d (D30) in MEA, and from lower the detection limit to 2.81 × 10^3 CFU/m^2/d (D32) in DG18. The most commonly found fungal species in MEA was *Penicillium* sp. (2.00x10^3 CFU/m^2/d; 89.43%), followed by *Cladosporium* sp. (1.59 × 10^2 CFU/m^2/d; 7.10%) and *Chrysosporium* sp. (2.56 × 10^1 CFU/m^2/d; 1.14%; Table 7.4). In DG18, the most prevalent species were *Cladosporium* sp. (2.81 × 10^3 CFU/m^2/d; 90.44%), *Penicillium* sp. (2.07 × 10^2 CFU/m^2/d; 6.67%) and *Aspergillus* sp. (1.05 × 10^2 CFU/m^2/d; 1.23%; Table 7.4). Four different *Aspergillus* sections were identified in the EDC samples from the bedrooms, two found in MEA (*Nigri* and *Fumigati*; 1.05 × 101 CFU/m^2/d), and two in DG18 (*Candidi* and *Circumdati*; 3.81x101 CFU/m^2/d; Figure 7.2).

In the 33 EDC collected from the living rooms, the fungal contamination ranged from lower the detection limit to 5.24 × 10^3 CFU/m^2/d (D3, D6 and D28) in MEA, and from lower the detection limit to 2.62 × 10^3 CFU/m^2/d (D32). In MEA, the most common was *Rhizopus* sp. (5.24 × 103 CFU/m^2/d; 38.11%), followed by *Chrysonilia* sp. (5.24 × 10^3 CFU/m^2/d; 38.11%) and *Chrysosporium* sp. (2.64 × 10^3 CFU/m^2/d; 19.19%); in DG18, *Chrysonilia* sp. (2.62 × 10^3 CFU/m^2/d; 76.55%), followed by *Penicillium* sp. (3.54 × 10^2 CFU/m^2/d; 10.33%) and *Cladosporium* sp. (1.7 × 10^2 CFU/m^2/d; 4.96%) were the most prevalent (Table 7.4). A total of eight *Aspergillus* sections were identified in the samples from the living room. Five different sections were found in MEA, including *Aspergillus* section *Fumigati* (6.18 × 101 CFU/m^2/d), *Flavi* and *Nigri* (2.62 × 10^1 CFU/m^2/d; Figure 7.2). In DG18, six *Aspergillus* sections were identified, with the most

prevalent being *Nidulantes* (7.89 × 10^1 CFU/m^2/d), followed by *Fumigati* (3.67 × 10^1 CFU/m^2/d) and *Clavati* (1.57 × 10^1 CFU/m^2/d; Figure 7.2).

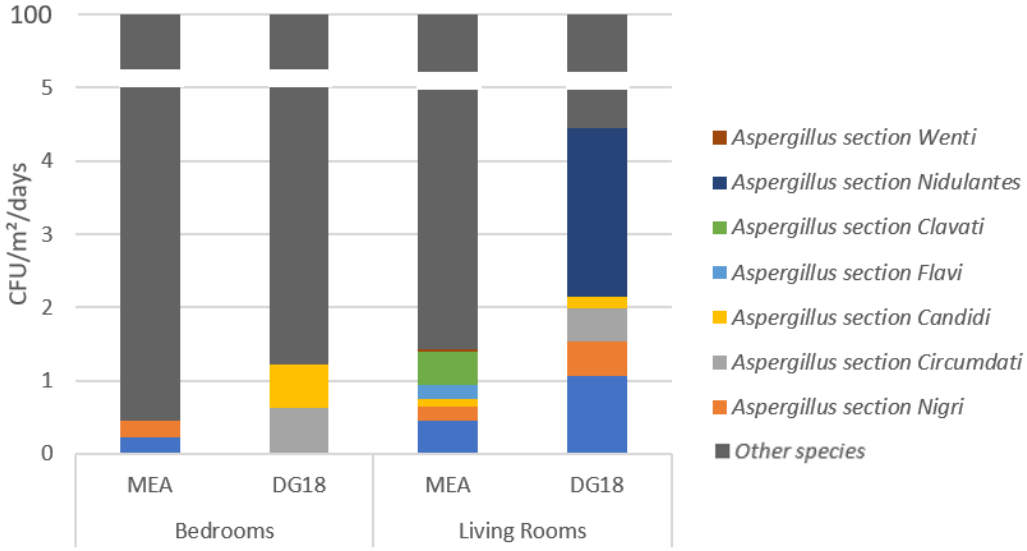

Figure 7.2 - Aspergillus sections identified in the electrostatic dust collectors (EDC) samples from the bedrooms and the living rooms.

Four EDC were recovered from classrooms. The fungal contamination in the MEA samples ranged from the lower detection limit (S1) to 1.76 × 10^1 CFU/m^2/d (in the three remaining samples), and in DG18 from the lower detection limit (S1 and S3) to 1.02 × 10^1 CFU/m^2/d (in S4). Three different fungal species were identified in the MEA samples: *Penicillium* sp. (1.76 × 10^1 CFU/m^2/d; 64.21%), *Chrysonilia* sp. and *Cladosporium* sp. (4.91 × 10^1 CFU/m^2/d; 17.90%; Table 7.4). Four fungal species were found in DG18: *Chrysosporium* sp. (1.02 × 10^1 CFU/m^2/d; 40.79%), *Aspergillus* section *Nidulantes*, *Chrysonilia* sp. and *Cladosporium* sp. (1.02 × 10^1 CFU/m^2/d; 19.74%; Table 7.4).

Table 7.4 - Fungal species found in each studied location.

Location	Genus/Species	MEA			DG18		
		N	CFU/m²/d	%	N	CFU/m²/d	%
Bedrooms	*Alternaria* sp.	2	1.05×10^{1}	0.47	1	1.05×10^{1}	0.34
	Aureobasidium sp.	1	5.24×10^{0}	0.23	1	5.24×10^{0}	0.17
	Chrysosporium sp.	3	2.56×10^{1}	1.14	2	9.49×10^{0}	0.31
	Cladosporium sp.	8	1.59×10^{2}	7.10	14	2.81×10^{3}	90.44
	Geotrichum sp.	1	4.14×10^{0}	0.18	1	5.24×10^{0}	0.17
	Penicillium sp.	17	2.00×10^{3}	89.43	12	2.07×10^{2}	6.67
	Aspergillus sp.	*2*	1.05×10^{1}	*0.47*	*2*	3.81×10^{1}	*1.23*
	Fusarium sp.	2	2.18×10^{1}	0.97	0	*	*
	Crysonilia sitophila	0	*	*	2	2.10×10^{1}	0.68
Living rooms	*Alternaria* sp.	1	5.24×10^{0}	0.04	0	*	*
	Aspergillus sp.	2	1.33×10^{2}	0.97	2	1.68×10^{2}	4.91
	Aureobasidium sp.	1	4.91×10^{0}	0.04	0	*	*
	Chrysonilia sp.	2	5.24×10^{3}	38.11	1	2.62×10^{3}	76.55
	Chrysosporium sp.	4	2.64×10^{3}	19.19	8	6.68×10^{1}	1.95
	Cladosporium sp.	13	2.22×10^{2}	1.61	12	1.7×10^{2}	4.96
	Fusarium sp.	0	*	*	1	2.46×10^{1}	0.72
	Geotrichum sp.	0	*	*	2	1.48×10^{1}	0.43
	Penicillium sp.	14	2.65×10^{2}	1.93	16	3.54×10^{2}	10.33
	Rhizopus sp.	2	5.24×10^{3}	38.11	0	*	*
	Ulocladium sp.	0	*	*	1	5.24×10^{0}	0.15
Classrooms	*Penicillium* sp.	2	1.76×10^{1}	64.21	0	*	*
	Chrysonilia sp.	1	4.91×10^{0}	17.90	1	4.91×10^{0}	19.74
	Cladosporium sp.	1	4.91×10^{0}	17.90	1	4.91×10^{0}	19.74
	Aspergillus sp.	0	*	*	1	4.91×10^{0}	19.74
	Chrysosporium sp.	0	*	*	1	1.02×10^{1}	40.79

N−Number of isolates observed. *−Lower the detection limit.

7.3.4. Azole-resistance screening

Seventeen different fungal species were detected on azole-resistance screening in 61 EDC samples, of which 11 were able to grow in at least one azole among the tested conditions. Noteworthy, *Aspergillus* sections *Candidi* and *Nigri* were able to grow on VOR in two distinct samples. Reduced susceptibility to multiazoles (i.e., fungal ability to grow in more than one azole) was observed in 14 EDC samples, for five different fungal species, including *Penicillium* sp. (VOR+POS in three samples), *Chrysosporium* sp. (VOR+POS in one sample, ITR+VOR in one sample) or *Cladosporium* sp. (ITR+VOR in two samples, VOR+POS in three samples, ITR+VOR+POS in one sample; Table 7.5). Similar to the results obtained with MEA in dwellings (Table 7.4), some of the most frequent fungal species were C. *sitophila* (83.05% SAB, 11.17% POS, 1.68 VOR), *Cladosporium* sp. (40.44% ITR, 38.33% VOR, 37.03% POS, 13.22% SAB) and *Penicillium* sp. (45.60% VOR, 27.21% ITR, 21.65% POS, 2.29% SAB; Table 7.5).

Table 7.5 - Fungal species found on azole-screening media.

Species/Sections/Complexes	SAB			ITR			VOR			POS		
	N	CFU/m²/d	%	N	CFU/m²/d	%	N	CFU/m²/d	%	N	CFU/m²/d	%
Alternaria sp.	8	4.91×10^{1}	0.22	0	*	0	1	5.24×10^{1}	0.94	0	*	0
Aspergillus section *Aspergilli*	1	5.24×10^{0}	0.02	0	*	0	0	*	0	0	*	0
Aspergillus section *Candidi*	0	*	0	0	*	0	1	5.24×10^{0}	0.94	0	*	0
Aspergillus section *Fumigati*	2	9.38×10^{0}	0.04	0	*	0	0	*	0	0	*	0
Aspergillus section *Nigri*	14	6.91×10^{1}	0.31	0	*	0	2	9.38×10^{0}	1.68	0	*	0
Aspergillus section *Nidulantes*	21	9.02×10^{1}	0.41	0	*	0	0	*	0	0	*	0
Aureobasidium sp.	0	*	0	2	1.05×10^{1}	16.18	5	2.40×10^{1}	4.30	1	4.14×10^{1}	4.41
Crysonilia sitophila	3000	1.84×10^{4}	83.05	0	*	0	2	9.38×10^{0}	1.68	2	1.05×10^{1}	11.17
Chrysosporium sp.	24	5.24×10^{1}	0.24	1	5.24×10^{0}	8.09	3	1.54×10^{1}	2.76	3	2.41×10^{1}	25.73
Cladosporium sp.	561	2.92×10^{3}	13.22	6	2.62×10^{1}	40.44	55	2.14×10^{2}	38.33	7	3.47×10^{1}	37.03
Fusarium incarnatum-equiseti species complex	2	1.05×10^{1}	0.05	0	*	0	0	*	0	0	*	0
Fusarium oxysporum species complex	0	*	0	1	5.24×10^{0}	8.09	0	*	0	0	*	0
Geotrichum sp.	0	*	0	0	*	0	2	1.05×10^{1}	1.88	0	*	0
Litchemia sp.	2	1.05×10^{1}	0.05	0	*	0	0	*	0	0	*	0
Penicillium sp.	162	5.07×10^{2}	2.29	3	1.76×10^{1}	27.21	53	2.54×10^{2}	45.60	5	2.03×10^{1}	21.65
Syncephalastrum racemosum	1	4.91×10^{0}	0.02	0	*	0	0	*	0	0	*	0
Paecilomyces sp.	1	1.57×10^{1}	0.07	0	*	0	0	*	0	0	*	0
Ulocladium sp.	0	*	0	0	*	0	2	1.05×10^{1}	1.88	0	*	0

*−Lower the detection limit.

7.3.5. Molecular Assessment

None of the *Aspergillus* sections targeted (*Circumdati, Flavi, Fumigati* and *Nidulantes*) on the EDC were amplified by RT-PCR.

7.3.6. Correlation Analysis

Regarding the EDC weight, significant correlations, with moderate or low intensity, were detected with particles PM2.5 ($rS = -0.395$, $p = 0.015$), particles PM10 ($rS = -0.486$, $p = 0.002$), bacterial contamination on TSA ($rS = -0.252$, $p = 0.042$) and with Aspergillus prevalence on MEA ($Rs = 0.555$, $p = 0.049$). These results show that higher EDC weights are related to lower concentrations of particles (PM2.5 and PM10), lower bacterial contamination on TSA and higher Aspergillus prevalence on MEA (Table 7.6).

Considering the concentration of PM, only a significant positive correlation was detected, with a strong intensity, between the PM2.5 and PM10 ($rS = 0.957$, $p < 0.0001$), which means that higher concentrations of particles PM2.5 are related to higher concentrations of PM10 (Table 7.6).

Regarding fungal contamination on MEA, significant positive and moderate correlations were detected with (i) fungal contamination on DG18 ($rS = 0.457$, $p < 0.0001$), (ii) fungal presence on VOR ($rS = 0.281$, $p = 0.020$) and (iii) fungal detection on POS ($rS = 0.280$, $p = 0.021$), indicating that higher fungal

contamination on MEA is related with higher fungal contamination on DG18 and with fungal counts on VOR and on POS (Table 7.6).

Regarding the fungal contamination on DG18, significant correlations of weak intensity and positive direction were detected with the fungal presence on VOR (rS = 0.262, p = 0.031) and on POS (rS = 0.276, p = 0.023), and with *Aspergillus* prevalence on DG18 (rS = 0.459, p = 0.042), revealing that higher fungal contamination on DG18 is related with the higher fungal counts on VOR and POS and *Aspergillus* prevalence on DG18 (Table 7.6).

Finally, a significant correlation, of weak intensity and in a positive direction, between fungal presence on VOR and POS (rS = 0.250, p = 0.039), which indicates that higher fungal counts on VOR are related with higher fungal counts on POS (Table 7.6).

Table 7.6 - Study of the relationship between the weight of EDCs, particulate matter (PM2.5 and PM10), bacterial (TSA and VRBA) and fungal (MEA and DG18) contamination, fungi in azole-screening media (ITR, VOR and POS) and Aspergillus prevalence (MEA and DG18).

Variables		Particles (µg/m^3)		Bacteria (CFU/m^2/d)		Fungi (CFU/m^2/d)		Fungi in Azole-Screening Media			*Aspergillus* Prevalence (CFU/m^2/d)	
		PM2.5	PM10	TSA	RB	MEA	DG18	ITR	VOR	POS	MEA	DG18
	EDC Weight (g/m^2/d)	−0.395*	−0.486**	−0.252*	0.118	0.038	0.210	0.030	.083	0.000	0.555*	0.253
Particles (µg/m^3)	PM2.5		0.957**	0.240	0.123	-0.084	−0.013	0.164	−0.084	−0.014	−0.386	−0.392
	PM10			0.220	0.114	-0.066	0.023	0.153	−0.064	0.027	−0.426	−0.447
Bacteria (CFU/m^2/d)	TSA				0.146	0.005	0.058	0.053	0.034	0.119	−0.379	−0.203
	RB					0.069	0.141	0.055	0.033	−0.009	0.019	−0.106
Fungi (CFU/m^2/d)	MEA						0.457**	−0.097	0.281*	0.280*	0.420	0.196
	DG18							−0.019	0.262*	0.276*	0.107	0.459*
Fungi in azole-screening media	ITR								0.078	0.026	−0.324	0.029
	VOR									0.250*	0.335	0.287
	POS										−0.032	−0.155
Aspergillus prevalence (CFU/m^2/d)	MEA											0.355

*. Correlation is significant at the 0.05 level (2-tailed).
**. Correlation is significant at the 0.01 level (2-tailed).

7.3.7. Comparison between Sampling Locations

From the comparison between sampling locations, only significant differences were detected in: (i) the EDC weight (χ_(K-W)^2 (2) = 6.74, p = 0.046), showing that in the classroom the EDC had less weight; (ii) the concentration of PM2.5 (U = 15.000, p = 0.013) and PM10 (U = 8.000, p = 0.005) particles presented the classroom as the sampling location with the highest concentrations (Table 7.7).

Table 7.7 - Comparison of EDC weight, particulate matter concentration, fungal and bacterial contamination, fungal presence in azole-screening media and Aspergillus prevalence between sampling locations (Kruskal–Wallis test or Mann–Whitney test).

Variables		Ranks			Test Statistics		
		Location	N	Mean Rank	χ^2 Kruskal–Wallis or Mann–Whitney U	Df	p
Particles	EDC Weight (g)	Classroom	4	11.75	6.174*	2	0.046***
		Living room	33	37.68			
		Bedroom	31	34.05			
		Total	68				
	PM2.5 (µg/m^3)	Classroom	4	31.75	15.000**		0.013***
		Living room	33	17.45			
		Total	37				
	PM10 (µg/m^3)	Classroom	4	33.50	8.000**		0.005***
		Living room	33	17.24			
		Total	37				
Bacterial	TSA (CFU/m^2/d)	Classroom	4	25.88	0.774*	2	0.679
		Living room	32	33.25			
		Bedroom	30	34.78			
		Total	66				
	RB (CFU/m$^{2/d}$)	Classroom	4	31.00	0.491*	2	0.782
		Living room	33	34.08			
		Bedroom	31	33.22			
		Total	68				
Fungal contamination	MEA (CFU/m^2/d)	Classroom	4	25.38	3.228*	2	0.199
		Living room	33	38.65			
		Bedroom	31	31.26			
		Total	68				
	DG18 (CFU/m^2/d)	Classroom	4	21.75	3.306*	2	0.192
		Living room	33	38.18			
		Bedroom	31	32.23			
		Total	68				
Fungal presence in Azoles	ITR	Classroom	4	46.00	5.049*	2	0.080
		Living room	33	35.12			
		Bedroom	31	32.35			
		Total	68				
	VOR	Classroom	4	26.50	5.273*	2	0.072
		Living room	33	39.77			
		Bedroom	31	29.92			
		Total	68				
	POS	Classroom	4	38.00	5.920*	2	0.052
		Living room	33	38.18			
		Bedroom	31	30.13			
		Total	68				
Aspergillus prevalence	MEA	Classroom	4	4.50	3.338*	2	0.188
		Living room	5	8.60			
		Bedroom	4	7.50			
		Total	13				
	DG18	Classroom	4	5.88	4.530	2	0.104
		Living room	8	13.25			
		Bedroom	8	10.06			
		Total	20				

*Kruskal–Wallis test. **Mann–Whitney test. ***Statistically significant differences at a 5% significance level

7.4. Discussion

To contribute to the assessment of children's exposure to particles and bioburden, EDC was exposed for an extended period to collect dust in two home locations and at schools (Viegas et al., 2020) (Figure 7.1). Although with some downsides, that rely mainly on the fact that bioaerosols are highly dynamic, thus difficult to collect in a representative way (Vissers et al., 2001), settled dust is considered to be a long-term integrated sample of particles that have been airborne. As such this method is more reliable to sample bioaerosols (Noss et al., 2008). Indeed, settled dust evidences a composite view of bioaerosols in the indoor environment that is being assessed (Madsen et al., 2012; Viegas et al., 2020, 2019). Therefore, EDC permits consistent estimation of exposure, since a single EDC analysis is equal to the sum of several air-impaction measurements (Institute of Medicine, 2004). Furthermore, EDC allows for an exclusive identification of some fungal species and higher fungal diversity, when compared to air samples obtained by impaction or even with other passive methods (Viegas et al., 2020). The coupling of this sampling method with particle measurement allowed a more complete analysis of children's exposure in their daily lives.

Indoor particle exposure constitutes a significant percentage of overall exposure, as children spend the majority of the time indoors (Faria et al., 2020). In our study, both fractions (PM2.5 and PM10) had higher concentrations in schools than in dwellings, which is related to children's activity during classes, resuspension of PM and inadequate ventilation (Faria et al., 2020). Studies carried out in European cities showed similar concentrations in schools (Rivas et al., 2014; Rovelli et al., 2014) and in dwellings (Hänninen et al., 2004; Langer et al., 2016; Stranger et al., 2007).

The settled dust presented a different pattern, characterized by higher levels in the dwellings. This difference between the PM and the collected dust by the EDC behavior has already been found in other studies, which indicated that settled dust is less influenced by the short-term variability of the indoor activities and ventilation (Cox et al., 2017; Estokova and Stevulova, 2012). Particle deposition depends on the size of the particles, their sedimentation processes (diffusion in the case of very small particles or gravity in the case of larger particles) (Estokova and Stevulova, 2012), the amount of furniture in the spaces (Thatcher et al., 2002), the type of ventilation and air turbulence (Thatcher and Layton, 1995).

The importance of using different culture media was validated and followed the same tendency as previously reported in studies performed in different indoor environments (Viegas et al., 2020, 2019, 2018a, 2018b, 2017a, 2017b). Regarding bacteria detection, no contamination by Gram-negative bacteria was detected in classrooms, which can partially be explained by less tolerance to the environmental conditions of these species (Adhikari et al., 2014). In what refers to fungal contamination, it was possible to detect different species in both culture media applied (MEA and DG18), with higher diversity of *Aspergillus* sections on living rooms as observed on DG18. Indeed, the exclusive identification by DG18 of *Aspergillus* sections *Circumdati* and *Nidulantes*, both with toxigenic potential (Varga et al., 2015), on living rooms

should be highlighted. Another concern regarding the toxigenic potential of the fungal species was the detection of *Aspergillus* section *Flavi* on the living rooms and of *Aspergillus* section *Fumigati* present in both sampling locations. Additionally, *Aspergillus* sections *Circumdati, Flavi, Fumigati* and *Nidulantes* identification should be emphasized since all the four *Aspergillus* sections are considered as indicators of harmful fungal contamination and, although our study has not detected these toxigenic species, their analysis should be performed in order to better contribute to the implementation of corrective measures (Dillon et al., 1996). Indeed, these species can produce mycotoxins that can become airborne on conidia or smaller fragments suggesting a potential inhalation or ingestion by indoor occupants (Borchers et al., 2017). Mycotoxins are known to have a wide array of adverse health effects or being carcinogenic to humans (Bennett and Klich, 2013).

Culture-based methods were able to provide positive results within *Aspergillus* genera, whereas the *Aspergillus* sections were not detected with molecular tools. Despite these observations, molecular tools are generally a suitable solution to overcome the nonviable/nonculturable limits of the commonly used culture-based methods as they might also provide a more exhaustive diversity profile (e.g., high throughput sequencing), unlike culture methods that might reveal less abundant taxa in an environment. However, culture-independent molecular methods often only identify most of the organisms until taxonomic levels (Cooley et al., 2000; Madsen et al., 2020; Mbareche et al., 2019) and this level of identification is insufficient for exposure assessment. Furthermore, it has already been reported that the viability of microorganisms can affect their inflammatory and/or cytotoxic potential and only viable microorganisms can cause infections, justifying the preference of culture-based methods (Cooley et al., 2000; Croston et al., 2016; Huttunen et al., 2003).

As fungal resistance to available azole drugs is an emergent global health problem (Fund et al., 2017), especially with *Aspergillus fumigatus* (Chowdhary and Meis, 2018; Sewell et al., 2019; Verweij et al., 2016), an exploratory screening of the frequency of fungal reduced susceptibility to azoles in dwellings and schools was conducted in this study. Some nonpathogenic species exhibited reduced susceptibility to one or more azoles, including *Aspergillus* sections *Nigri* and *Candidi*. In order to confirm the resistance phenotype of these species, further susceptibility tests and/or molecular detection of resistance mutations must be performed. So far, azole-resistant isolates with identical genetic profiles were found to be globally distributed and sourced from both clinical and environmental locations, thus, reinforcing azole resistance as an international public health concern (Sewell et al., 2019). In Portugal, some resistant *Aspergillus* sp. have already been found in the environment (data not published), but never in this context. If the resistance phenotype is confirmed, it will be a novelty as it has never been described in these environments.

The statistical analysis revealed some positive correlations that suggest (more evident on MEA than on DG18) that fungal reduced susceptibility to azole drugs, such as voriconazole and posaconazole, might

be developed when higher fungal contamination is present in those environments. Moreover, it seems that reduced susceptibility to voriconazole and posaconazole are also related among these two azoles. This can be important (if azole resistance is confirmed) to understand the development of resistance, since voriconazole and posaconazole, though belonging to the same azole class, differ in their molecular structure: voriconazole is a short-tailed triazole (similar to triazole fungicides used in agriculture), whereas posaconazole (such as itraconazole) is a long-tailed triazole (Caramalho et al., 2017). Understanding how fungal mutations affect drug affinity is necessary for the design of improved azoles that might overcome fungal resistance (Sagatova et al., 2016).

7.5 Conclusions

The indoor exposure to PM and bioburden at children's dwellings and schools was assessed by particle measurement and by using EDC. Results showed that the PM concentrations in classrooms highly exceeded the limit values established by the Portuguese legislation for indoor air quality. Although not correlated with PM, EDC provided information regarding the bioburden present indoors unveiling the presence of fungal species with toxigenic potential and nonpathogenic species exhibited reduced susceptibility to one or more azoles, including *Aspergillus* sections *Nigri* and *Candidi.*

Future studies at a larger scale, applying the same sampling approach—EDC coupled with particulate matter assessment—should be implemented to allow for a long-term integrated sample of organic dust.

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Chapter 8

Chapter 8. Children's exposure to size-fractioned particulate matter: chemical composition and internal dose

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Published in: Science of the Total Environment. Accepted.

Journal Impact Factor (2021): 7.963

Abstract

The health effects of the particulate matter depend not only on its aerodynamic diameter and chemical composition, but also on the time activity pattern of the individuals and on their age. The main objective of this work was to assess the exposure of children to aerosol particles by using personal instruments, to study the particle size and composition of the inhaled PM, and to estimate their transport and deposition into the human respiratory tract. The average daily PM2.5 exposure was 19 μg/m^3 and the size fractions with the greatest contribution to PM2.5 concentrations were 1 < AD <2.5 μm and AD <0.25 μm. Results indicated a contribution of 9% from the mineral aerosol, 7.2% from anthropogenic sulphate, 6.7% from black carbon and 5% from anthropogenic trace elements to the daily exposure to PM2.5. The levels of mineral and marine elements increased with increasing particle size, while anthropogenic elements were present in higher concentrations in the finest particles. Particle size has been shown to influence the variability of daily dose deposited between the extrathoracic and alveolar-interstitial zones. On average, 3% of the PM deposited in the bronchial region, whereas 5% to 8% were found in the bronchiolar region. The level of physical activity had a significant contribution to the total daily dose.

Keywords: PM2.5, personal sampling, elements, dosimetry model, respiratory tract

8.1. Introduction

Particulate Matter is one of the major environmental concerns due to its harmful effects on human health (Liu et al., 2019; Ren et al., 2021). Exposure to PM2.5, particulate matter with an aerodynamic diameter less than 2.5 μm, increases the risk of hospital admission for cardiovascular and respiratory diseases (Amsalu et al., 2019; Danesh Yazdi et al., 2019). According to the European Environment Agency's 'Air Quality in Europe — 2020 report', in 2018, long-term exposure to PM2.5 was responsible for approximately 417,000 premature deaths in Europe (EEA, 2020).

The health effects of PM depend on its chemical, physical and biological properties and on the place where it deposits in the respiratory system (Sturm, 2020). PM enters in the human body mainly through the inhalation route and the estimation of the aerosol deposition in the human respiratory tract during breathing provides valuable evidence on the complete exposure–dose–response relation (Mitsakou et al., 2007).

The health outcomes of PM are most noticeable in some susceptible groups of the population. Children belong to one of these groups because their respiratory and immune systems are still developing and they have higher rates of inhalation and oxygen consumption per unit of body weight, due to their physiology, physiognomy, and behavioural characteristics (Buonanno et al., 2011; Burtscher and Schüepp, 2012; Landrigan et al., 2004; Moya et al., 2004).

The PM concentrations in urban areas are commonly measured and controlled by fixed air quality monitoring stations, equipped with automated instruments and with sufficient time resolution to study temporal variability. However, concentrations of air pollutants vary, in time and space, depending on variations in emission sources, meteorology, and topography (Wilson and Zawar-Reza, 2006). Since these factors can significantly change the concentrations across a city, and people spend more than 85% of their time indoors (Cunha-Lopes et al., 2019; Faria et al., 2020), fixed air quality monitoring stations are not representative of the actual population exposure to pollutants (Kaur et al., 2005; Tran et al., 2020). The exposure assessment must consider the time spent in all the microenvironment visited by an individual during the day and the concentration of the pollutants in these MEs, which can be achieved by direct methods that use personal equipment, or indirect methods that considers measurements performed with fix instruments installed in the different MEs. The direct methods have a higher correlation with personal exposure because they take into account all the MEs affecting the daily exposure and because the time activity pattern of each individual is taking into account (Huang et al., 2017). However, they are difficult to apply on a large scale as they require that each individual carry personal equipment during all his daily activities (Steinle et al., 2013). The main advantages of the indirect methods are their easier application on a large scale, as less equipment is needed to reach a larger population and the possibility of studying in detail the MEs that most affect the personal exposure (Steinle et al., 2013).

The dose can be studied as inhaled dose, integrating exposure and inhalation rates, as done in Almeida-Silva et al. (2015) and Faria et al. (2020), or as a deposited dose (Almeida-Silva et al., 2018), through the use of numerical models as described in Mitsakou et al. (2007) and applied in this study. This last approach allows a more detailed analysis of the deposition of PM along the HRT but requires the knowledge of the aerosol size distribution, to which an individual is exposed, density, shape, hygroscopic, and chemical reactions of the PM (Yeh et al., 1976).

This work aims 1) to study the size distribution of the aerosol particles to which children are exposed in their daily life, and their chemical composition and 2) to link the external personal exposure to the internal dose by inhalation using a computational model that estimates the transport and deposition of PM into the HRT.

8.2. Methods

8.2.1 Size-segregated PM sampling

Nine children, living and studying in the metropolitan area of Lisbon (Figure 8.1), were selected to perform personal measurements of PM for a period of 72 hours continuously, during working days, between May and June 2018. As shown in Table S8.1, in the supplementary material, the children, eight girls and one boy, were between 7 and 10 years old.

Each child carried a trolley with a portable monitoring device, Sioutas Cascade Impactor five-stage SKC (SKC Inc., U.S. Patent No. 6,786,105), with an air inlet tube placed in the breathing zone. The impactor was connected to a Leland Legacy® sampler pump that operated at a constant flow rate of 9 L/min, calibrated by a DryCal primary flowmeter (Bios Defender 510, MesaLabs, USA). During some activities like bathing or sports, children were allowed to place the trolley aside but close to protect instruments from moisture and vibration.

PM was collected at five 50% size cut-off ranges: > 2.5 μm, 1.0–2.5 μm, 0.50–1.0 μm, 0.25–0.50 μm and < 0.25 μm. The smallest diameter of 0.03 μm was assumed for the last stage of the particulate filter < 0.25 μm. Polytetrafluoroethylene filters (PTFE, SKC) with 37 mm diameter and 2.0 μm pore size were used for sampling of PM0.25, while 25 mm filters with 0.5 μm pore size were selected for the other stages. The filters were weighed before and after sampling with a microbalance (Sartorius R160P) following the procedure described in EN12341. PM mass concentrations were determined by dividing the filter loads by the sampled air volume. The methodology is in accordance with that applied by Cunha-Lopes et al. (2019), which preceded this one

Figure 8.1 - Location and classification of homes and schools of the 9 selected children, and the fixed urban background station.

8.2.2 Chemical characterisation

The samples were analysed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS from THERMO, X Series II) and Inductively Coupled Plasma - Atomic Emission Spectrometry (ICP-AES from THERMO, IRIS Advantage TJA Solutions) to determine major (Al, CA, Fe, K, Mg, Na, P, S) and trace elements (Li, B, Ti, V, Mn, Ni, Cu, Zn, Ga, As, Rb, Sr, Y, Zr, Nb, Mo, Cd, Sn, Sb, Ba, La, Ce, Nd, Pb, Bi, Th, among others). Each filter was subjected to acid digestion (1.25 mL HNO_3: 2.5 mL HF: 1.25 mL $HClO_4$). For every batch of acid digested samples, the corresponding blanks followed the same analytical procedures. Three multi-elemental solutions Spec® 1 (rare earth elements, REE), Spec® 2 (alkalis, earth alkalis, and metals) and Spec® 4 (Nb) were used to elaborate external calibration curves. The detection limits are close to 0.005 μg m^{-3} for major elements and 0.05 ng m^{-3} for most trace elements. Repeated measurements were performed with quality control standard solutions and a standard reference material (SRM 1633b, fly ash). Additionally, a multi standard composed of the same elements was introduced in each batch of samples to check the accuracy of measurements. The methodology enables quantification with relative errors < 5% for most elements, and around 10% for Al and Na.

8.2.3 Black Carbon

The BC was measured through a MicroAeth AE51 model aetalometer (AethLabs, USA). The AE51 measures the changes in light absorption, transmitted at 880 nm, which occur during the deposition of the

BC particles onto a small Teflon-coated borosilicate fibreglass filter. Data were recorded every 1 minute at a flow rate of 100 mL/min.

The captured data was corrected using the "Optimized Noise-Reduction" (ONA) software to reduce signal noise.

8.2.4 Mass closure

Chemical mass closure was calculated including the contribution of BC, non-sea salt sulphate ($nssSO_4^{2-}$), mineral dust (MD), sea salt (SS), and trace elements (Trace) to the total mass, to better understand the chemical composition and sources affecting the children daily exposure.

The contribution of each aerosol type was calculated according to the equations presented in Table 8.1 and followed the same criteria used in Faria et al. (2022). The mineral dust was determined considering the oxides of Al, Ca, Fe, K, La, Mn, Si, and Ti (Calvo et al., 2013; Kong et al., 2015; Zhang et al., 2013). The soil fractions of Ca (soilCa), Fe (soilFe) and K (soilK) were calculated using their typical crustal ratios, 0.45, 0.63, and 0.32 of aluminium, respectively (Mason, 1966). Silicon was estimated through the soil Si/Al ratio (3.14) (Mason, 1966). Sea salt was calculated through the sum of Cl, Na, Mg, sea salt Ca (ssCa), sea salt K (ssK), and sea salt SO_4^{2-} ($ssSO_4^{2-}$) (Calvo et al., 2013; Diapouli et al., 2017). The sea salt fractions of Ca, K, and SO_4^{2-} were calculated using their typical ratios for sea water (Ca/Na, K/Na, and SO_4^{2-}/Na). Chlorine was estimated using the sea water Cl/Na ratio (1.798) (Calzolai et al., 2015; Henderson and Henderson, 2009). The elements As, Ba, Ce, Cr, Cu, Li, Ni, P, Pb, Rb, Sb, Sn, Sr, V, Zn, and Zr and the anthropogenic fractions of K (anthropoK), Ca (anthropoCa), and Fe (anthropoFe) were associated with the trace elements group (Calvo et al., 2013) (Table 8.1). BC and $nssSO_4^{2-}$ were considered separately from any group.

Table 8.1 - Equations used in the mass closure assessment

	Equations	**Where**
Mineral dust	1.89 × [Al] + 1.4 × [soilCa] + 1.4 × [soilFe] + 1.2 × [soilK] + 1.17 x La +1.58 x Mn + 2.14 × [Si] + 1.67 × [Ti]	[soilCa] = 0.45 × [Al] [soilFe] = 0.62 × [Al] [soilK] = 0.32 × [Al] [Si] = 3.14 × [Al]
Sea Salt	[Cl] + [Mg] + [Na] + [ssK] + [ssCa] + [$ssSO_4^{2-}$]	[Cl] = 1.798 × [Na] [ssCa] = 0.038 × [Na] [ssK] = 0.037 × [Na] [$ssSO_4^{2-}$] = 0.253 × [Na]
Trace elements	[anthropoCa] + [anthropoFe] + [anthropoK] + [As] + [Ba] + [Ce] + [Cr] + [Cu] + [Li] + [Ni] + [P] + [Pb] + [Rb] + [Sb] + [Sn] + [Sr] + [V] + [Zn]+[Zr]	[anthropoCa] = Ca -soilCa – ssCa [anthropoFe] = Fe - soilFe [anthropoK] = K - soilK – ssK
$nssSO_4^{2-}$	SO_4^{2-} - $ssSO_4^{2-}$	

8.2.5 Particle transport and deposition in the respiratory tract

A mechanistic numerical model that describes aerosol dynamics was employed to determine particle deposition in the respiratory tract of the children as a whole and in its regions: the extrathoracic (ET) and the main thoracic regions, i.e., the bronchial (BB), the bronchiolar (bb) and the alveolar-interstitial (AI). The model predicts the temporal variation of particle concentration and the regional deposition of the inhaled particles during a breathing cycle by solving the aerosol general dynamic equation (GDE) taking into account breathing dynamics:

$$\overbrace{\frac{\partial}{\partial t}(A_t\, n_i)}^{\text{temporal variation}} = \overbrace{-\frac{\partial}{\partial x}(A_A\, u\, n_i)}^{\text{convection}} + \overbrace{\frac{\partial}{\partial x}\left(A_t\, D_i\, \frac{\partial n_i}{\partial x}\right)}^{\text{diffusion}} - \overbrace{U_{d_i}\, \Gamma\, n_i}^{\text{deposition}} + \overbrace{\left(\frac{\partial}{\partial t}(A_t\, n_i)\right)_{\text{growth}}}^{\text{condensation}} + \overbrace{\left(\frac{\partial}{\partial t}(A_t\, n_i)\right)_{\text{coagulation}}}^{\text{coagulation}}, \qquad \text{Equation 8.1}$$

where t is the time, n_i the particle number concentration in section i of the size distribution, u the fluid velocity, D_i the diffusion coefficient of particles with size i, A_i and A_A the time dependent and constant cross-section of all air ducts, respectively, at distance x from the respiratory system entrance, Γ the circumference of air ducts and U_{di} the particle deposition velocity. The GDE is considered in a one-dimensional form and describes the different external (convection, axial diffusion, deposition) and internal (growth, coagulation) processes acting simultaneously on the inhaled particle population. The description of the above deposition mechanisms is based on standard theory for the respective aerosol processes. The thoracic region of the respiratory tract is described with the help of the classical morphometric model “A” by Weibel (Weibel, 1963). The volume of the alveolated section of the lung is left to vary with time to accommodate effects due to breathing dynamics. A simplified morphological scheme that consists of sequential cylindrical airways describes the extrathoracic region through the mouth pathway. The air velocity along the airways of the respiratory tract is determined by solving the equation of continuity.

A detailed description of the model, its validation against experimental data, as well as its application potential have already been published (Almeida-Silva et al., 2018; Mitsakou et al., 2007, 2005; Pilou, 2020; Pilou et al., 2015).

8.2.6 Particle density

Density is one of those particle physicochemical characteristics that influence the deposition of particles in the respiratory tract (Yeh et al., 1976). In order to use a realistic density, representative of the

sampled particles, rather than use a reference density, the following equation, based on the species chemical composition, was applied (adapted from DeCarlo et al. (2004)

$$\rho_\rho = \frac{\sum_{x=1}^{n} C_x}{\sum_{x=1}^{n} \frac{C_x}{\rho_x}}, \qquad \text{Equation 8.2}$$

where

C_x is the mass concentration and ρ_x is the density of specie x, and n is the total number of species.

The species and respective densities used to calculate the particle density are in Table S8.2, in the supplementary material. The calculated density of particles in the city of Lisbon ranged from 1.5 to 3.8 g/cm^3.

8.2.7 Time activity pattern

To understand the impact of different physical activities on the daily inhaled dose, it was necessary to understand which activities with different levels of physical arousal each child performed per day and for how long. Each child filled a time activity diary, where the main activities performed throughout the day of the measurements were recorded. The microenvironments and times entered in the diary by the children during the measurements were validated using a portable GPS (Garmin model eTrex 20) placed next to the equipment's.

As can be seen in Figure 8.2, among the nine children, the time spent sleeping varied between 33 and 43% and the time spent sitting awake ranged between 35 and 54%. On average, the total time spent on exercise (light and heavy) was 20%. Among the children, C8 stands out as the one who spent the most time on light exercise (18%) and C3 on heavy exercise (19%).

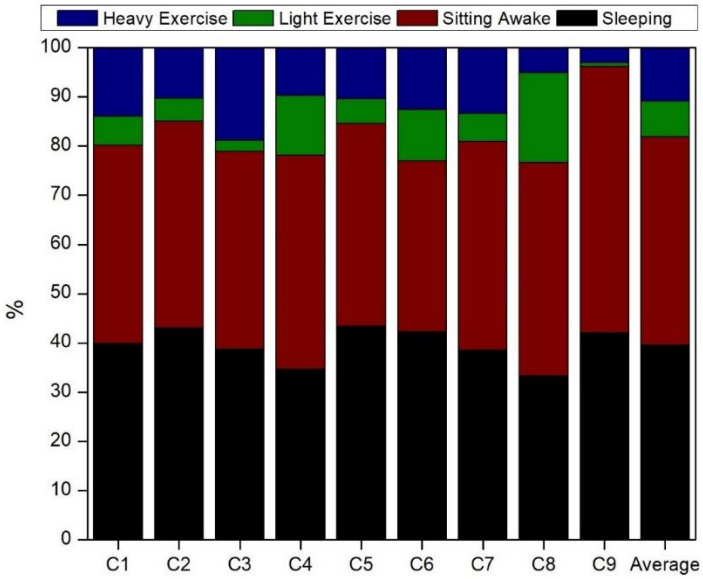

Figure 8.2 - Time spent in a day on each type of activity (%)

8.3. Results and discussion

8.3.1 Exposure to PM2.5

Figure 8.3 presents the average concentrations of PM2.5 and respective chemical composition. The average PM2.5 exposure was 19 μg/m^3, which is above the new World Health Organisation daily reference value of 15 μg/m^3 (WHO, 2021).

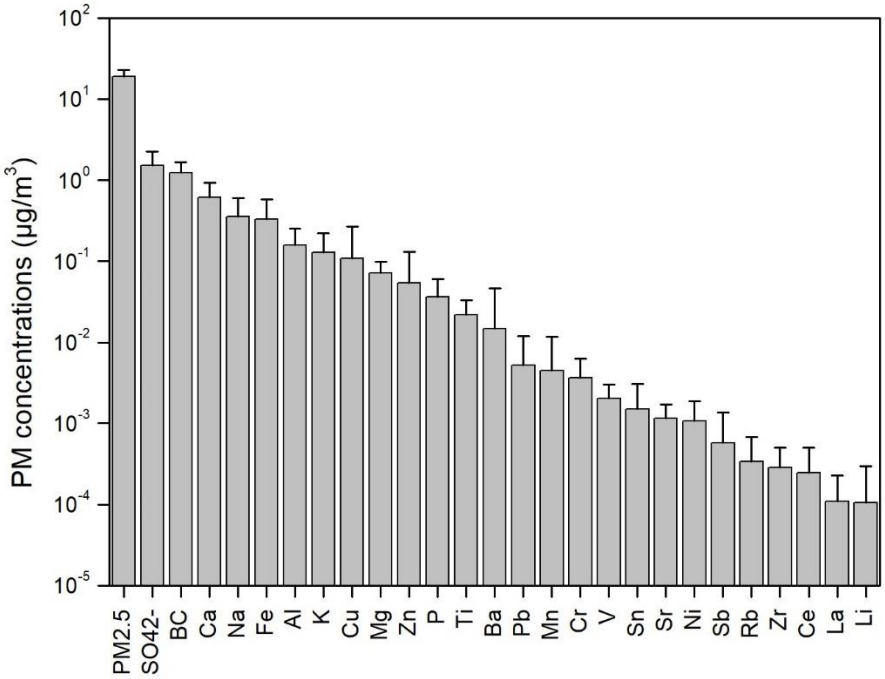

Figure 8.3 - Mass concentrations in PM2.5 collected by a personal sampler carried by 9 children (values in μg/m^3). The whiskers represent standard deviation.

The average $PM_{2.5}$ exposure obtained using personal monitoring was higher than the average concentrations measured in the nearest fixed urban background station (Figure 8.1) for the correspondent sampling period of each child (9.3 μg/m^3). Figure 8.4 shows that there is a poor correlation between the children's exposure to PM2.5 and the correspondent PM2.5 concentrations measured at the nearest urban background monitoring station ($R^2 = 0.31$). These results reinforce the importance of assessing the personal daily exposure since it depends on the concentrations of PM in different outdoor and indoor MEs frequented by the children during the day and the time activity pattern. Similar conclusions were taken by Kim et al. (2006) in a study conducted in Toronto, Canada, where the average personal exposure to PM2.5 (22 μg/m^3) was greater and more variable than the average ambient level of PM2.5 measured at the central fixed location (11 μg/m^3). In a study conducted in Bologna, Italy, regarding police and parking wardens' exposure to PM10 (among other pollutants), the mean personal exposure measurements (185.10 ± 38.52 μg/m^3) were higher than the concentrations measured in the fixed monitoring stations (43.56 ± 24.10 μg/m^3) (Violante

et al., 2006). It can be then concluded that the daily exposure to PM is undervalued by the fixed monitoring stations.

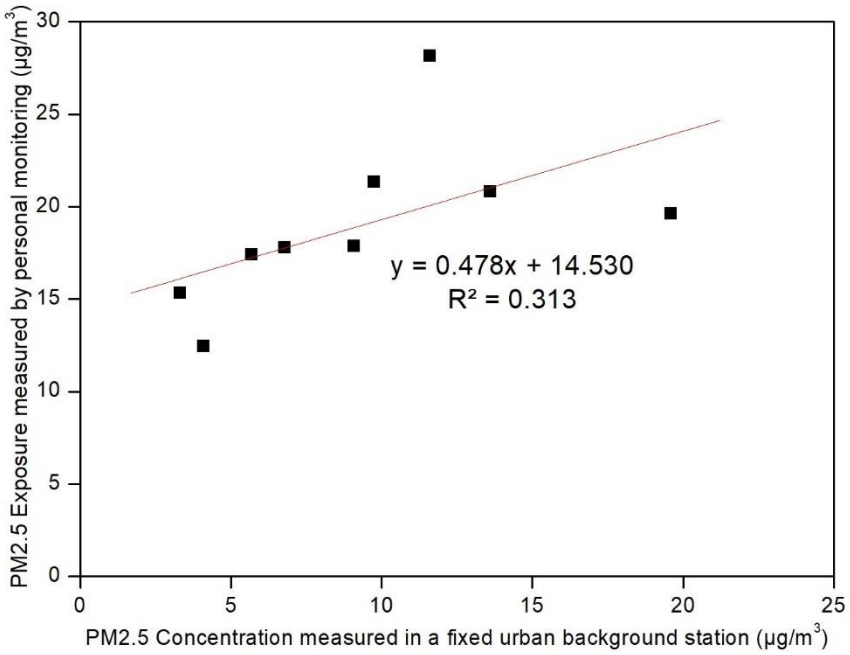

Figure 8.4 - Correlation between the PM2.5 exposure of the nine children to PM2.5 measured with a personal sampler and the PM2.5 concentrations measured in the near fixed urban background station.

8.3.2 Mass closure and PM2.5 chemical composition

Mass closure reconstructed the PM mass levels by achieving closure between PM2.5 mass measured by gravimetry and the sum of the analysed PM chemical compounds. On average, the sum of the chemical compounds accounted for 33% of the PM2.5 mass. The remaining fraction can be attributed to important PM compounds which are very relevant for the share of the PM mass but were not measured, such as organic carbon, nitrates and ammonium. For instance, in Lisbon, Faria et al. (2022) showed that the particulate organic matter was the dominant contributor to the total mass of PM inside homes (63%) and schools (57%), which are the MEs that most contribute to the PM daily exposure.

Figure 8.5 shows the contribution of each particle category to the PM2.5 concentration assessed in this work by a direct method and compares it with the results obtained by Faria et al. (2022), who studied the children's exposure in Lisbon by an indirect method, i.e., exposure was estimated by the integration of time activity patterns and the concentrations of pollutants measured in the MEs where children spend most of their day (home, school, outdoor, and transports) with fixed instruments. The integrated exposure to PM2.5 estimated by Faria et al. (2022) was 21.2 µg/m^3 agreeing with the average exposure to PM2.5 measured in the present study using personal equipment (19 µg/m^3).

Mineral dust accounted for 9% of the PM2.5, which is in the same range of values of the work developed by Faria et al (2022) in Lisbon (7.5%). In the work performed by Rivas et al. (2014) about the exposure of children in schools, mineral dust elements had a contribution of 27% in the indoor and 37% in the outdoor to the PM2.5 total mass, while the work developed by Oliveira et al. (2019) reported mineral dust contributions between 2 and 15%.

SO_4^{2-} was the chemical compound with the highest average concentration (Figure 8.3) and $nssSO_4^{2-}$ was the second main contributor to the total PM2.5 (7.2%) (Figure 8.5). Child C2 had the highest exposure to $nssSO_4^{2}$, with concentrations of 2.96 $\mu g/m^3$ and at the same time the highest exposure to PM2.5 (28.1 $\mu g/m^3$). SO_4^{2-} results from industrial processes, energy production, and road traffic (Amato et al., 2014; Calvo et al., 2013). The results were similar to those found in the study developed by Faria et al. (2022), who showed a $nssSO_4^{2-}$ contribution of 7.5% to the PM2.5 exposure.

BC represented 6.7% of the total mass of PM2.5. which is in agreement with the results obtained by Faria et al. (2022) in Lisbon (5.4%). BC is a good indicator of traffic-related PM pollution since its emissions are closely related to the combustion of carbonaceous fuels (Jeong and Park, 2017). Child C4, who presented the highest exposure to BC (2.17 $\mu g/m^3$), spent more time commuting than all the others (10% of the daily time). Child C9 had the second highest exposure to BC (1.84 $\mu g/m^3$). The time trend for this pollutant showed that the home was the ME that most contributed to the C9 daily exposure to BC. Knowing that cooking is an important source of BC in indoor environments (Sankhyan et al., 2021), and for example, grilling, even on an electric plate, emits large concentrations of BC, as demonstrated in the study carried out by Alves et al.(2021), this result can be explained by the fact that the home of this child has an open kitchen, which allows a higher dispersion of BC particles through the home.

The SS accounted, on average, to 5.9% of the total PM2.5 mass. The city of Lisbon is bathed by the Tagus River and is 7 km away from the Atlantic ocean, which contributes to relevant concentrations of marine aerosols (Almeida et al., 2013).

The average percentage of the anthropogenic trace elements in the PM2.5 was 5% and varied between 3.5 and 9.3%, with child C9 standing out with an average exposure of 1.82 $\mu g/m^3$. The contribution of the anthropogenic elements to the PM2.5 estimated by Faria et al. (2022) was 5.2%, which showed, once again, that the concentration measured by the personal monitors and estimated by the integration of MEs concentrations and time activity pattern is in agreement.

C7 levels for the different compounds is not presented in Figure 8.5, because it was not possible to measure some of the concentrations of the major elements.

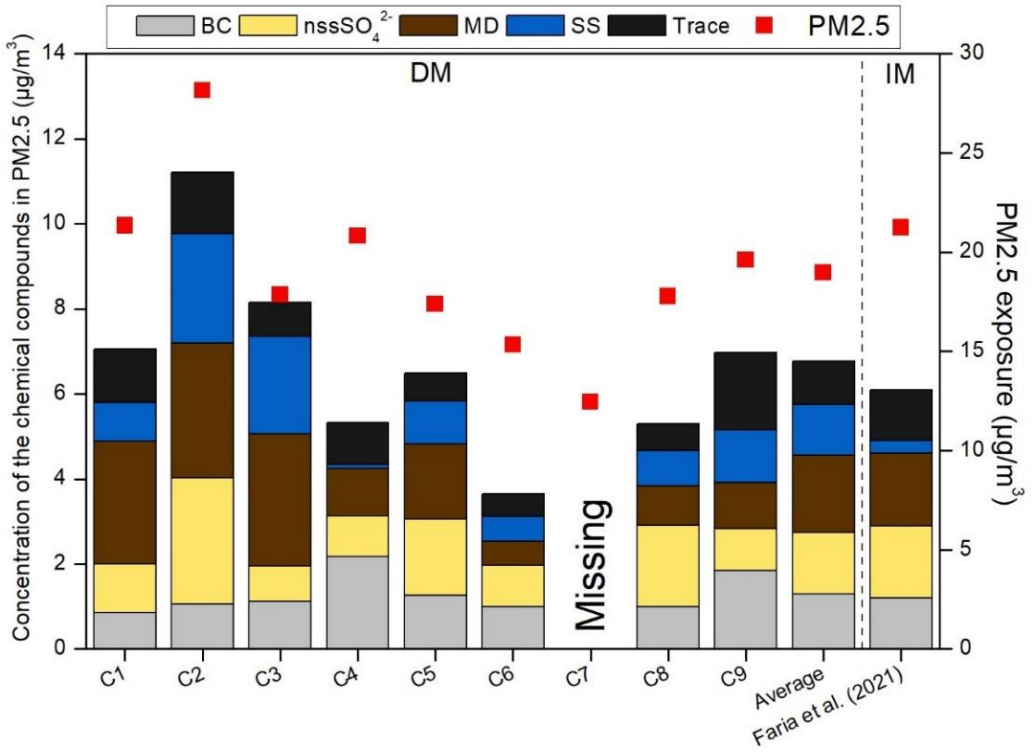

Figure 8.5 - Main chemical compounds affecting the exposure of children to PM2.5 in Lisbon, measured in the present study through a direct method (DM) and estimated by an indirect method (IM) by Faria et al. (2022).

8.3.3 PM2.5 mass size distribution

The children's exposure to PM2.5 varied between 12 and 28 µg/m^3 (Table 8.2), among the nine children, and no clear trend on the size distribution was found. The size fractions with the greatest contribution to PM2.5 concentrations were 1 <AD <2.5 µm and AD <0.25 µm. The particles with an AD<0.25 µm represented the greatest contribution to the PM2.5 concentration for all the children with exception of C1, C3, and C7, which had a higher contribution of particles in the 1.0–2.5 µm fraction. The smaller the diameter of the particle is, the better it can penetrate the respiratory system. Particles with an AD<0.25 include ultrafine particles that can enter the bloodstream and reach the organs (Anderson et al., 2012). The standard deviation are presented in Table S8.3, in the supplementary material.

Table 8.2 - PM2.5 concentration to which each child was exposed and the respective size distribution (values in $\mu g/m^3$).

	<0.25 µm	**0.25–0.50 µm**	**0.50–1.0 µm**	**1.0–2.5 µm**	**PM2.5**
C1	7.51	2.16	3.71	7.94	21.33
C2	9.32	6.52	3.35	8.94	28.13
C3	6.39	1.97	2.16	7.33	17.86
C4	10.20	5.59	2.37	2.65	20.81
C5	5.55	4.09	3.21	4.53	17.39
C6	7.66	1.63	1.47	4.56	15.32
C7	3.68	2.16	1.40	5.20	12.44
C8	9.45	3.52	2.08	2.72	17.77
C9	9.18	4.59	2.92	2.92	19.60

The mass size distribution of PM chemical components is shown in Figures 8.6 and Figure 8.7. The PM chemical components were grouped into three categories: mineral dust, sea salt, and trace elements.

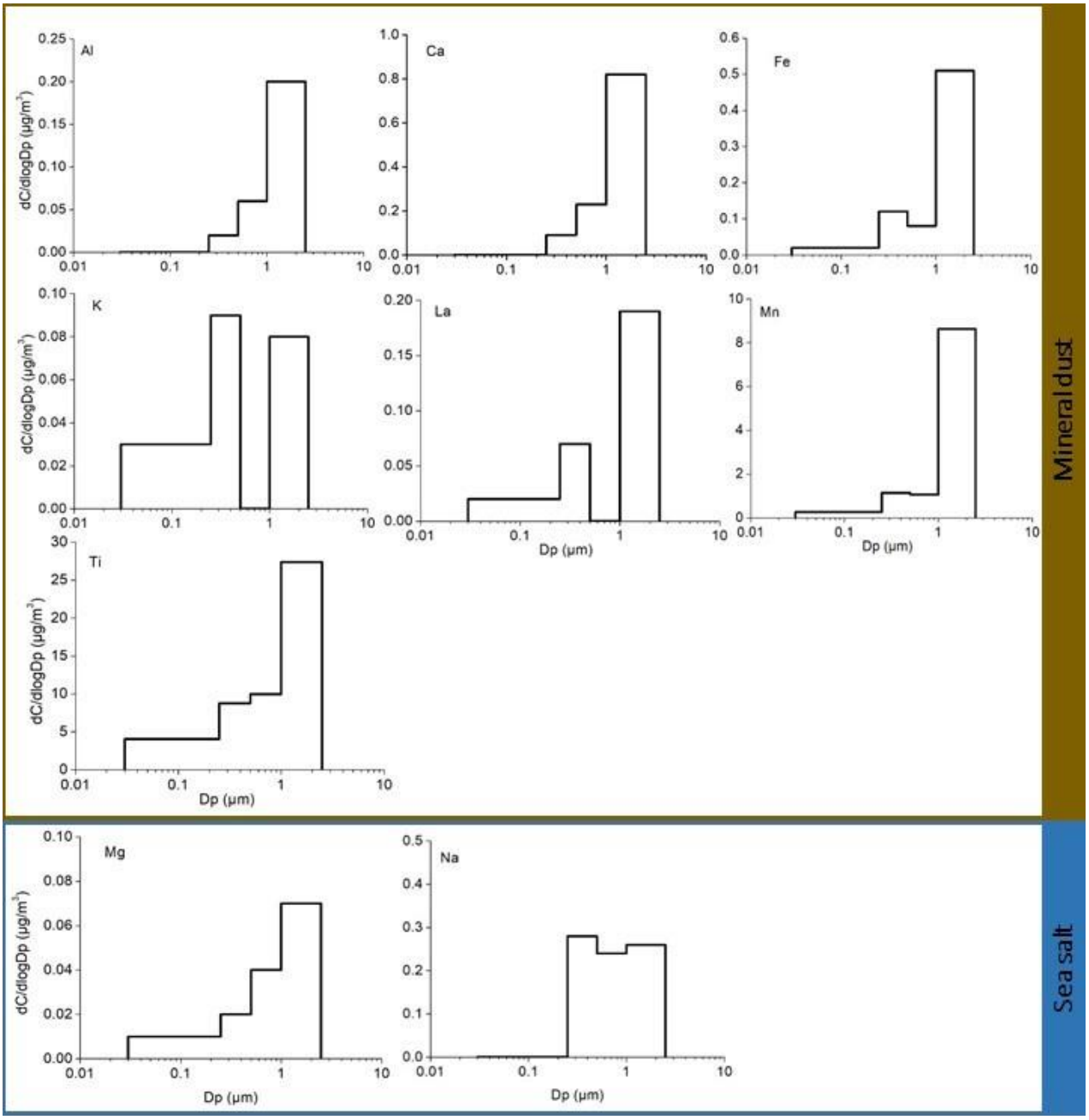

Figure 8.6 - Average mass size distribution of mineral dust and sea salt elements for the 9 children

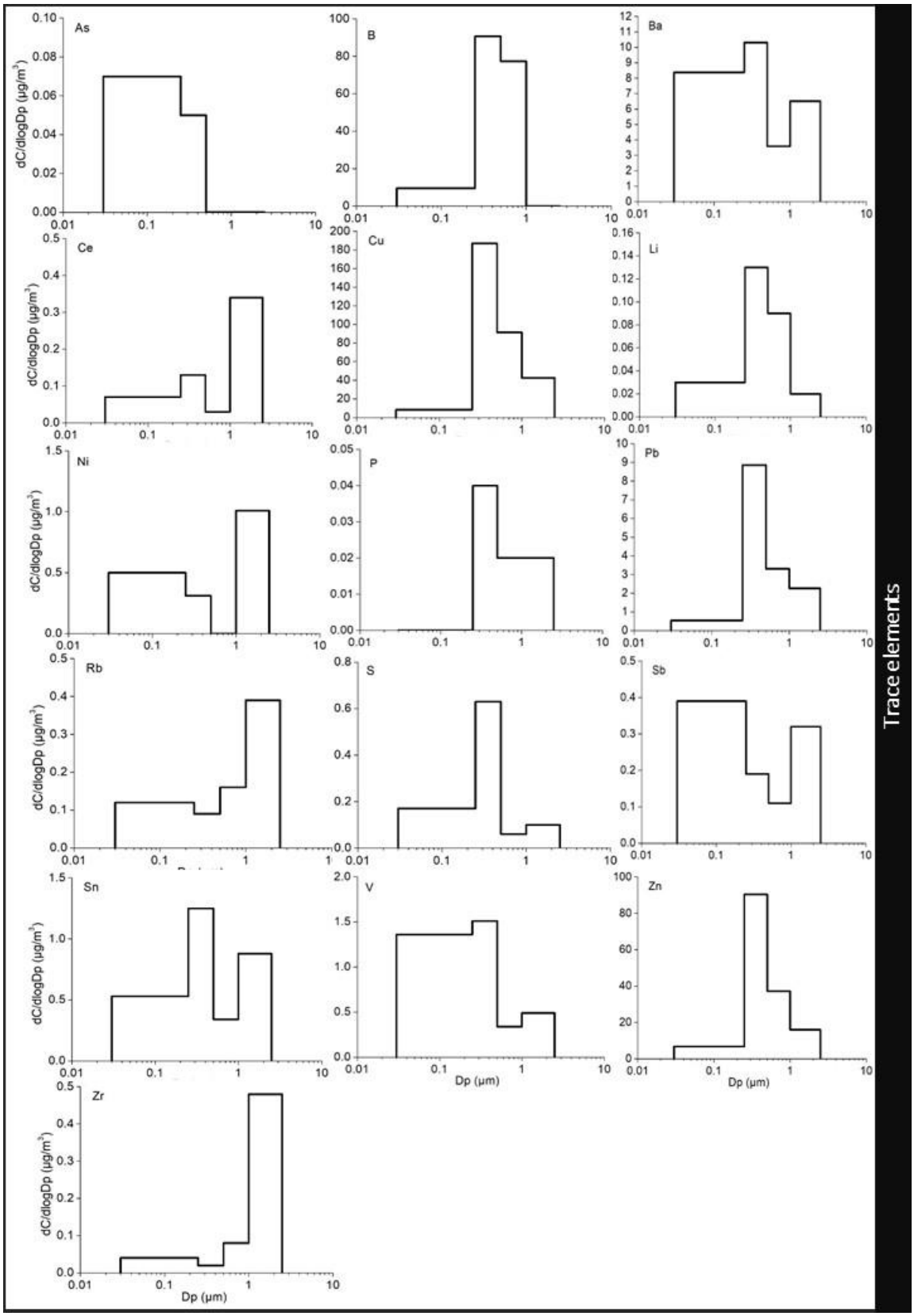

Figure 8.7 - Average mass size distribution of trace elements for the 9 children

Elements associated with mineral dust (Al, Ca, Fe, K, Ti, Mn, and La) were found in higher concentrations in the coarse fraction, with the peak occurring generally more consistently in the range 1-2.5 μm. These results are in agreement with other studies (Martins et al., 2020; Waheed et al., 2011; Zhi et al., 2021). Mineral dust is associated with land surface sediments that have been eroded by wind and transported over long distances until deposited (Mahowald et al., 2005). In urban environments, the mineral dust is related to the resuspension of dust caused by vehicles, works in the city, or, especially in the Mediterranean area where the study site is located, with long-range transport events from North of Africa (Almeida et al., 2005; Artíñano et al., 2001; Calvo et al., 2013; Mahowald et al., 2005). In indoor environments, especially in schools, mineral dust is transported from the outdoor to the indoor and resuspended by the movement of the occupants. In general, the elements associated with the soil have a unimodal distribution, although, in the case of potassium, a different behaviour was observed, characterised by a bimodal distribution. The fine K fraction is related to biomass burning (Calvo et al., 2013), covering the 0.25-1.0 μm fraction, which was also found in the studies by Taiwo et al. (2014) and Zhang et al. (2015) and the coarser fraction of K is related to marine aerosol and soil dust (Diapouli et al., 2017; Z. Zhang et al., 2015).

The elements associated with SS (Mg and Na) followed the same trend as MD elements. These elements were found in greater concentration in coarser fractions, which is according to the existing literature (Diapouli et al., 2017).

The concentrations of trace elements associated with anthropogenic sources, such as As, Ba, Ce, Cu, Ni, Pb, Rb, S, Sb, Sn, V, and Zn, showed a prevalence in the finer fractions (<0.25 μm and 0.25–0.50 μm), although at low concentrations. These elements are associated with industrial processes, fossil fuel combustion, vehicle exhaust, biomass burning, waste, and chemical reactions in the atmosphere (Calvo et al., 2013; Harrison et al., 2003). Some of them seem to have a bimodal distribution. For instance, nickel peaked in the <0.25 μm fraction, followed by a decrease and further increase in the 1.0–2.5 μm fraction. Ni in the fine fraction is associated with the industry, oil burning, and car exhaust (Calvo et al., 2013; Rogula-Kozłowska et al., 2015) and in the coarse fraction with soil dust resuspension (Duan et al., 2012). Several studies have found a bimodal distribution (<0.25 μm and >2.5 μm) of Ni (Alver Şahin et al., 2013; Duan et al., 2012; Waheed et al., 2011; Zhi et al., 2021).

Regarding Sb and Ba, it was found a bimodal behaviour. The 0.1–2.5 μm fraction is usually associated with fuel combustion (Calvo et al., 2013; Rogula-Kozłowska et al., 2015), while the 1-2.5 μm fraction in urban environments is emitted by the abrasion of tyres and the resuspension of road dust (Calvo et al., 2013; Gietl et al., 2010; Rogula-Kozłowska et al., 2015). The study on brake wear particles performed by Gietl et al. (2010) found the peak concentration in the 3 μm fraction.

Regarding sulphur, and its presence in the air as SO_4^{2-}, its peak occurred between the 0.25–0.5 μm fraction, indicating a possible anthropogenic influence (Rogula-Kozłowska et al., 2015), such as energy production and industrial processes, brought to the city by regional transport of ammonium sulphate, or road traffic (Amato et al., 2014; Calvo et al., 2013; Taiwo et al., 2014). Taiwo et al. (2014) developed a study in a steel industrial area with the steel production and in an urban background site and registered an association between SO_4^{2-} and Pb and Zn in the modal peaks of 0.5 μm and a small mode between 1 and 2 μm, as a result of a possible mixture between them, giving rise to $PbSO_4$ and $ZnSO_4$. In our study, the same behaviour was found.

8.3.4 Average daily dose

The particle transport and deposition model was used to calculate the average daily dose in the children's respiratory tract. The necessary parameters of the respiratory tract physiology used in the model were obtained from ICRP (ICRP, 1994) and are shown in Table 8.3.

Table 8.3 - Reference respiratory values at different physical excitation levels for 10-year-old children with functional residual capacity, V_{FRC} = 1.484Lt (ICRP, 1994). V_T: tidal volume, f_R: respiration frequency, V_R: ventilation rate.

Activity		**V_T [Lt]**	**f_R [/min]**	**V_R [m^3/h^1]**
Sleeping		0.304	17	0.31
Sitting Awake		0.333	19	0.38
Light Exercise		0.583	32	1.12
Heavy Exercise	**Male**	0.841	44	2.22
	Female	0.667	46	1.84

The total daily dose and its distribution in the different regions of the respiratory tract was calculated for each child, based on the individual exposure to PM and activity pattern (Figure 8.8). The total daily dose varied from 92 μg (C7) to 177 μg (C2). For all children ~3% of the total daily dose is in the bronchial region, whereas 4.7% to 8% is found in the bronchiolar. However, there is a greater variability regarding the extrathoracic and alveolar-interstitial daily dose, depending on the children: dose in ET region accounts for 42% (C9) to 65% (C3 and C7) of the total daily dose, whereas dose in AI region fluctuates from 27% (C3 and C7) to 47% (C9).

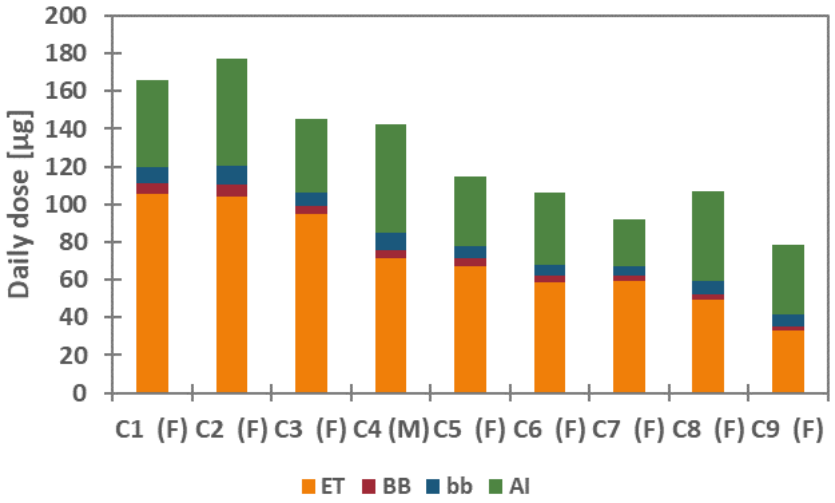

Figure 8.8 - Daily dose per child and its distribution in the regions of the respiratory tract: extrathoracic (ET), bronchial (BB), bronchiolar (bb) and alveolar-interstitial (AI). Female (F) and male (M).

It is also obvious that the ratio of daily dose in the extrathoracic region to that in the alveolar-interstitial region is different for each child (Figure 8.8), varying from 0.9 (C9) to 2.4 (C3 and C7). This can be attributed to the contribution of each particle size bin to the total daily dose, as seen in Figure 8.9. The higher the contribution of sub-micrometre particles to the child's daily dose, the higher the deposition in the alveolar-interstitial region, and thus the lower the ET to AI dose ratio (e.g., C4, C8 and C9). Conversely, when particles with diameters >1 µm have a significant contribution to the daily dose, the ratio is well larger than unity and deposition in the extrathoracic region is high (e.g., C1, C3 and C7).

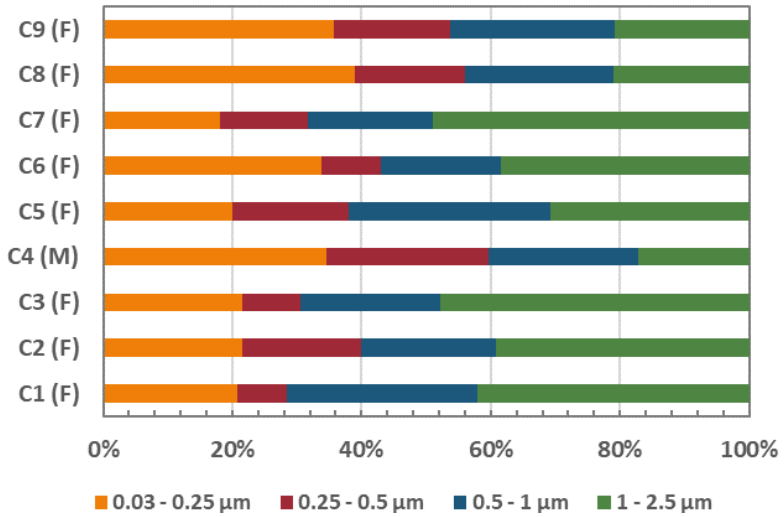

Figure 8.9 - Contribution of particle size to total daily dose per child. Female (F) and male (M).

The total daily dose for each child depends also on the time spent in activities of different physical excitation level, as shown in Figure 8.10. Even if only a small amount of time is spent on daily exercise, it has a significant contribution to the total daily dose. This is obvious even for C9, who spends only 4% of her time being physically active, but this accounts for 20% of her daily dose. Of course, for all other children, who dedicate more time to exercise (15% to 23% daily), the effect on their daily dose is stronger (54% to 64%). This is a result of the higher ventilation rates during exercise comparing to sleeping or sitting awake (Table 8.1), i.e., a child consumes larger amounts of particle laden air during exercise than when sitting or sleeping.

The PM deposit in different regions of the respiratory tract also depends on the physical excitation level (Figure 8.11). As a child becomes more active and ventilation rate increases, deposition of particles occurs earlier in the respiratory tract; more particles deposit in the extrathoracic region and less in the alveolar interstitial as the air reaching this area is already depleted of particles due to earlier deposition. Deposition in the bronchial region is not affected by the activity, whereas there is a slow decrease in deposition in the bronchiolar region as the ventilation rate increases (from 9% to 3%).

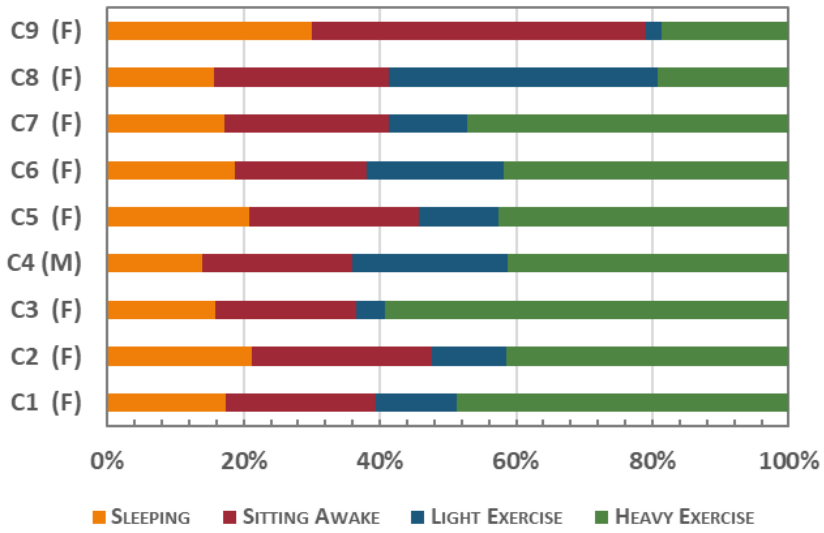

Figure 8.10 - Contribution of each physical excitation level to total daily dose per child. Female (F) and male (M).

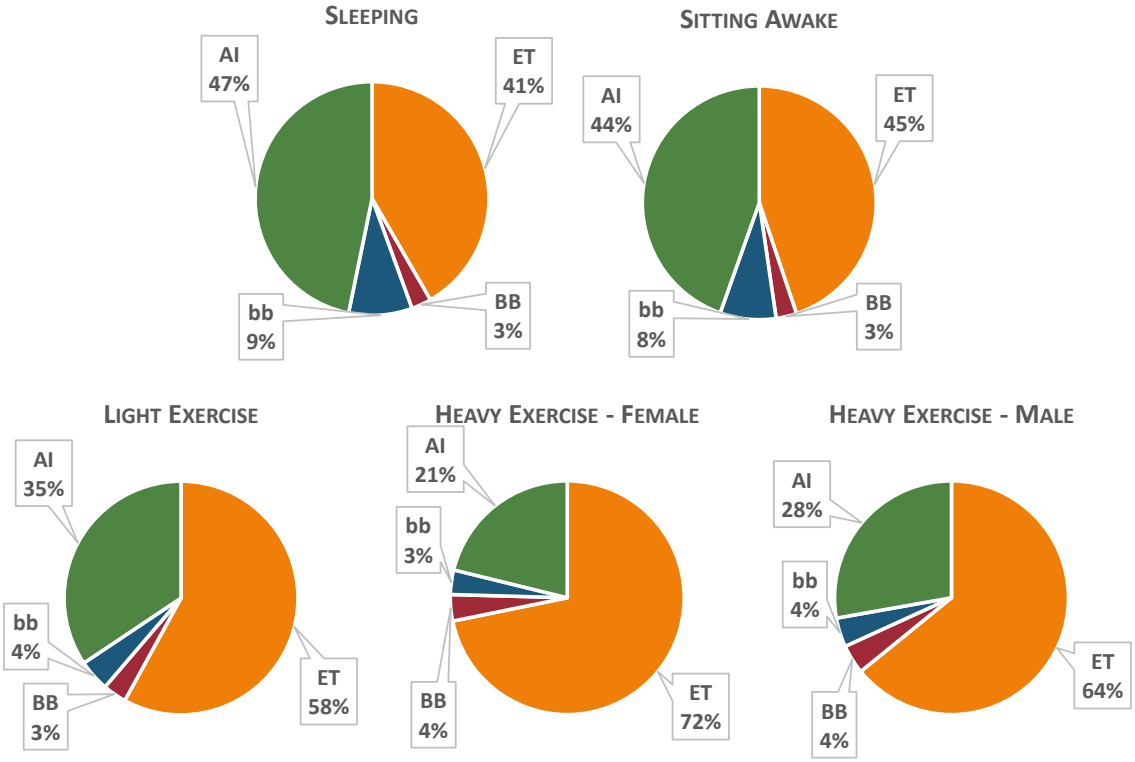

Figure 8.11 - Total dose distribution in the respiratory tract regions for different physical excitation levels (ET – extrathoracic, BB – bronchial, bb – bronchiolar, AI – alveolar-interstitial).

8.4. Conclusion

The personal exposure of children living and studying in Lisbon to size segregated PM2.5 and respective chemical composition was evaluated by a direct method using personal instruments. The measurements of exposure were combined with mathematical models to estimate the average daily dose to PM2.5 in the different regions of the children's respiratory tract, as well as the particle build up in extrathoracic, bronchial, bronchiolar, and alveolar-interstitial regions.

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

- The children average PM2.5 exposure in Lisbon was 19 μg/m^3, which is above the WHO daily reference value of 15 μg/m^3.

- The levels of mineral and marine elements increased with increasing PM size, while anthropogenic elements were present in higher concentrations in the finest particles.

- 3% of the particles deposited in the bronchial region, whereas 4.7% to 8% were found in the bronchiolar region.

- There is an important variability in the extrathoracic and alveolar-interstitial daily dose among children, which can be attributed to the contribution of each particle size bin and level of physical excitation.

- The urban monitoring stations undervalue the daily children exposure to PM.

- The direct method used in this work to evaluate the children exposure to PM in Lisbon was compared with the exposure estimated by the indirect method and similar results were obtained, showing that both methods are valuable alternatives for studying daily exposure to pollutants.

As an overall remark, the measurement of exposure and the PM mass size distribution provides essential data for determining the internal doses in the HRT of children. The results reported may be useful for epidemiological studies, and to establish practical and effective mitigation strategies to reduce the children's exposure to PM and consequently decrease adverse health effects.

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Supplementary material

Table S8.1 - Age and sex of the children under study.

Children	Sex	Age
C1	Female	9
C2	Female	7
C3	Female	9
C4	Male	10
C5	Female	9
C6	Female	10
C7	Female	9
C8	Female	9
C9	Female	8

Table S8.2 - Density of all elements measured.

Element	Density (g/cm^3)	Element	Density (g/cm^3)
Al_2O_3	3.95	As	5.70
CaO	3.34	Se	4.81
Fe_2O_3	5.24	Rb	1.53
K2O	2.35	Sr	2.64
Mg	1.74	Y	4.47
Na	0.97	Zr	6.49
P	1.82	Nb	8.57
SO_4^{2-}	1.75	Mo	1.03
Li	0.53	Cd	8.65
Be	1.85	Sn	6.99
B	2.08	Sb	6.68
Sc_2O_3	3.86	Cs	1.90
TiO2	4.23	Ba	3.50
V	6.10	La_2O_3	6.51
Cr	7.20	Ce	6.76
MnO_2	5.03	Pr	6.50
Co	8.90	Nd	7.01
Ni	8.91	Sm_2O_3	8.35
Cu	8.96	Pb	11.34
Zn	7.14	Bi	9.78
Ga	5.91	Th	11.70
Ge	5.32		

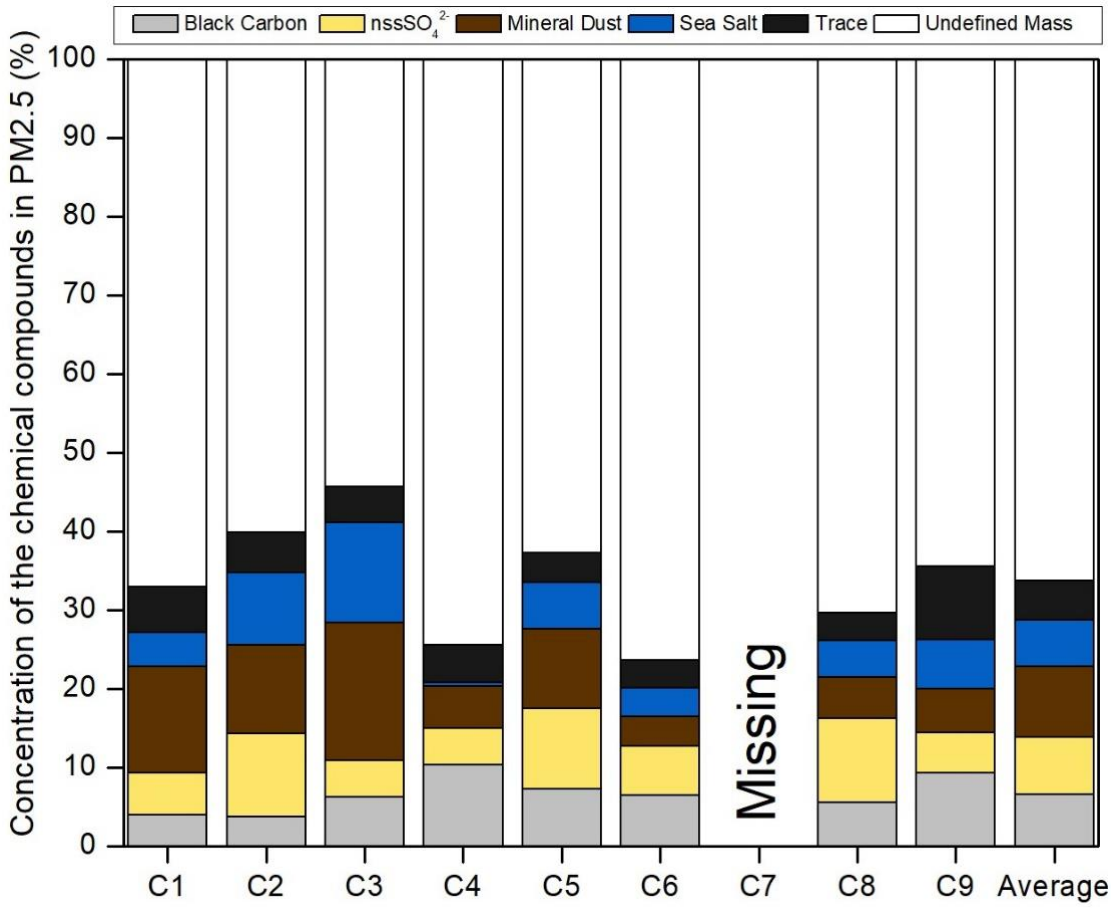

Figure S8.1- Main chemical compounds affecting the exposure of children to PM2.5 in Lisbon (values in %).

Table S8.3 - The standard deviation of the PM2.5 concentration to which each child was exposed to and the respective size distribution (values in μg/m^3).

	<0.25 μm	**0.25–0.50 μm**	**0.50–1.0 μm**	**1.0–2.5 μm**	**PM2.5**
C1	0.23	0.27	0.23	0.19	0.06
C2	0.26	0.26	0.19	0.49	0.65
C3	0.21	0.21	0.23	0.21	0.43
C4	0.28	0.28	0.31	0.28	0.58
C5	0.29	0.29	0.21	0.29	0.55
C6	0.18	0.12	0.12	0.18	0.30
C7	0.18	0.25	0.25	0.18	0.44
C8	0.23	0.36	0.42	0.23	0.64
C9	0.93	0.83	0.59	0.59	1.50

Chapter 9

Chapter 9. Source apportionment of children daily exposure to particulate matter

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Accepted to publication (13 April 2022): Science of the Total Environment.

Journal Impact Factor (2021): 7.963

Abstract

The present study aims to investigate the sources of particulate pollution in indoor and outdoor environments, with focus on determining their contribution to the exposure of children to airborne particulate matter (PM). To this end, parallel indoor and outdoor measurements were carried out for a selection of 40 homes and 5 schools between September 2017 and October 2018. PM2.5 and PM2.5-10 samples were collected during five days in each microenvironment (ME) and analysed by X-Ray Fluorescence (XRF), for the determination of elements, and by a thermal-optical technique, for the measurement of organic and elemental carbon. The source apportionment analysis of the PM composition data, by means of the receptor model SoFi (Source Finder) 8 Pro, resulted in the identification of nine sources: exhaust and non-exhaust emissions from traffic, secondary particles, heavy oil combustion, industry, sea salt, soil, city dust, and an indoor source characterized by high levels of organic carbon. Integrated daily exposure to PM2.5 was on average 21 µg/m3. The organic matter, resulting from cleaning, cooking, smoking and biological material, was the major source contributing by 31% to the PM2.5 exposure. The source city dust, which was highly influenced by the resuspension of dust in classrooms, was the second main source (26%), followed by traffic (24%). The major sources affecting the integrated exposure to PM10, which was on average 33 µg/m3, were the city dust (39%), indoor organics (24%) and traffic (16%). This study provides important information for the design of measures to reduce the exposure of children to PM.

Keywords: Aerosol, indoor, outdoor, homes, schools, receptor models

9.1. Introduction

Air quality management policies, aiming at protecting the citizens' health, are based on ambient concentration levels, assessed by national air quality measurement networks, assuming that the corresponding monitoring stations are representative of the population exposure across a given city. However, ambient outdoor concentrations may lead to exposure misclassification, which is likely to be determined by the individual's time-activity profiles including time spent in indoor environments (Almeida et al., 2016; Faria et al., 2020, 2022). Since people spend about 90% of their time indoors, individual's exposure to air pollutants is dominated by indoor air quality, which is affected by both the building characteristics and indoor pollution sources (Morawska et al., 2013). Indoor air pollutants result from outdoor air and from indoor sources, including the presence of occupants, human activities, combustion processes, building materials, and consumer products (MacNeill et al., 2014; Morawska et al., 2017; Urso et al., 2015). Indoor chemistry is itself a source of chemicals that might otherwise not be present indoors (Abbatt & Wang, 2020). Indoor chemistry is governed by different factors and processes than those that control outdoor atmospheric chemistry for several reasons, such as absence of direct sunlight and rain, less extreme temperature fluctuations, much larger surface-to-volume ratios, and much higher concentrations of organic compounds (Farmer & Vance, 2019; Weschler & Carslaw, 2018). Therefore, highly variable exposure conditions among different buildings can result in large exposures and health risks for a subset of the population, which may not correspond only to people living in areas identified by the national air quality networks as heavily polluted.

Particulate matter (PM) is a key air pollutant in terms of adverse health effects. Epidemiological and clinical studies have demonstrated particles to be a risk factor for several respiratory disease, such as lung cancer, chronic obstructive pulmonary disease and asthma (Kulhánová et al., 2018; Lu et al., 2020; Mateen & Brook, 2011), along with numerous cardiovascular disease, such as stroke, coronary events, myocardial infarction, cerebrovascular events, atherosclerosis, and deep vein thrombosis (Gu et al., 2017; Mateen & Brook, 2011; Miller et al., 2007). In general, children are more susceptible to PM than adults, because their respiratory, immune, central nervous, digestive and reproductive systems are still evolving (Salvi, 2007; Suwanwaiphatthana et al., 2010). Moreover, children have higher inhalation rates per body weight and higher pulmonary specific surface area as compared to adults (Bateson & Schwartz, 2008). Deep breathing pulls PM faster and further into the lungs, bypassing initial areas of deposition (Zwozdziak et al., 2016). According to Ginsberg et al. (2005) the pulmonary region of the lung has slower clearance, therefore PM remain there longer, and consequently the particle dose can be two to four fold higher among young children.

Europe is moving towards the implementation of the Thematic Strategy on Air Pollution, where Member States are required to draw up plans and programs to guarantee compliance with legally binding

limit values for air pollutants. However, the current policy efforts, at European and national level, have not fully delivered the expected results. In spite of the numerous efforts, 97% of the urban population in Europe is exposed to concentrations of fine particles (PM2.5) above the new World Health Organization (WHO) guideline level of 5 μg/m^3 (WHO, 2021) and serious air pollution impacts on health still persist. Prompt action through efficient air quality management, considering outdoor and indoor sources, is required not only to ensure that the outdoor air legal limits are not exceeded, but principally to guarantee that the consequences of poor air quality on human heath are controlled and minimized. Therefore, management of air quality requires quantitative estimates of population integrated exposure to pollutants, considering all the microenvironments (MEs) frequented by the individuals during their daily activities, as well as the influence of the different PM sources and factors affecting this exposure (Morawska et al., 2013).

While the major sources of indoor air PM have been identified, few studies have attempted to estimate the contribution of specific sources using receptor-modelling techniques. Receptor models are statistical procedures for identifying and quantifying the sources of air pollutants at a receptor location. Receptor models have been extensively used for outdoor air quality (Almeida et al., 2020; Amato et al., 2016; Karagulian et al., 2015) but few studies on indoor PM have been conducted (Amato et al., 2014; Kalaiarasan et al., 2017; Zhao et al., 2007), mainly because the presence of both indoor and outdoor sources, the building-related mechanisms (e.g. ventilation and infiltration), as well as the outdoor meteorology and long range transport of pollutants makes Source Apportionment (SA) challenging (Bekö et al., 2020).

This study aims at improving the understanding of the sources affecting the indoor and outdoor environments and how these sources contribute to the overall exposure, focusing on elementary school children. To the best of our knowledge, there is a limited number of SA studies at indoor school and home MEs, while the contribution of the different sources to the daily exposure of children is still far from being well understood.

9.2. Methodology

9.2.1 Assessment of Time-Microenvironment-Activity Pattern in Lisbon

A necessary step in measuring the extent of children's exposure to air pollutants and assessing the sources affecting this exposure is to evaluate where they spend their time. Therefore, data on children time-microenvironment-activity was collected using a questionnaire that was distributed in 26 schools and applied to children, aged between 5 and 10 years-old, living and studying in Lisbon. The questionnaire was developed in two main parts: the first part was dedicated to the characterization of the children and location of their houses and schools; and the second part focused on the characterization of the time activity pattern of children during the weekdays and weekends. The time was divided in periods of 30 minutes and 17 MEs were considered. The questionnaires were filled by the parents of the children. To increase the interest of

the school community and the response rate, the teamwork put into action the awareness campaign "The air belongs to everyone" that aimed to aware students and teachers to the problem of air quality. 6096 questionnaires were delivered, 1251 of the parents returned the questionnaires, but only 1189 were completed, representing a response rate of 20%. The questionnaire and more details about its application and results can be consulted in LIFE Index Air (2017) report. The results of the questionnaire were essential to identify the MEs where children spend more time and to select the sampling locations.

9.2.2 Air Quality Measurements

Air quality measurements were carried out indoors and outdoors of 40 homes and 5 primary schools located in Lisbon, between September 2017 and October 2018. Homes and schools were carefully selected in order to represent different zones of the city and different building characteristics (age, envelope, materials, etc). The sampling was made in more homes than classrooms due to the higher variability of the conditions, sources and concentrations in dwellings and to the less number of works focusing the indoor air quality in this ME, which increases the need of more knowledge about processes and sources inside homes. The sampling at each home and school lasted for 5 days, during the occupancy hours, i.e. in schools, 8 h from Monday to Friday and in homes 15 h during the week (from 18:00 to 9:00) and 24 h during the weekend. Outdoor air measurements followed the same time schedule as indoor sampling.

PM was sampled concurrently indoors and outdoors using four medium volume samplers (MVS6, Leckel, Sven Leckel, Germany). The Leckel samplers were equipped with a sampling head for the simultaneous collection of PM2.5 and PM2.5-10 at a constant flow rate of 2.3 m^3 (Faria et al., 2020). Two samplers were installed indoors (in living-room or classroom) with air inlets at roughly 1 m above the floor level, corresponding to the breathing level of the children, and away from the door, thus avoiding disturbances resulting from air currents. The other two samplers were installed outdoors, in the balcony or playground. The use of two samplers in each site allowed the collection of PM at two different filter substrates and consequently the chemical analyses of filters by different techniques. One sampler collected PM2.5 and PM2.5-10 on Quartz fibre filters (Pall) and the other sampler collected PM2.5-10 in Nuclepore filters with 0.4 μm pore size (Whatman) and PM2.5 in polytetrafluoroethylene filters (PTFE) with 2 μm pore size (Whatman).

Filters were weighted before and after sampling in a laboratory with controlled temperature and humidity, using a microbalance (Sartorius R160P, Greifensee, Switzerland). PM mass concentrations were determined by dividing filter loads by the volume of air filtered. PM10 concentrations were obtained by summing PM2.5 and PM2.5-10 concentrations. PM samples collected on Nuclepore and PTFE filters were analysed by X-Ray Fluorescence (XRF), to determine the concentrations of Na, Mg, Al, Si, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Br, Sr, Ba, and Pb, using an Energy Dispersive X-ray Spectrometer (ED-

XRF) Laboratory Instrument (Epsilon 5, PANalytical, the Netherlands), following the methodology described at Manousakas et al. (2018). PM samples collected on Quartz filters were analysed by the Thermo-Optical Transmittance method for the determination of Organic Carbon (OC) and Elemental Carbon (EC) using the Lab OC-EC Aerosol Analyzer (Sunset Laboratory Inc., USA) and the EUSAAR2 protocol. More details about sampling, chemical analysis and quality assurance and control are described in Faria et al. (2020) and Faria et al. (2022).

9.2.3 Source apportionment

Source apportionment was implemented through the multilinear engine-2 (ME-2) solver and controlled via SoFi (Source Finder) 8 Pro, which allows for a comprehensive and systematic PMF analysis (Canonaco et al., 2013).

Source apportionment of PM was performed by receptor modelling that is based on the mass conservation principle:

$$xij = \sum_{k-1}^{p} gik\ fkj\ +\ eij \qquad \text{Equation 1}$$

where xij is the concentration of the j^{th} species in the i^{th} sample, gik is the contribution of the k^{th} source in the i^{th} sample, fkj is the concentration of the j^{th} species in the source k^{th}, and eij is the uncertainty of each individual measurement result.

Data below the limit of detection (LOD) were substituted by half of the LOD and the uncertainties were set to 5/6 of the LOD. Missing data were substituted by the geometric mean of the measured concentrations and the corresponding uncertainties were set as 4 times these geometric mean (Polissar et al., 2001).

Chemical species with high noise were down-weighted based on their signal-to-noise (S/N) ratio to reduce the influence of poor variables on the analysis. Species with S/N lower than 0.5 were considered as bad variables and excluded from the analysis, and species with S/N between 0.5 and 1 were defined as weak variables and down-weighted by increasing the uncertainty.

ME-2 allows exploring the rotational space around the base solution by introducing limits into the Positive Matrix Factorization (PMF) model for deviation from predetermined values for *gik* and/or *fkj* for one or more factors (Paatero, 1999). This approach is referred to as constraining. In the current study a constraining technique that is called *a*-value approach was used. In this approach one or more output factor profiles are required to be within predefined limits of a reference profile, with the tightness of constraint defined by the scalar a ($0 \leq a \leq 1$). The scalar a defined the degree of freedom (a=0 means 0% allowed deviation from the anchor profile, and a=1 means 100% allowed deviation).

For identifying the indoor and outdoor sources, four different datasets were used: PM2.5 indoor and outdoor combining data from schools and houses in each case, as wells as PM10 indoor and outdoor combining data from schools and houses in each case. The total number of variables used was 22 (OC, EC, Na, Al, Si, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Br, Sr, Ba, Pb). To estimate the factor contribution, PM was also used as species in the analysis with a 300% uncertainty assigned.

A novel methodology was used for the identification of indoor and outdoor sources, based on the *a*-value approach. First, the outdoor sources for both PM10 and PM2.5 datasets were identified by performing fully unconstrained analysis on the datasets. Then, the factor profiles that were obtained from the analysis of the outdoor data, were used to constrain the indoor data analysis. In particular, the indoor data source apportionment analysis was performed by constraining the outdoor profiles on the indoor runs with an *a*-value of 0.2 (all species except PM were constrained), and adding an additional unconstrained source. Since the indoor PM levels are the sum of outdoor contributions plus indoor contributions, by using this approach we were able to successfully characterize the influence of the outdoor sources in the indoors environment, as opposed to those that are exclusively indoor. The chemical profiles of the outdoor sources are not expected to remain unchanged in the indoor MEs, due to infiltration or/and other processes that can take place in an indoor environment; the selected *a*-value of 0.2 (20% change allowed) provides enough space to the model to adapt the outdoor source profiles to those changes. By following this approach two main goals are achieved: (i) the contribution/effect of outdoor sources to the indoor environment is accurately estimated, and (ii) the contribution of exclusively indoor sources is accurately estimated.

A sensitivity analysis was performed to determine the used *a*-value and the number of extra sources indoors in comparison to the outdoor ones. As stated before, an *a*-value equal to 0.2 and one extra indoor source provided the optimum results. Including more indoor sources did not lead to extra sources with reasonable source profiles (more OC sources with no other tracers were produced), while increasing the *a*-value did not lead to significant changes in the factor profiles. The small change in the Q values (<1%) before and after the application of the constraints, indicates that the solutions are mathematically equal and the model is not forced to deviate too much from the unconstrained solution.

Three main reasons are the cause of uncertainties in source apportionment analysis: random errors in data values, rotational ambiguity, and modeling errors. Modeling errors are identified by monitoring the residuals of the solution. The residuals were normally distributed, unstructured over time and variables throughout all ranges as suggested by Reff et al. (2007). The rotational ambiguity was investigated using the methodology described in Canonaco et al. (2021). This method is based on a combination of the *a*-value approach (information about the rotational ambiguity) and the classical bootstrapping approach (information about the statistical uncertainty and random errors) (Ulbrich et al., 2009). All mathematical indicators suggest source apportionment solution with low uncertainty. The optimum number of factors

was decided by examining the mathematical diagnostics (Q/Q_{exp}, scaled residuals, structure of the residuals, unexplained variation), as well as the physical meaning of the factors.

The contribution of each source to the daily exposure of children (S) was calculated by integrating the time-activity data, provided from the time activity questionnaire, with the contribution of the source in the different MEs, according to Equation 2:

$$S = \frac{\sum_{j=1}^{m} s_j . t_j}{\sum_{j=1}^{m} t_j} \quad \text{Equation 2}$$

Where S_j is the source contribution in the ME (j) and t_j is the time spent in the ME (j).

9.2.4 Statistical analysis

The non-parametric Wilcoxon Matched pairs test was applied to assess the differences between pairs of indoor and outdoor levels and source contributions and the Mann–Whitney U test was selected to evaluate the differences between schools and homes. Spearman's correlation coefficients were calculated to assess the contribution from infiltration and/ or indoor sources to the observed chemical species concentrations. Statistical significance refers to $p < 0.05$. All statistical analysis were implemented in STATISTICA software.

9.3. Results and discussion

9.3.1 Children's daily time activity patterns

In this work a time activity pattern survey targeting children between 5 and 10 years old from Lisbon was performed based on a questionnaire. Results showed that during the weekday, children spent 89% of their time indoors – 57% in home and 26% in classrooms and that only 10% of their time was spent outdoors. During the weekend, children spent 87% of their time indoors, increasing the time spent in home and leisure places, in comparison to the weekdays (Figure 9.1). The analysis of the children's time activity pattern showed the importance of the indoor MEs for the children's daily exposure.

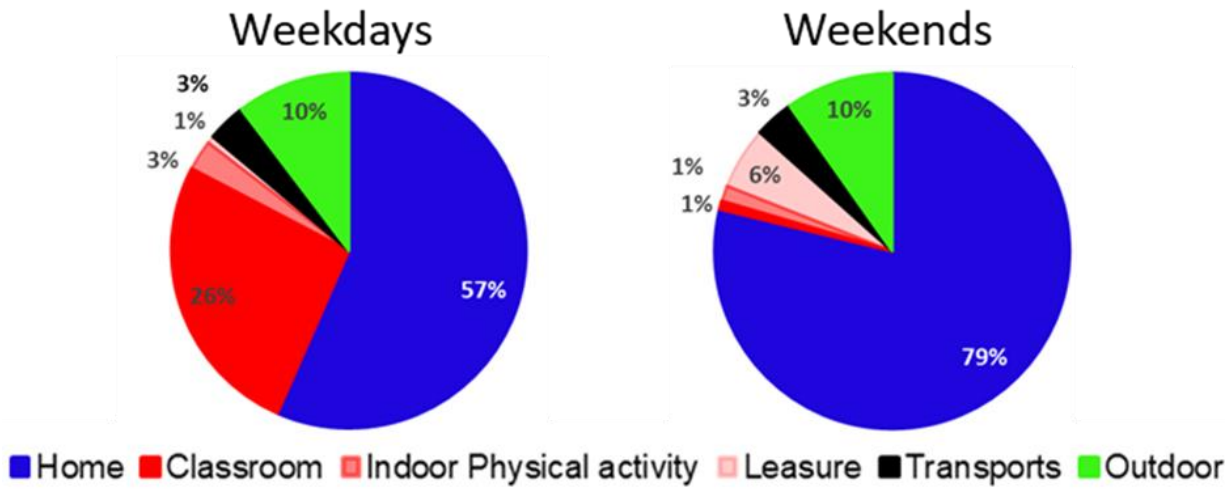

Figure 9.1 - Time activity pattern for children between 5 and 10 years old from Lisbon for weekdays and weekends.

9.3.2 PM concentrations

Table 9.1 reports the average concentrations of indoor and outdoor PM total and chemical compounds mass, as well as the children integrated exposure levels calculated by integrating the time-activity data with the concentrations in the different MEs according to Equation 3.

$$E = \frac{\sum_{j=1}^{m} C_j . t_j}{\sum_{j=1}^{m} t_j} \quad \text{Equation 3}$$

Where C_j is the PM concentration measured in the ME (j) and t_j is the time spent in the ME (j).

The concentrations and size distribution of the particles sampled in schools and homes differed significantly (Martins et al., 2020). The schools displayed higher concentrations (PM2.5: 35 μg/m^3 and 14 μg/m^3; PM10: 65 μg/m^3 and 18 μg/m^3, for school and homes, respectively) and I/O ratios (PM2.5: 2.4 and 1.4; PM10: 2.3 and 0.9, for school and homes, respectively), and lower PM2.5/PM10 ratios (schools: 0.57; homes: 0.78).

While the school environment normally lacks typical indoor PM sources such as cooking and heating, results indicated that the classrooms is a ME characterized by high concentration of PM, principally in coarse fraction. The reason for that can be attributed to insufficient ventilation in schools, unappropriated cleaning practices, a large number of students in a limited room area over a period of several hours (average density of 2 m^2 per student), a constant resuspension of particles from room surfaces, and the close proximity of the schools to busy roads. Faria et al. (2020) used a laser photometer (DustTrak, model 8533, TSI) in the same five schools of the present study to measure PM2.5 and PM10 in real-time providing information on the diurnal variability, as well as impact of the occupancy and emission sources. This work showed that there is an increase of PM concentrations before the beginning of the classes (9:00) due to the

cleaning of the room, which takes place every day before the first class, and during the class-hours due to the presence of students in the room, leading to the generation and resuspension of particles.

Although students spent less time in classrooms (6.1 hours) than in homes (13.2 hours), exposure in schools led to a substantial contribution to their total daily exposure to PM, due to the higher concentrations measured in this ME. The personal exposure to PM2.5 and PM10, calculated based on the children time-microenvironment-activity pattern and the concentrations measured in homes, classrooms and outdoor, was 21 μg/m^3 and 33 μg/m^3, respectively. PM2.5 exposure exceeded the new 24h WHO guideline of 15 μg/m^3 and the annual guideline of 5 μg/m^3 (WHO, 2021). PM10 exposure did not exceed the 24h WHO guideline of 45 μg/m^3, but highly exceeded the annual guideline of 15 μg/m^3.

9.3.3 Composition of PM

The major compounds found in the PM were OC, EC, S, Ca, Na, Cl, Si, K and Fe. Although the other compounds did not contribute significantly to the PM mass, they provided valuable insights in the identification of PM sources and health impact assessment, as we will observe in the source apportionment section.

Spearman's correlation coefficients (Rs) were calculated to evaluate the contribution from infiltration and/ or indoor sources to the observed chemical species concentrations. The highest correlations were calculated for those species of exclusively outdoor origin, such as traffic related pollutants (EC, 0.89-0.93) and secondary aerosol (S, 0.70-0.95).

OC average concentrations were significantly higher in homes (PM2.5: 6.2 μg/m^3; PM10: 7.5 μg/m^3) and schools (PM2.5: 13 μg/m^3; PM10: 21 μg/m^3) than in the respective outdoors, which indicates the importance of indoor sources of OC, such as cleaning, cooking, heating and smoking. In the homes of smokers, OC and K increased 4.7 and 5.9 times in PM2.5 and 4.0 and 5.1 times in PM10, respectively, indicating that these two compounds are good indicators of smoking, as already indicated by the study developed by Zhao et al. (2007).

In homes, the ratio I/O for the major part of the chemical compounds was higher in PM2.5 than in PM10, probably due to the contribution of the coarse fraction that has reduced penetration efficiency and faster settling times, as showed by Hussein et al. (2007) and Martins et al. (2020).

In schools the I/O ratios were higher than in homes, principally for mineral species, reflecting the importance of the particle resuspension by the children's activity, which is a significant source of indoor coarse particles in schools (Almeida et al., 2011; Fromme et al., 2008; Kim et al., 2017). According to Morawska et al. (2017) this source is likely the main reason for the elevated PM10 concentrations in this ME.

Table 9.1 - Average concentrations measured in the indoor and outdoor of homes and schools and average individual exposure. PM, OC and EC in µg/m3 and elements in ng/m3. Indoor/outdoor (I/O) ratios (significant differences at p<0.05 in bold) and Spearman correlation (Rs) between indoor and outdoor concentrations (significant correlations at p<0.05 in bold).

	PM2.5									PM10							
	Houses				Schools				Exposure	Houses				Schools				Exposure
	Indoor	Outdoor	I/O	Rs	Indoor	Outdoor	I/O	Rs		Indoor	Outdoor	I/O	Rs	Indoor	Outdoor	I/O	Rs	
PM	14	13	1.4	**0.63**	35	21	**2.4**	**0.47**	21	18	22	**0.9**	**0.57**	65	32	**2.3**	0.24	33
OC	6.2	3.0	**2.8**	**0.59**	13	5.1	**2.7**	0.34	7.9	7.5	3.8	**2.6**	**0.50**	21	6.7	**3.4**	0.25	11
EC	1.0	1.2	**0.9**	**0.92**	1.3	1.3	1.0	**0.92**	1.2	1.1	1.3	**1.0**	**0.89**	1.7	1.4	**1.3**	**0.93**	1.3
Al	56	69	**2.1**	**0.64**	410	170	**2.7**	0.16	170	87	130	**1.6**	**0.59**	660	310	**2.4**	**0.56**	280
Ba	1.5	1.7	0.9	0.20	6.9	15	0.5	-0.09	3.0	3.4	8.4	0.9	-0.11	17	27	1.2	-0.40	7.5
Br	1.9	2.4	**0.9**	**0.73**	5.8	2.5	1.0	-0.80	3.1	2.8	5.0	**0.8**	**0.32**	7.1	5.2	0.8	0.61	4.3
Ca	200	200	1.5	**0.59**	2500	720	**5.9**	**0.59**	918	380	560	**0.9**	**0.50**	5900	1500	**5.3**	0.30	2100
Cl	170	160	**2.6**	**0.77**	240	230	3.1	**0.81**	195	480	1000	**0.5**	**0.84**	670	1000	**0.9**	**0.87**	590
Cr	0.54	0.83	**1.0**	**0.46**	2.6	0.71	1.6	0.50	1.15	0.91	2.0	**0.8**	**0.56**	5.1	1.8	**3.3**	**0.53**	2.2
Cu	10	10	1.8	**0.26**	16	14	1.9	0.45	12	13	17	**1.4**	**0.35**	19	19	1.3	**0.49**	15
Fe	100	190	**0.7**	**0.83**	400	270	**1.4**	**0.81**	208	180	460	**0.4**	**0.75**	800	600	1.2	**0.80**	400
K	160	140	1.8	**0.82**	370	300	**1.3**	**0.76**	239	190	200	**1.1**	**0.76**	500	400	1.3	**0.73**	300
Mg	13	19	1.3	**0.63**	100	21	3.2	0.49	41	18	52	**0.8**	**0.52**	120	49	3.9	0.80	50
Mn	2.0	3.1	1.0	**0.60**	8.9	5.7	**1.6**	0.36	4.4	3.3	7.1	**0.7**	**0.47**	16	9.8	**1.9**	**0.46**	7.8
Na	200	240	**1.0**	**0.78**	300	240	1.3	**0.84**	234	290	440	**0.8**	**0.77**	450	440	1.4	**0.78**	360
Ni	0.94	0.90	**1.0**	**0.66**	0.78	0.56	1.4	-0.11	0.85	1.2	1.4	1.5	**0.56**	1.5	1.2	2.3	-0.30	1.3
Pb	3.6	4.2	1.0	**0.58**	13	11	**1.4**	0.45	7.1	5.4	6.5	1.2	**0.42**	18	14	2.5	0.37	9.9
S	480	540	**0.9**	**0.95**	720	550	1.2	**0.91**	557	530	640	**0.9**	**0.70**	810	660	1.2	**0.81**	620
Si	160	190	1.8	**0.54**	1100	480	**2.4**	**0.62**	453	240	320	**1.6**	**0.47**	1600	780	**2.4**	**0.63**	700
Sr	0.42	0.48	0.9	0.27	3.04	0.79	1.2	0.37	1.2	1.1	2.1	**0.7**	**0.39**	11	3.0	**3.7**	**0.65**	4.1
Ti	7.2	6.9	1.4	**0.54**	66	45	**3.3**	**0.59**	28	12	16	**1.2**	**0.52**	140	77	**3.7**	**0.75**	55
V	2.0	2.5	**1.1**	**0.74**	2.5	2.1	1.1	-0.02	2.1	2.2	2.9	1.1	**0.68**	2.7	2.3	2.0	-0.10	2.4
Zn	12	13	**1.3**	**0.78**	33	30	1.5	0.38	20	15	22	**1.0**	**0.69**	60	40	**2.1**	0.31	31

9.3.4 Source apportionment

The source apportionment analysis was conducted to resolve the sources and quantify their contribution to PM in homes, schools and ambient environment. The most reliable solution identified nine source factors. Figure 9.2 shows that a very good agreement was obtained between the gravimetric and the sum of the source contributions ($0.77 < R^2 < 0.86$).

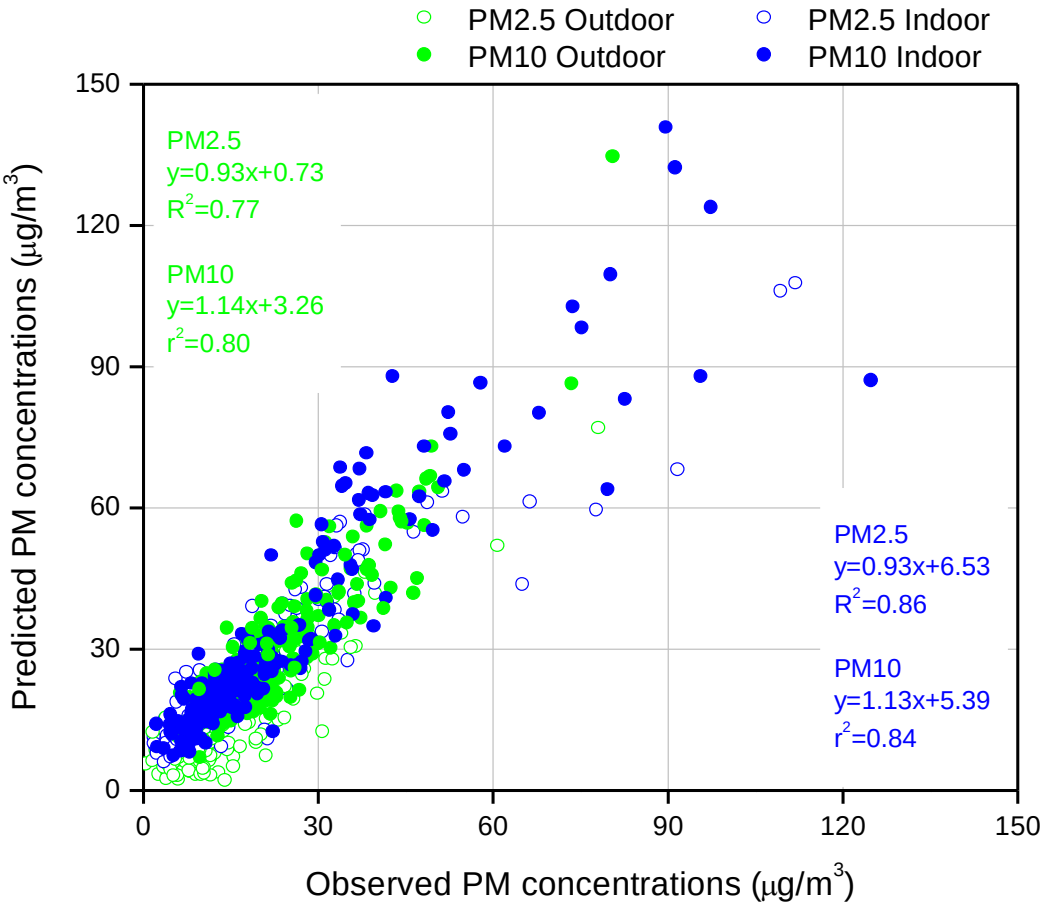

Figure 9.2 - Observed versus predicted PM2.5 and PM10 concentrations (values in µg/m^3).

The nine sources were identified as exhaust traffic, non-exhaust traffic, secondary sulfate, heavy oil combustion, industry, sea salt, soil, city dust and indoor organics. Factor profiles are displayed in Tables S9.1 to S9.4 in the supplementary material. Figure 9.3 and Table S9.5 present the contribution of the identified sources to PM2.5 and PM10 sampled in the indoor and outdoor of homes and schools.

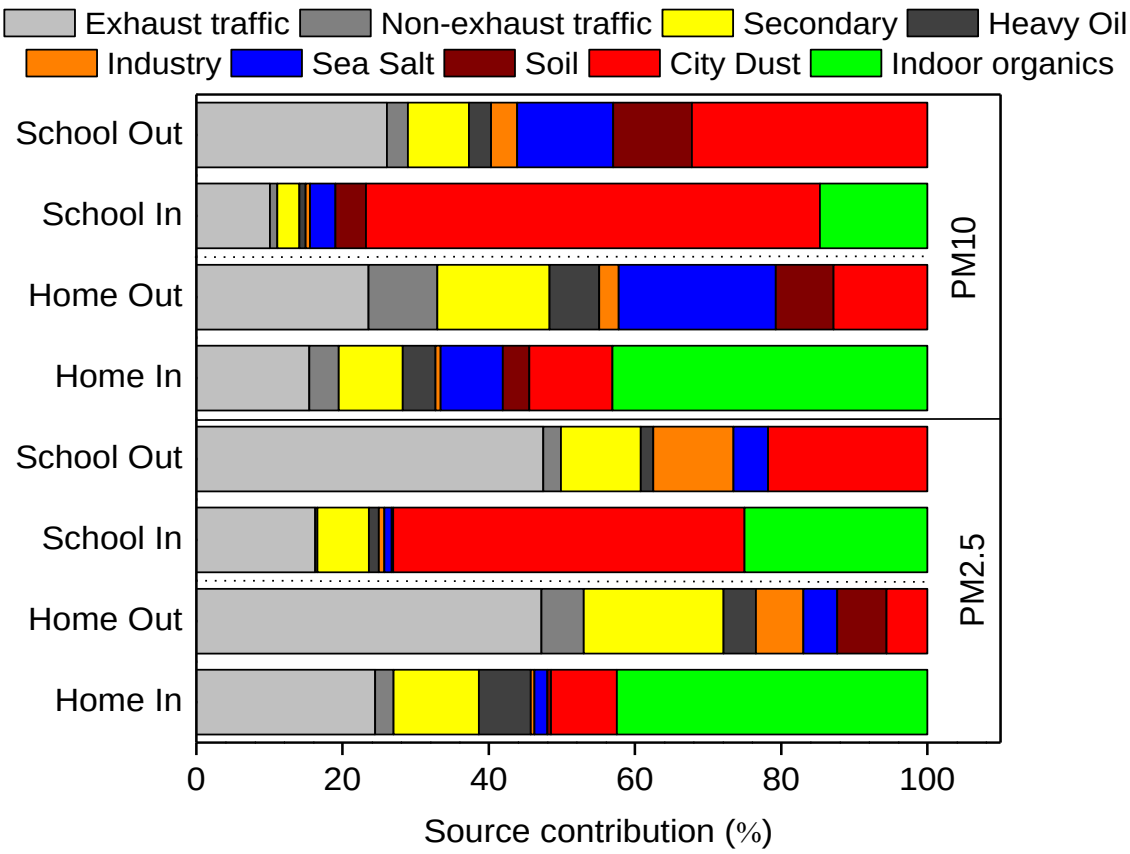

Figure 9.3 - Average relative source contribution for PM2.5 and PM10 sampled in the indoor and outdoor of schools and homes.

- Traffic exhaust emissions

Traffic is a source of three different contributions to outdoor PM, comprising combustion emissions, mechanical/abrasive processes and resuspension. The exhaust emissions were traced by OC and EC. In this source, the ratio OC/EC was 0.98 for PM2.5 and 1.2 for PM10, which is comparable with the OC/EC ratio typically found in traffic monitoring sites, which varies between 1.6 and 1.7, while in remote sites varies between 12 and 15 (Querol et al., 2013).

Particles from vehicle exhaust are mainly in the fine fraction of PM, and are able to efficiently infiltrate in indoor environments. As expected the contribution of this source was higher in the outdoor than in the indoor and the correlations between indoor and outdoor levels were strong for both places (homes: Rs = 0.82; schools: Rs = 0.57) (Figure 9.4 and Table S9.5), indicating the importance of the infiltration of traffic related pollutants. The average contribution of the traffic exhaust emissions to PM2.5 measured in homes and schools was 4.5 μg/m^3 (24%) and 7.3 μg/m^3 (16%), respectively.

The higher contribution of traffic in schools was partly caused by the fact that sampling was performed during the occupied periods, which means during the day in schools and mainly during the night

and weekends in homes. These results agree with those from Amato et al. (2014) that estimated an average traffic exhaust contribution of 13% for PM2.5 measured inside schools in Barcelona.

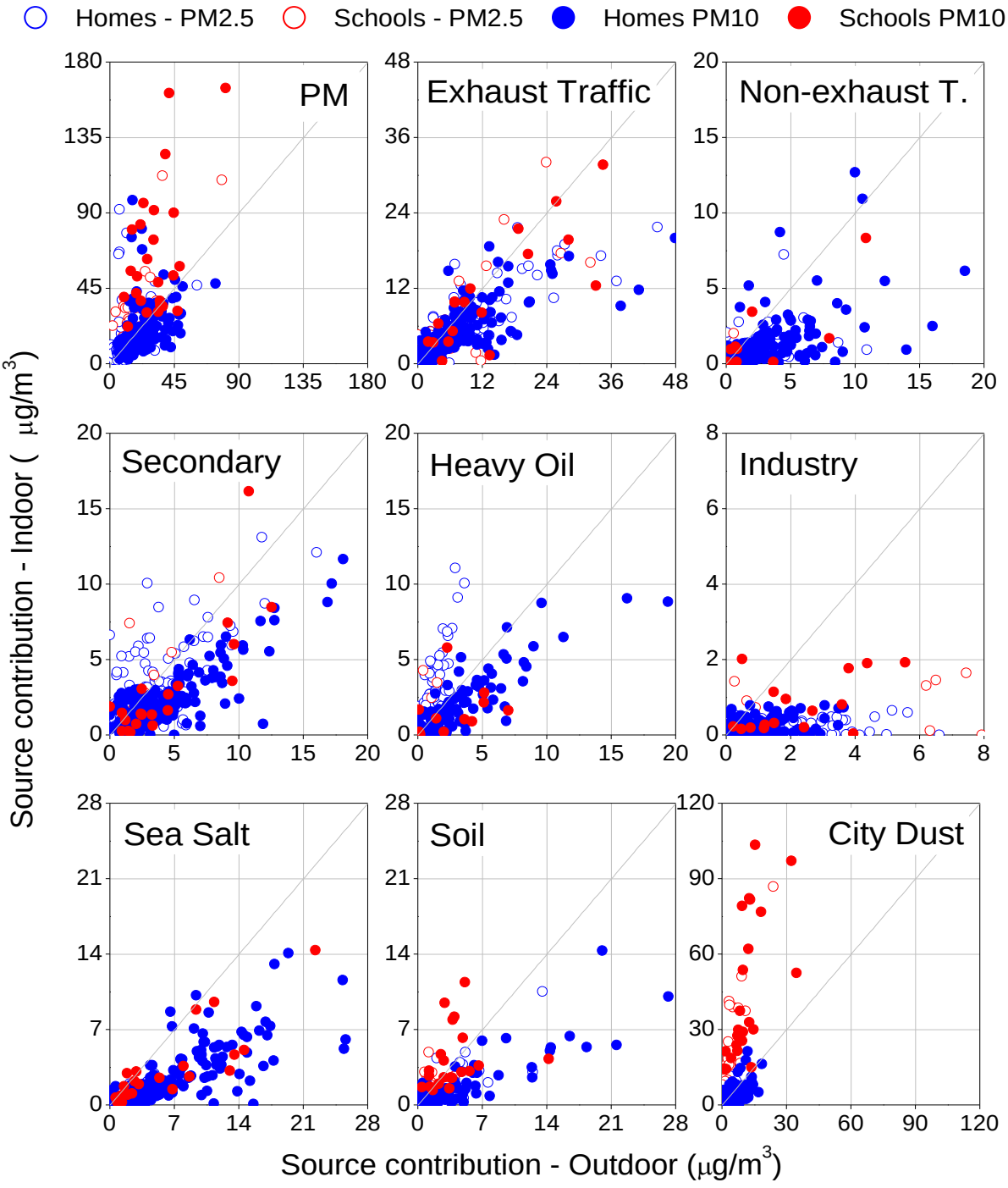

Figure 9.4 - Correlation between source contribution for indoor and outdoor PM2.5 and PM10 levels (values in ng/m^3).

- Traffic non-exhaust emissions

As stringent policies and technological developments have led to sizeable reductions in exhaust emissions, the contribution of non-exhaust emissions is becoming more relevant (Padoan and Amato, 2018). Traffic non-exhaust emissions include (i) Fe, Ba, Sb, Sn, and Cu from brake wear (fraction of pad, disc, and clutch), (ii) carbonaceous, Al, Si, Zn, and S from tire wear, (iii) mineral aggregates bond by bitumen from road wear and (iv) a mix of exhaust emissions, road sanding and salting, and geogenic material carried onto the road from road dust resuspension (Padoan and Amato, 2018). In this study, the traffic non-exhaust emission factor explains most of the variance of Cu, Cr, Fe, Mn, Zn and EC, which result from break and tire wear, road wear and dust resuspension (Table S9.1-S9.4).

The contribution of this source for PM2.5 and PM10 was 2.5% (0.47 $\mu g/m^3$) and 4.0% (1.0 $\mu g/m^3$) for homes and 0.32% (0.15 $\mu g/m^3$) and 1.0% (0.84 $\mu g/m^3$) for schools, respectively. The contribution of traffic non-exhaust emissions was higher outdoor than indoor and the contributions outdoors were less correlated with those indoors than in the exhaust emissions, probably because non-exhausts particles are mainly contained in the coarse fraction and the infiltration of coarse particles is lower (Bennett & Koutrakis, 2006). Some indoor sources of the tracers of the non-exhaust emissions can also contribute to these poor correlations. For instance, several studies have already reported that vacuum cleaners, air dryers and electrical heathers are important sources of Cu (Tofful et al., 2021).

- Secondary sulfate

Secondary Secondary aerosols are not emitted directly into the atmosphere by a single source, they result from the atmospheric chemical transformations of gaseous precursors emitted by combustion processes, mostly in industry and transports, at shorter or longer timescales, often involving heterogeneous processes. In source apportionment studies, secondary aerosols are often not allocated to the primary source of their precursor, which might complicate the interpretation of results (Karagulian et al., 2015). The secondary sulfate factor was traced by S and to a lesser extent by As. Since the secondary aerosol is mainly in the fine fraction, the correlation between indoor and outdoor contributions was strong (Rs between 0.59 and 0.77) due to the high infiltration of fine particles. The contribution of this source to PM2.5 was 2.2 $\mu g/m^3$ (11%) and 3.1 $\mu g/m^3$ (6.8%) for homes and classrooms, respectively. In Barcelona schools, Amato et al. (2014) estimated a contribution of secondary sulfate of 11% to the indoor PM2.5 concentrations.

- Heavy Oil Combustion

The Heavy Oil Combustion factor, mostly associated with combustion processes from industry and shipping, was traced by V and Ni and to a lesser extent by S and Br, as it has already been reported in other

studies (Almeida et al., 2020). According to Amato et al. (2009), since industries and shipping typically burn high sulfur content residual oil, the sulfate related to V and Ni probably represents the direct SO_3 emission, condensed in particulate sulfate at the receptor site. The contribution of this source in homes was 6.9% for PM2.5 and 4.5% for PM10 and in schools was 1.3% for PM2.5 and 0.80% for PM10.

- Industrial emissions

Industrial emissions are a complex mixture of stationary and diffuse emissions associated with the main processes and operations (Almeida et al., 2015). While, the contribution from industry is incorporated in other factors such as secondary sulfate and fuel oil combustion, SoFI identified a factor related principally with Pb but also with Cu and Mn. The contribution of this source in homes and schools was 0.51% and 0.71% for PM.5 and 0.73% and 0.60% for PM10, respectively. The relative contribution of this source was higher for PM2.5 and outdoors (balcony: 6.5% and playground: 10%); however, the indoor and outdoor concentrations were uncorrelated (Rs between 0.27 and 0.42), which can indicate an additional source of Pb indoors. Old lead-based paint is the most significant source of Pb exposure indoors. Harmful exposures to Pb can be created when Pb-based paint is improperly removed from surfaces by dry scraping, sanding, or open-flame burning (EPA, 2022).

- Sea Salt

The Sea Salt factor was traced by Na and Cl and to a lesser extent by Br and Sr in PM10. The ratio Cl/Na in this factor was 2.0 (outdoor) and 1.7 (indoor) for PM2.5 and 1.4 (outdoor) and 1.5 (indoor) for PM10, which is comparable to the ratio of these elements for sea water (1.8). The contribution of this factor was similar in the two indoor MEs, 2.2 $\mu g/m^3$ and 3.0 $\mu g/m^3$ for the PM10 sampled in the indoor of homes and schools, respectively. The contribution of this source to the PM10 was significantly higher in the outdoor (homes: 5.9; schools: 5.6 $\mu g/m^3$) but the indoor and outdoor contributions were highly correlated (Rs = 0.84 for homes and Rs = 0.83 for schools), indicating the importance of the penetration from outdoor to indoor environments, even though sea salt particles are mainly contained in the coarse fraction. The contribution of the Sea Salt source was higher indoors than outdoors in 35% and 38% of the PM2.5 samples collected in homes and schools, respectively, probably because particles with high salt content found indoors can be formed by absorption of cleaning agents (Fromme et al., 2008; Zhao et al., 2007).

- Soil

The Soil factor was identified by typical crustal species such as Al, Si and Ti, which result from the erosion of earth crust but also from the suspension from unpaved playgrounds. Consequently, the average contribution of this source for PM was higher in classrooms (PM2.5: 1.4 μg/m^3; PM10: 3.5 μg/m^3) than in homes (PM2.5: 0.50 μg/m^3; PM10: 0.92 μg/m^3). In homes the soil contribution was significantly higher in the outdoor (PM2.5: 0.85 μg/m^3; PM10: 2.2 μg/m^3) than in the indoor and the correlation between indoor and outdoor for fine fraction was strong (Rs = 0.77), indicating the importance of infiltration for this source. In schools, the soil contribution for PM10 was also higher in the outdoor (4.6 μg/m^3).

- City Dust

This This source is characterized by abundance of Ca, Ti, Si, Fe and Sr and the absence of Al, which makes the main difference for not identifying this source as a mineral source.

This is the largest source in classrooms contributing with 22 μg/m^3 (47%) for PM2.5 and 52 μg/m^3 (62%) for PM10. In addition to the infiltration of dust from the outdoor, this source is related to the continuous resuspension of particles brought inside directly by the children on their shoes or clothing and with indoor sources of Ca-rich particles, such as chalk and building deterioration. This source also explains the high variation in Sr concentrations, due to its common substitution for Ca atoms in $CaCO_3$ used for chalk. In classrooms using chalk, PM2.5 and PM10 average concentrations doubled and the contribution of city dust increased to 55% for PM2.5 and 71% for PM10. In the playground, the contribution of city dust is still significant (20% for PM2.5 and 32% for PM10). However, as the I/O ratio of this source is 6.83 for PM2.5 and 3.87 for PM10, it is expected that the increase of ventilation will promote the dilution of the PM concentrations inside classrooms, once the effect of the outflow of internal pollutants will be larger than the inflow of external particles. In schools with mechanical ventilation, air handling units should be equipped with filters, with efficiency selected according to the concentration of PM outdoors, which will avoid the entrance of particles to the indoor.

In homes the contribution of this source to PM2.5 (1.7 μg/m^3, 8.8%) and PM10 (2.9 μg/m^3, 11%) was significantly lower than in schools. In Barcelona, Minguillón et al. (2012) also found a factor contributing to the indoor of homes characterized by abundance of Ca, Li, Ti and Sr and the absence of Al and attributed this source to cosmetics. Ti and Ca are included in the European inventory of cosmetics ingredients (Commission Decision, 2006/257/EC) and their presence in cosmetics has been documented by several studies (Di Maiuta & Schwarzentruber, 2011; Kaida et al., 2004). Moreover, sunscreen products may use nanoparticles of titanium dioxide as an active ingredient (Cengiz et al., 2006).

- Organic Matter

In indoor environments, a factor characterized by the high abundance of OC was identified. On average, this factor represented the most important contribution in homes, explaining 42% of the PM2.5 and 43% of the PM10. These results are in agreement with Tofful et al. (2021) who also identified the organic matter as the main contributor to PM2.5 in home (54%). The occupants in homes are considered one of the most important sources of coarse PM because they are responsible for the emission of primary biological material such as skin flakes, debris and hair (Fromme et al., 2008). In addition, the re-suspension of the deposited dust caused by the occupants movement and cleaning activities, such as vacuuming, dusting, house-keeping, also contribute to the organic carbon levels in the coarse fraction. Other domestic activities such as cooking, smoking and burning of candles and incenses, are also responsible for the emission of OC but in the fine and ultra-fine fraction of PM. According to Géhin et al. (2008), combustion generated particles are generally considerably smaller than 2.5 µm, often smaller than 300 nm, therefore the number concentration of ultrafine particles can be more relevant than PM2.5 mass to assess the impact of residential exposure to combustion-related particles (Isaxon et al., 2015). The fact that the indoor sources could not be separated further and appear as one source, is attributed to the lack of suitable tracers, and especially organic tracers.

In schools, the relative contribution of this source decreased to 24% for PM2.5 and 15% for PM10, respectively. However, the absolute contribution of this source in schools (PM2.5: 11 µg/m^3; PM10: 12 µg/m^3) was higher than in homes (PM2.5: 7.8 µg/m^3; PM10: 11 µg/m^3), probably due to the higher occupational density and dust resuspension. In schools, the sources of fine particles are less frequent and therefore the OC PM2.5/PM10 was 0.60, while in homes was 0.82. In Barcelona primary schools, Amato et al. (2014) estimated a contribution to PM2.5 of 45% (16 µg/m^3) for the factor associated with OC and also with Ca.

9.3.5 Contribution of the sources to the children exposure to particles

In order to consider the variability between the different days of the week, the contribution of the sources to total exposure was firstly calculated separately for weekdays and weekends. In the weekdays we considered the outdoor measured in the schools for the calculation of the source contribution to exposure, while in the weekends we used the outdoor measured in homes. For the indoor environments / activities that were not monitored (indoor physical activity, leasure and transports), which represented 7% and 10% of time during the week and weekend, respectively, we considered the concentrations measured in the schools. Afterwards, the average contribution of the sources was calculated by weighting the contribution of the weekdays (71%) and weekends (29%) during the week. The average contribution of the sources to the children's exposure to PM2.5 and PM10 is presented in Figure 9.5 and Table S9.6.

Although children spent less time at school than at home, the contribution of the main sources in the classroom highly affected the integrated daily exposure. During the week the exposure was mainly affected by the factor indoor organics (29%, 8.1 μg/m^3) and city dust (29%, 8.0 μg/m^3), which is highly influenced by the resuspension of dust inside the classrooms. The contribution of vehicular traffic, both exhaust and non-exhaust, contributed by 23% (6.2 μg/m^3). As source apportionment inside transports was not carried out, the contribution of traffic related sources for the exposure should be underestimated. Although children only spent 3% of time in-transit, it is known that commuting lead to a substantial contribution to their total daily exposure (Cunha-Lopes et al., 2019; Faria et al., 2020), especially in high vehicle-density metropolitan areas, because transport MEs have higher air pollutant concentrations than other settings children occupy in their daily routines (Buitrago et al., 2021; Correia et al., 2020; Martins et al., 2021). The contribution of the secondary sulfate was 9.3% (2.6 μg/m^3) and the other sources contributed less than 3% to the exposure.

During the weekend, the exposure to PM2.5 decreased from 22 to 15 μg/m^3, because children were not exposed to high concentration of pollutants at the school, along with the decrease of the contribution of some outdoor sources, such as traffic exhaust, traffic non-exhaust, secondary sulfate and industry (-24%, -15%, -42% and -27%, respectively). The contribution of the city dust during the weekend decreased to 3.0 μg/m^3 (16%) and the major sources were the indoor organics (36%, 6.9 μg/m^3) and traffic (25%, 4.9 μg/m^3).

In PM10, the major source during weekdays was city dust, accounting by 42% (19 μg/m^3). The indoor organics and traffic displayed a relative contribution of 23% and 15%, respectively. During the weekends, the exposure reduced from 34 to 22 μg/m^3, and the main source affecting the exposure was the indoor organics with 30% (8.6 μg/m^3).

The high exposure levels verified in this study do not necessarily result in higher risks to the children, since the composition of PM and sources are key factors for the health impacts.

Our results showed that city dust, indoor organics and traffic were the main sources affecting the children exposure to PM. On average city dust was responsible for 26% and 38% of the exposure to PM2.5 and PM10, respectively. This factor was mainly identified by mineral material and, epidemiological studies developed, by Hoek et al. (2002) and Janssen et al. (2005) support the hypothesis that PM derived from earth crust material have less health impacts than particles generated by combustion processes. Indoor organics accounted on average for 31% and 24% of the exposure to PM2.5 and PM10, respectively. This source was identified by OC that refers to the carbon found in the form of organic compounds, and comprises a complex mixture of different classes of organic compounds, some of them related to primary biological material but other resulting from the use of some cleaning products that can have carcinogenic, neurotoxic, immunogenic, and estrogenic activities (Gunathilake et al., 2021). Moreover, traffic contributed on average by 24% and 16% to the exposure to PM2.5 and PM10, respectively. Jung et al. (2015) showed that exposure to traffic-related air pollution may be associated with increased risk of asthma,

allergic rhinitis, allergic sensitization, and with reduced lung function in schoolchildren. Traffic-related air pollution exposure was also associated with brain changes of a functional nature and slower cognitive growth (Pujol et al., 2016; Sunyer et al., 2017). Children from schools with higher traffic-related pollution showed lower functional integration and segregation in key brain networks (Pujol et al., 2016). The most recent research results show that non-exhaust particles can be more harmful than exhaust PM. Oxidative stress is one of the principal biological mechanisms causing toxicity and is frequently related to transition metals and/or redox active organics. Yanosky et al. (2012) showed that brake and tire wear particles have higher oxidative potential than other traffic-related sources and their effect is very local (50-100 m from the source), yielding more oxidant PM at road sites rather than at urban background sites.

Therefore, this study showed that emission sources contributing to children's exposure to PM can lead to major health problems and therefore it is urgent to clarify the toxicological and biological relevance of this exposure.

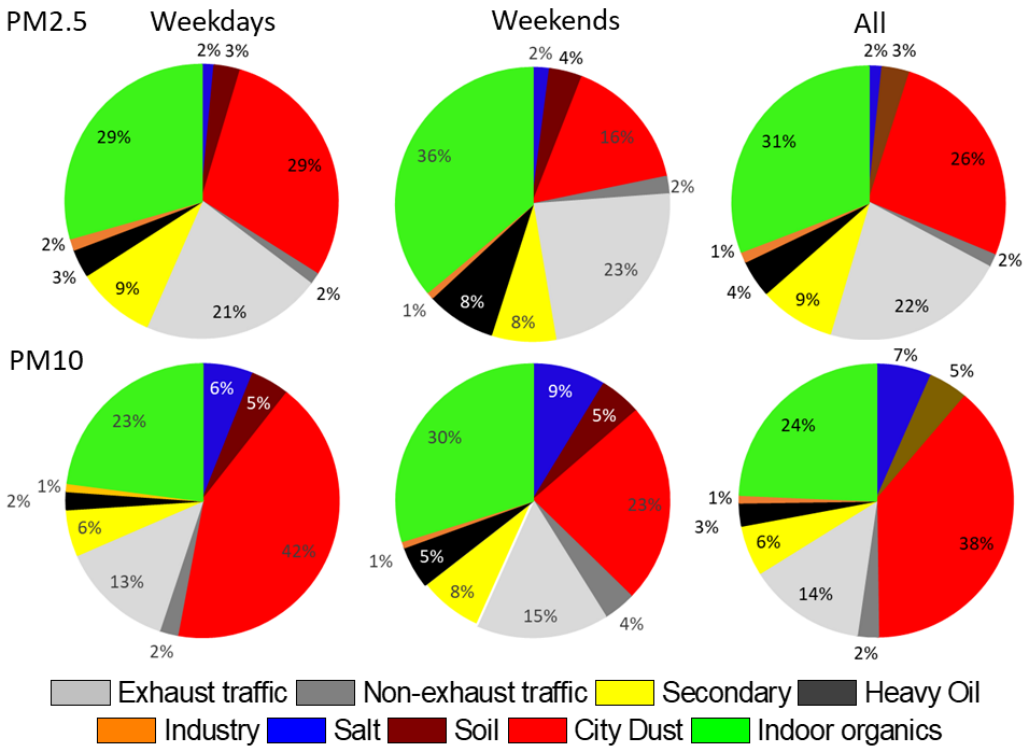

Figure 9.5 - Source contribution for the PM2.5 and PM10 daily exposure.

Conclusions

This work provides information on the sources contributing to children exposure to PM2.5 and PM10 concentration and supports the identification of actions to reduce the concentration of PM in indoor and outdoor environments, and consequently reduce their exposure and health impacts.

Source apportionment showed that the major sources contributing to exposure are related with the emission of organic carbon in indoor environments, from cooking, cleaning, smoking, biomass burning, candles and occupation; resuspension of mineral particles in schools and traffic.

The results of this study highlights the importance of:

- Promoting a good ventilation in order to effectively dilute and remove contaminants emitted by occupants and indoor activities;
- Exhausting air in the vicinity of localized indoor sources such as cooking;
- Regulating measures that prohibit smoking inside and near the buildings;
- Avoiding the use of candles, incense, diffusers and air fresheners;
- Changing the cleaning routines to reduce the resuspension of mineral particles, selecting low emission products and vacuum cleaners or mops instead of brooms, and in the schools scheduling the cleaning operations in the afternoon after the school hours.
- Giving preference to the whiteboard, but if the classroom is equipped with a chalkboard cleaning it with a damp cloth, to avoid high concentrations of chalk particles suspended in the air.
- Developing sustainable transport solutions and urban planning to reduce the exposure of children to traffic related pollutants.

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Supplementary material

Table S9.1 - Source profiles for the outdoors PM2.5 (%)

PM2.5 Outdoors	City Dust	Secondary	Non-exhaust Traffic	Exhaust traffic	Heavy Oil	Soil	Sea Salt	Industry
PM	5.6	22.6	3.8	45.0	3.5	5.9	4.6	9.0
OC	11.8	10.2	3.6	66.8	0.0	3.5	0.9	3.2
EC	6.0	0.0	19.3	68.0	0.0	4.6	1.6	0.5
Na	0.0	7.9	1.7	0.0	21.9	21.8	46.6	0.0
Al	0.0	2.3	0.0	0.0	0.0	96.5	0.5	0.7
Si	47.8	0.0	0.0	0.0	0.0	52.2	0.0	0.0
S	2.4	47.4	0.0	0.3	35.6	3.8	2.9	7.5
Cl	0.0	2.5	1.4	0.0	0.1	0.0	94.7	1.4
K	2.7	0.0	0.0	68.2	7.1	16.0	3.8	2.1
Ca	55.1	7.6	2.2	19.5	2.3	10.9	2.4	0.0
Ti	43.2	0.9	1.8	5.3	7.6	40.3	0.7	0.2
V	0.8	2.6	0.5	0.0	96.1	0.0	0.1	0.0
Cr	6.1	0.0	33.4	38.3	15.5	5.0	0.0	1.7
Mn	1.2	0.3	16.6	13.1	3.1	13.4	0.6	51.7
Fe	23.8	3.7	24.3	27.5	0.0	19.7	1.0	0.0
Ni	0.0	0.0	0.0	1.6	90.1	0.0	4.3	4.0
Cu	0.0	0.0	34.7	0.0	0.3	0.0	0.3	64.7
Zn	9.5	0.9	14.9	67.2	3.5	0.0	0.0	4.0
As	0.0	28.2	5.3	25.5	8.8	2.9	18.7	10.7
Br	0.0	1.5	1.2	55.9	27.8	0.0	13.5	0.0
Sr	17.4	13.8	2.5	15.1	10.5	21.1	19.6	0.0
Ba	0.0	16.7	43.8	33.0	0.0	4.4	0.0	2.2
Pb	4.1	0.0	0.0	0.0	0.0	0.0	0.0	95.9

Table S9.2 - Source profile for the indoors PM2.5 (%)

PM2.5 Indoors	City Dust	Secondary	Non-exhaust Traffic	Exhaust traffic	Heavy Oil	Soil	Sea Salt	Industry	Indoor organics
PM	21.6	12.8	1.9	23.7	8.0	2.3	0.4	0.0	29.4
OC	9.0	5.3	0.8	17.7	0.0	0.8	0.3	1.1	65.0
EC	6.8	0.0	12.6	55.1	0.0	3.3	2.0	0.3	19.8
Na	0.0	5.7	0.8	0.0	20.7	16.3	56.5	0.0	0.0
Al	0.0	3.3	0.0	0.0	0.0	94.5	0.8	0.7	0.8
Si	63.3	0.0	0.0	0.0	0.0	35.5	0.0	0.0	1.3
S	4.2	50.0	0.0	0.2	32.6	2.8	2.3	8.0	0.0
Cl	0.0	2.0	0.7	0.0	0.0	0.0	96.2	1.1	0.0
K	3.7	0.0	0.0	66.3	7.9	14.0	5.4	2.7	0.0
Ca	74.5	6.4	1.1	8.3	1.1	6.3	2.3	0.0	0.0
Ti	63.7	0.8	0.7	3.7	4.9	25.4	0.7	0.1	0.0
V	1.4	2.9	0.3	0.0	95.1	0.0	0.2	0.0	0.0
Cr	12.6	0.0	26.3	37.4	17.2	4.4	0.0	2.2	0.0
Mn	1.9	0.3	10.2	10.0	2.7	9.3	0.7	64.9	0.0
Fe	41.3	4.0	16.1	22.7	0.0	14.6	1.2	0.0	0.0
Ni	0.0	0.0	0.0	1.3	88.5	0.0	5.5	4.6	0.0
Cu	0.0	0.0	24.5	0.0	0.3	0.0	0.3	74.8	0.0
Zn	13.4	0.8	12.1	67.5	2.7	0.0	0.0	3.5	0.0
As	0.0	26.4	3.9	23.7	9.3	2.4	25.5	8.8	0.0
Br	0.0	1.8	0.9	50.4	29.1	0.0	17.8	0.0	0.0
Sr	36.6	12.1	1.3	10.1	8.0	12.7	19.2	0.0	0.0
Ba	0.0	22.5	36.4	34.0	0.0	4.1	0.0	3.0	0.0
Pb	4.9	0.0	0.0	0.0	0.0	0.0	0.0	95.1	0.0

Table S9.3 - Source profiles for the outdoors PM10 (%)

PM10 Outdoors	City Dust	Secondary	Non-exhaust Traffic	Exhaust traffic	Heavy Oil	Soil	Sea Salt	Industry
PM	16.3	14.9	6.2	22.6	8.1	7.9	21.2	2.8
OC	17.0	16.9	9.7	44.5	0.0	4.8	2.8	4.4
EC	7.3	0.0	44.3	38.1	0.0	5.2	4.5	0.5
Na	0.0	6.1	2.2	0.0	6.6	13.9	71.2	0.0
Al	0.0	2.4	0.0	0.0	0.0	95.2	1.5	0.9
Si	49.3	0.0	0.0	0.0	0.0	50.7	0.0	0.0
S	2.7	61.2	0.0	0.1	14.6	4.0	9.1	8.2
Cl	0.0	1.3	1.2	0.0	0.0	0.0	96.9	0.6
K	4.7	0.0	0.0	53.6	4.5	18.6	14.9	3.6
Ca	58.9	9.3	4.4	9.7	0.9	11.0	5.8	0.0
Ti	46.9	1.2	4.3	2.5	3.5	39.4	1.9	0.2
V	1.9	7.4	2.2	0.0	88.1	0.0	0.3	0.0
Cr	4.4	0.0	68.2	14.6	6.1	5.1	0.0	1.8
Mn	1.3	0.4	35.8	6.9	1.3	14.4	1.7	38.1
Fe	16.2	4.3	47.1	13.0	0.0	17.0	2.3	0.0
Ni	0.0	0.0	0.0	1.6	72.3	0.0	17.5	8.6
Cu	0.0	0.0	50.9	0.0	0.1	0.0	0.5	48.6
Zn	15.1	1.7	34.5	40.5	2.1	0.0	0.0	6.1
As	0.0	26.9	8.3	14.6	2.7	3.4	35.4	8.7
Br	0.0	1.7	2.3	39.3	10.3	0.0	46.4	0.0
Sr	15.3	14.0	4.1	6.2	3.4	17.6	39.3	0.0
Ba	0.0	15.5	67.1	12.4	0.0	3.3	0.0	1.7
Pb	6.1	0.0	0.0	0.0	0.0	0.0	0.0	93.9

Table S9.4 - Source profiles for the indoors PM10 (%)

PM10 Indoors	City Dust	Secondary	Non-exhaust Traffic	Exhaust traffic	Heavy Oil	Soil	Sea Salt	Industry	Indoor organics
PM	32.1	6.4	2.9	14.6	4.9	3.4	7.5	0.1	28.1
OC	12.9	6.8	1.8	12.1	0.0	1.5	0.8	1.4	62.8
EC	10.6	0.0	23.1	41.8	0.0	3.2	2.6	0.5	18.1
Na	0.0	8.5	0.9	0.0	8.8	15.4	66.4	0.0	0.0
Al	0.0	1.9	0.0	0.0	0.0	94.0	1.3	0.8	2.0
Si	62.4	0.0	0.0	0.0	0.0	34.0	0.0	0.0	3.6
S	3.6	63.6	0.0	0.1	13.1	2.2	4.2	9.7	3.3
Cl	0.0	1.6	0.7	0.0	0.0	0.0	96.9	0.9	0.0
K	6.2	0.0	0.0	46.8	3.0	10.4	7.0	2.9	23.8
Ca	78.8	4.4	1.0	4.4	0.4	6.3	2.8	0.0	1.9
Ti	67.3	0.9	1.5	1.8	2.4	23.9	1.0	0.2	1.0
V	2.8	5.7	0.8	0.0	88.1	0.0	0.2	0.0	2.4
Cr	16.1	0.0	40.0	20.8	7.6	5.2	0.0	3.9	6.4
Mn	4.0	0.4	17.4	7.1	1.3	14.9	1.3	53.6	0.0
Fe	36.6	5.2	25.4	14.8	0.0	16.2	1.9	0.0	0.0
Ni	0.0	0.0	0.0	2.0	72.6	0.0	12.8	10.3	2.3
Cu	0.0	0.0	26.7	0.0	0.1	0.0	0.3	72.0	0.9
Zn	25.8	1.2	17.2	42.5	2.2	0.0	0.0	5.1	5.9
As	0.0	26.5	3.7	13.7	2.5	2.7	23.4	9.7	17.7
Br	0.0	2.5	1.0	36.2	14.3	0.0	30.2	0.0	15.8
Sr	36.6	11.8	2.4	4.9	2.7	15.2	23.2	0.0	3.2
Ba	0.0	20.7	46.1	15.7	0.0	5.4	0.0	2.6	9.5
Pb	7.8	0.0	0.0	0.0	0.0	0.0	0.0	92.2	0.0

Table S9.5 - Average contribution of the sources to the indoor and outdoor of homes and schools. Ratio between the contribution of the sources to the indoor and outdoor (significant differences at $p<0.05$ in bold) and Spearman Correlation (Rs) between contribution of the sources to the indoor and outdoor concentrations (significant correlations at $p<0.05$ in bold).

		PM2.5								PM10							
		Homes				Schools				Homes				Schools			
		Indoor	Outdoor	I/O	Rs	Indoor	Outdoor	I/O	Rs	Indoor	Outdoor	I/O	Rs	Indoor	Outdoor	I/O	Rs
Exhaust traffic	ng/m^3	4.5	5.9	**0.76**	**0.82**	7.3	8.9	0.96	**0.57**	3.9	6.4	**0.66**	**0.79**	8.5	11	0.96	**0.60**
	%	24	47			16	44			15	24			10	26		
Non-exhaust traffic	ng/m^3	0.47	0.73	**0.68**	**0.53**	0.15	0.45	0.53	**0.47**	1.0	2.6	**0.43**	**0.68**	0.84	1.2	0.76	0.36
	%	2.5	5.8			0.32	2.2			4.0	9.4			1.0	2.9		
Secondary	ng/m^3	2.2	2.4	**0.75**	**0.64**	3.1	2.1	0.99	**0.65**	2.2	4.2	**0.50**	**0.59**	2.6	3.6	**0.58**	**0.77**
	%	11	19			6.8	10			8.8	15			3.0	8.4		
Heavy Oil	ng/m^3	1.3	0.56	**2.45**	**0.80**	0.62	0.31	1.35	**0.64**	1.1	1.9	**0.76**	**0.74**	0.72	1.3	0.54	**0.74**
	%	6.9	4.4			1.3	1.6			4.5	6.8			0.80	3.0		
Industry	ng/m^3	0.10	0.82	**0.10**	**0.40**	0.33	2.1	**0.22**	**0.42**	0.19	0.74	**0.27**	**0.27**	0.51	1.5	**0.29**	**0.69**
	%	0.51	6.5			0.71	10			0.73	2.7			0.60	3.6		
Sea Salt	ng/m^3	0.33	0.58	**0.60**	**0.93**	0.45	0.89	**0.59**	**0.76**	2.2	5.9	**0.34**	**0.84**	3.0	5.6	**0.60**	**0.83**
	%	1.7	4.6			1.0	4.4			8.5	21			3.5	13		
Soil	ng/m^3	0.50	0.85	**0.53**	**0.77**	1.4	1.4	1.54	0.40	0.92	2.2	**0.48**	**0.57**	3.5	4.6	1.26	0.24
	%	2.6	6.8			3.1	6.9			3.6	7.9			4.2	11		
City Dust	ng/m^3	1.7	0.7	**2.98**	**0.62**	21.6	4.1	**6.83**	**0.76**	2.9	3.5	**0.80**	**0.54**	52.4	13.7	**3.87**	**0.75**
	%	8.8	5.6			47	20			11	13			62	32		
Indoor organics	ng/m^3	7.9				11				11				12			
	%	42				24				43				15			

Table S9.6 - Average contribution of the sources to the children exposure to PM2.5 and PM10.

		PM2.5			PM10		
		Weekday	Weekend	All	Weekday	Weekend	All
Exhaust traffic	ng/m^3	5.9	4.5	5.5	6.1	4.5	5.6
	%	21	23	22	13	15	14
Non-exhaust traffic	ng/m^3	0.37	0.39	0.38	1.0	1.1	1.0
	%	1.4	2.1	1.5	2.2	3.8	2.5
Secondary	ng/m^3	2.6	1.5	2.2	2.5	2.2	2.4
	%	9.3	7.6	8.9	5.5	7.7	5.9
Heavy Oil	ng/m^3	0.91	1.6	1.1	1.0	1.4	1.1
	%	3.3	8.2	4.4	2.1	5.0	2.7
Industry	ng/m^3	0.38	0.16	0.32	0.43	0.22	0.37
	%	1.4	0.84	1.3	0.95	0.77	0.91
Salt	ng/m^3	0.42	0.39	0.41	2.7	2.5	2.7
	%	1.5	2.0	1.6	6.1	8.7	6.6
Soil	ng/m^3	0.85	0.74	0.82	2.1	1.4	1.9
	%	3.1	3.9	3.3	4.6	4.9	4.6
City dust	ng/m^3	8.0	3.0	6.6	19	6.8	16
	%	29	16	26	42	24	39
Indoor organics	ng/m^3	8.1	6.9	7.7	10	8.6	9.9
	%	29	36	31	23	30	24

Chapter 10

Chapter 10. Conclusions, Recommendations, and Future Perspectives

This study evaluated the exposure of children to organic and inorganic compounds in PM, identified the main factors affecting the exposure, and contributed to the definition of actions to improve the children health and wellbeing. The main conclusions from the work presented in this thesis can be summarised as follows.

Time activity pattern

Children are becoming an increasingly important focus for exposure and risk assessment because they are more sensitive than adults to pollutants. A necessary step in measuring the extent of children's exposure is to assess where children spend their time. A questionnaire about time activity patterns, targeting children between 5 and 10 years, was distributed to parents from 24 schools from Lisbon.

The most important finding of the survey was that children spent more than 87% of their time indoors (during the week, 55% inside home and 27% inside classroom), indicating that risk assessment should focus on indoor MEs.

Schools

The classrooms were the ME with the highest average concentrations of PM2.5 (35 $\mu g/m^3$) and PM10 (65 $\mu g/m^3$), which exceeded the limit values defined by the Portuguese legislation for IAQ. The I/O ratio in this ME was higher than 1, indicating the importance of indoor sources, and the PM2.5/PM10 ratio showed that the coarse fraction is predominant.

Organic carbon and mineral matter were the main contributors to the total mass in this ME, which result from outdoor sources, occupation, resuspension of dust caused by the intense movement of children, the use of chalk on blackboards, and from an inadequate ventilation of the spaces. OC presented a bimodal distribution, characterised by high OC concentrations in the fine fraction, associated with emissions from the traffic, and by a high correlation between coarse OC and the mineral matter. A unimodal distribution was detected for mineral elements characterised by higher levels in the coarse fraction.

Source apportionment indicated that resuspended dust, indoor organics and vehicle exhaust contributed to 62%, 15% and 10% of the PM10. These results indicated that IAQ in schools can be improved with the reinforcement of cleaning procedures, increase of the ventilation and urban planning to reduce the exposure of children to traffic related pollutants.

Homes

The concentrations of PM2.5 (14 μg/m^3) and PM10 (18 μg/m^3) were significantly lower in the homes than in the schools. POM was the dominant contributor to the total mass of PM inside homes (63% for PM2.5 and 61% for PM10). The I/O ratio for OC (3.2 for PM2.5 and 2.7 for PM10) indicated that besides the infiltration of outdoor particles, there was an important contribution of indoor sources. The occupants in homes are considered one of the most important sources of coarse OC because they are responsible by the emission of primary biological material, such as skin flakes, debris and hair. In addition, the resuspension of the deposited dust caused by the occupants' movement and cleaning activities, such as vacuuming, dusting, house-keeping, also contribute to the OC levels in coarse fraction. Other domestic activities such as cooking, biomass burning for domestic heating, smoking and burning of candles and incenses, are also responsible for the emission of OC but in the fine and ultra-fine fraction of PM.

Source apportionment results showed that the indoor organics and traffic exhaust, both identified by high levels of OC, were the main sources of PM2.5 (42% and 24%, respectively) and PM10 (43% and 15%, respectively) in homes. These results indicated that it is essential to avoid some indoor sources (e.g. smoking, candles, incense, diffusers), promote a good ventilation and exhaust air in the vicinity of localized indoor sources such as cooking. The houses located in the city centre, where traffic is more intense, presented higher concentrations of PM, which confirm the importance of traffic emissions for the IAQ. Ventilation of the homes should be performed during periods with less traffic and sustainable transport solutions should be developed to reduce the exposure even inside home.

Besides the chemical pollutants, settled dust was sampled and analysed by culture methods and qPCR to identify fungal species with toxigenic potential. *Aspergillus* sections (such as *Nigri* and *Candidi*) with toxigenic potential were found in bedrooms and living rooms and exhibited reduced susceptibility to one or more azoles. The most prevalent fungal species were *Penicillium* sp. (92%) in the rooms and *Rhizopus* sp. (38%) in the living rooms.

Exposure and inhaled dose

The average exposure of children to PM2.5 in Lisbon was above the new WHO daily reference value of 15 μg/m^3. Although children spent less time at school than at home, the classroom was the ME that most contributed to the exposure of children to PM2.5 (42%) and PM10 (50%), followed by the house, mainly during bedtime (PM2.5 – 27%; PM10 – 22%). Together these two MEs contributed to 79% of the children's daily exposure and to more than 64% of the inhaled dose. Although children only spent 10% of time in-

transit, commuting leaded to a substantial contribution to their total daily exposure, because transport MEs presented higher air pollutant concentrations than other settings occupied by kids in their daily routines.

The contribution from outside was higher to the inhaled dose (24%) than to the exposure (12%), due to the higher inhalation rates associated with outdoor activities. This fact reinforces the importance of a good urban planning that avoid the construction of schools and outdoor places frequented by children near areas with high levels of pollutants, such as traffic roads.

Source apportionment indicated that indoor organic matter, resulting from personnel care products, cleaning, cooking, smoking and biological material, was the major PM2.5 source, contributing to 31% of the exposure. The source city dust, which was highly influenced by the resuspension of dust in classrooms, was the second main source (26%), followed by traffic (24%). The major sources affecting the integrated exposure to PM10 were the city dust (39%), indoor organics (24%) and traffic (16%).

The exposure of children to PM was assessed in Lisbon through the direct and indirect methods and similar results were obtained, showing that both alternatives are valuable approaches to study the daily exposure to pollutants, as long as indoor MEs are considered. The exposure results obtained by the direct method were also compared with the concentrations obtained by the nearest fixed urban monitoring station. The results showed that fixed urban stations underestimated the exposure. This fact is due to the great heterogeneity in the distribution of pollutants in the city, different time activity patterns of the children and the weight that indoor environments have on the daily exposure. The assessment of children's integrated daily exposure, considering all the visited MEs during the day, is essential to estimate the inhaled and internal dose, which are key factors in health impacts.

Deposited dose

The measurements of exposure were combined with mathematical models to estimate the average daily dose of PM2.5 in the different regions of the respiratory tract of the children, as well as the particle build up in extrathoracic, bronchial, bronchiolar, and alveolar-interstitial regions. It was concluded that 3% of the particles were deposited in the bronchial region, while 5% to 8% were found in the bronchiolar region. There is an important variability among children regarding the extrathoracic and alveolar-interstitial daily dose, which can be attributed to the contribution of each particle size bin and level of physical excitation.

The measurement of exposure and the PM mass size distribution provide essential data for determining the internal doses in the HRT of children and are determinant for the evaluation of risk.

General observations

This thesis characterised the PM sampled in the main MEs frequented by the children in their daily routines and identified the main factors and sources influencing their levels. The results demonstrated that indoor MEs are the main contributors to personal exposure and respective inhaled dose.

The results obtained pointed to the need for an integrated exposure assessment, in order to reduce the uncertainty associated with the calculation of exposure and dose, allowing stronger associations between these parameters and health outcomes.

The outputs of this work are useful for epidemiological studies and for establishing practical and effective mitigation strategies to reduce children's exposure to PM and, consequently, reduce adverse health effects, improving their well-being.

Recommendations for improving air quality in different microenvironments

Science and knowledge must play a leading role in transforming society. Contributing to the development of scientific research and seeking answers to its gaps is extremely important. However, transmitting the knowledge acquired to the stakeholders and population, so that they can be an active part of a positive, informed, and science-based change, is essential.

For this purpose, several recommendations are suggested to the decision-makers at the political, urban, and school level and to the general population.

For schools

• Do not wear street shoes inside classrooms to reduce particle concentrations.

• Do not eat in the classroom and keep it clean to prevent the spread of microorganisms, accumulation of dust, and the spread of contagious diseases.

• Give preference to the whiteboard, but if the classroom is equipped with a blackboard, clean it with a damp cloth to avoid high concentrations of airborne chalk particles.

• Ventilate classrooms by opening windows and doors, in case the windows face a high traffic road, ventilate the room by leaving the door open and letting the windows open when the room is empty.

• Give preference to damp mops and cloths instead of brooms and dry cloths to reduce particle levels.

• Clean school spaces at the end of each day to reduce the concentration of substances emitted by cleaning products.

• Schedule furniture renovation and school maintenance activities for periods of non-occupancy or school holidays to avoid exposure to toxic substances.

• Create solutions to reduce the density of road traffic around schools (e.g., plantation of green curtains).

• Promote public transport as an option for commuting, reducing the number of cars around the school and their respective emissions.

For houses

• Do not smoke indoors.

• Do not wear street shoes indoors to avoid transferring external particles to indoor spaces.

• Do not use candles, incense, diffusers, air fresheners, aerosol products and mothballs.

• Avoid the accumulation of objects around the house, which favour the accumulation of dust and make cleaning difficult.

• Clean the house regularly, avoiding the accumulation of dust and microorganisms.

• Keep the house clean using a vacuum cleaner with high levels of filtration or mop instead of brooms, as the sweeping action promotes the resuspension of particles. Use a damp cloth instead of a dry cloth.

• If using cleaning products, open windows to promote the dispersion of emitted pollutants.

• Open windows to ventilate indoor environments, but avoid traffic rush hours.

• Exhaust air in the vicinity of localized indoor sources such as cooking.

• Keep humidity levels between 30% and 50% to prevent the proliferation of fungi, promoting air extraction in the kitchen and bathrooms (e.g., avoid drying clothes indoors).

• Reduce the use of rugs and carpets to reduce the accumulation of dust and dirt. Give preference to short pile carpets/rugs or rugs that can be washed.

For policymakers/authorities

• Develop air quality plans, which aim to reduce the emission of pollutants and ensure compliance with air quality objectives.

• Do not approve school projects near roads with high traffic.

• Demand that new schools have mechanical ventilation that allows for the renewal of indoor air

• Select the best locations to plant trees in urban areas to ensure the dispersion of pollutants.

• Invest in conditions to encourage public transport, cycling, and walking.

• Wash roads with water at dawn and decrease speed limits to reduce road dust resuspension

• Take into account children's exposure to air pollutants in urban planning.

Future research and open questions

The research carried out in this study opens the way to other gaps and open questions that future research can answer:

- Indoor sources of air pollutants should be further investigated, especially those that showed to have a higher impact on IAQ. The creation of a complete database of indoor sources, with information about their fingerprint and impacts, would support source apportionment studies and allow a more effective application of measures.

- Organic carbon stood out as the pollutant that most contributed to the indoor MEs. Some indoor organic compounds are considered emergent pollutants and have important health impacts. Identifying and quantifying the organic compounds in the indoor MEs is essential to evaluate their possible health impacts and to identify the contribution of sources.

- Knowledge about indoor/outdoor relationships in buildings, taking into account the influence of infiltration, the age of the building, the construction characteristics, among others, is essential to assess the population exposure to pollutants using modelling techniques.

- The effects of the children's exposure to pollutants on health and on their school performance should be clarified by carrying out long-term studies that follow groups of children over the years.

- The quantification of the impact of indoor and outdoor mitigation measures on air quality, exposure, dose and health is essential to identify cost effective actions to be implemented in cities, homes and schools.

ANNEX I - Participation in scientific meetings

1. Oral communications

1.1 Author and presenter

– T. Faria, I. Cunha-Lopes, M. Pilou, C. Housiadas, X. Querol, C. Alves, S. M. Almeida. Children's exposure to size-fractioned particulate matter: chemical composition and internal dose assessment. European Aerosol Conference. EAC 2021. 30 August - 3 September.

- T. Faria, A.S.S. Daoudi, R. Bossi, M.S. Johnson, K. Vorkamp, S. M. Almeida. Assessment of children's exposure to organic pollutants in homes in Portugal. European Aerosol Conference. EAC 2021. 30 August - 3 September.

- T. Faria, V. Martins, C. Correia, N. Canha, E. Diapouli, M. Manousakas, K. Eleftheriadis, SM. Almeida. Children integrated exposure to chemical compounds in particulate matter. International Congress on Environmental Health. ICEH 2019. Lisbon, Portugal. 25-27 September 2019.

- T. Faria, V. Martins, C. Correia, N. Canha, E. Diapouli, M. Manousakas, K. Eleftheriadis, SM. Almeida. Children exposure and dose assessment to chemical compounds in particulate matter in Lisbon. European Aerosol Conference. EAC 2019. Gothenburg, Sweden. 25-30 August 2019.

- T. Faria, V. Martins, C. Correia, N. Canha, E. Diapouli, M. Manousakas, K. Eleftheriadis, SM. Almeida. Spatial variability of personal exposure to particles in Lisbon. 7th Iberian Meeting on Aerosol Science and Technology. RICTA 2019. Lisbon, Portugal. 9 - 11 July 2019.

- T. Faria, V. Martins, I. Cunha-Lopes, C. Correia, N. Canha, E. Diapouli, M. Manousakas, K. Eleftheriadis, C. Alves, S.M. Almeida (2018) Avaliação da exposição de crianças a matéria particulada em ambiente urbano. Conferência Internacional de Ambiente em Língua Portuguesa (CIALP). 8 a 10 de maio de 2018

1.1.1 Author

- I. Cunha-Lopes, I. Rienda, T. Faria, F. Lucarelli, F. Amato, C. Alves, SM. Almeida. Characterization of non-exhaust emissions from road traffic in Lisbon. European Aerosol. Conference. EAC 2021. 30 August - 3 September.

– V. Martins, T. Faria, E. Diapouli, M. Manousakas, K. Eleftheriadis, M. Viana, SM. Almeida. Assessment of size-segregated particulate matter in urban microenvironments. European Aerosol Conference. EAC 2021. 30 August - 3 September.

- V. Martins, C. Correia, I. Cunha-Lopes, T. Faria, E. Diapouli, M. Manousakas, K. Eleftheriadis, SM. Almeida. Concentration and chemical composition of PM in urban transport modes. European Aerosol Conference. EAC 2021. 30 August - 3 September.

- E. Diapouli, V. Martins, T. Faria, M. Dionisi, N. Canha, M. Manousakas, K. Eleftheriadis, A. Miranda, J. Ferreira, H. Relvas, A. Korhonen, H. Lehtomäki, O. Hänninen, M. Lazaridis, E. Chalvatzaki, S.M. Almeida. Implementation of the LIFE Index-Air Exposure - Dose Management Tool in 5 European Cities. European Aerosol Conference. EAC 2021. 30 August - 3 September.

- E. Diapouli, S.M. Almeida, A. Kalogridis, V. Martins, T. Faria, N. Canha, A. Miranda, J. Ferreira, H. Relvas, D. Lopes, A. Korhonen, H. Lehtomäki, O. Hänninen, M. Lazaridis, E. Chalvatzaki, K. Eleftheriadis. LIFE Index-Air: Development of an integrated exposure - dose management tool for the reduction of PM pollution and the protection of public health. European Aerosol Conference. EAC 2020. 30 August - 4 September.

- I. Cunha-Lopes, V. Martins, T. Faria, C. Correia, SM. Almeida. Children's exposure assessment to particulate matter in Lisbon metropolitan area. International Congress on Environmental Health. ICEH 2019. Lisbon, Portugal. 25-27 September 2019.

- S.M. Almeida, T. Faria, V. Martins, C. Correia, N. Canha, E. Diapouli, M. Manousakas, K. Eleftheriadis. Exposure to source-related components of particle air pollution. International Congress on Environmental Health. ICEH 2019. Lisbon, Portugal. 25-27 September 2019.

- V. Martins, T. Faria, E. Diapouli, M. Manousakas, K. Eleftheriadis, M. Viana, SM. Almeida. Indoor-to-outdoor levels of size-segregated particulate matter in urban microenvironments. International Congress on Environmental Health. ICEH 2019. Lisbon, Portugal. 25-27 September 2019.

- C. Correia, V. Martins, I. Cunha-Lopes, T. Faria, E. Diapouli, K. Eleftheriadis, S.M. Almeida. Commuter exposure and inhaled dose of particulate matter in four common modes of transport in Lisbon. International Congress on Environmental Health. ICEH 2019. Lisbon, Portugal. 25-27 September 2019.

- S.M. Almeida, T. Faria, V. Martins, C. Correia, N. Canha, E. Diapouli, M. Manousakas, K. Eleftheriadis. Source Apportionment of Children Exposure to Particulate Matter in Lisbon. European Aerosol Conference. EAC 2019. Gothenburg, Sweden. 25-30 August 2019.

- E. Diapouli, M. Manousakas, S.M. Almeida, V. Martins, T. Faria, V. Vasilatou, K. Eleftheriadis. Chemical characterization of indoor and outdoor PM at residences and schools, in Lisbon, Portugal. European Aerosol Conference. EAC 2019. Gothenburg, Sweden. 25-30 August 2019.

– E. Diapouli, S.M. Almeida, V. Martins, T. Faria, N. Canha, A. Miranda, J. Ferreira, H. Relvas, A. Korhonen, H. Lehtomäki, O. Hänninen, M. Lazaridis, E. Chalvatzaki, K. Eleftheriadi. LIFE Index-Air - development of an integrated exposure - dose management tool for the reduction of particulate matter in air and the protection of public health. 7th Iberian Meeting on Aerosol Science and Technology. RICTA 2019. Lisbon, Portugal. 9 - 11 July 2019.

– H. Lehtomäki, A. Korhonen, S.M. Almeida, V. Martins, T. Faria, A.I. Miranda, J. Ferreira, D. Lopes, S. Rafael, E. Diapouli, K. Eleftheriadis, O. Hänninen. Burden of disease attributed to airborne particulate

matter in five selected European cities. 7th Iberian Meeting on Aerosol Science and Technology. RICTA 2019. Lisbon, Portugal. 9 - 11 July 2019.

- S.M. Almeida, T. Faria, V. Martins, C. Correia, N. Canha, E. Diapouli, M. Manousakas, K. Eleftheriadis. Sources of children's exposure to particulate matter. 7th Iberian Meeting on Aerosol Science and Technology. RICTA 2019. Lisbon, Portugal. 9 - 11 July 2019.

- V. Martins, T. Faria, E. Diapouli, M. Manousakas, K. Eleftheriadis, M. Viana, SM. Almeida. Relationship between indoor and outdoor size-fractionated particulate matter collected in urban homes and schools. 7th Iberian Meeting on Aerosol Science and Technology. RICTA 2019. Lisbon, Portugal. 9 - 11 July 2019.

- C. Correia, V. Martins, I. Cunha-Lopes, T. Faria, E. Diapouli, K. Eleftheriadis, S.M. Almeida. Exposure and inhaled dose of particulate matter by commuters in Lisbon. 7th Iberian Meeting on Aerosol Science and Technology. RICTA 2019. Lisbon, Portugal. 9 - 11 July 2019.

- I. Cunha-Lopes, V. Martins, T. Faria, C. Correia, SM. Almeida. Assessment of children's exposure to sized-fractioned particulate matter and black carbon in Lisbon metropolitan area. 7th Iberian Meeting on Aerosol Science and Technology. RICTA 2019. Lisbon, Portugal. 9 - 11 July 2019.

– M. Gini, E. Diapouli, M. Manousakas, E. Chalvatzaki, M. Lazaridis, V. Martins, T. Faria, S.M. Almeida, O. Hänninen, K. Eleftheriadis. The effect of variability in size distribution metrics of aerosol chemical components on the deposited dose for urban areas in Lisbon. 7th Iberian Meeting on Aerosol Science and Technology. RICTA 2019. Lisbon, Portugal. 9 - 11 July 2019.

– J. Ferreira, D. Lopes, H. Relvas, T. Faria, V. Martins, E. Diapouli, S.M. Almeida, A.I. Miranda. Modelling population exposure to PM2.5 in Lisbon. 7th Iberian Meeting on Aerosol Science and Technology. RICTA 2019. Lisbon, Portugal. 9 - 11 July 2019.

- F. Sá, M. Mateus, P. Santos, A. Monteiro, T. Faria, C. Viegas. Bioburden characterization in Portuguese dwellings. Vertentes e Desafios da Segurança (VDS 2018). October 25 to 27, 2018. Leiria, Portugal.

- V. Martins, S.M. Almeida, T. Faria, C. Correia, I. Cunha-Lopes, N. Canha, E. Diapouli, M. Manousakas, K. Eleftheriadis (2018) Child Exposure to Indoor and Outdoor PM at Schools and Homes in the Lisbon Metropolitan Area, Portugal. 10th International Aerosol Conference. September 2 to 7, 2018. St. Louis, Missouri, USA

– S.M. Almeida, P. Blondeau, V. Manteigas, J. Lage, A. D'Espiney, M. Almeida-Silva, N. Canha, V. Martins, T. Faria, K. Gonçalves, J.L. Alexandre, R. Chacartegui, J. Lizana, J.A. Becera, A. Gamarra, Y.L. Perez, A. Fernandes (2018) Managing Indoor Air Quality in ClimACT Schools. 10th International Aerosol Conference. September 2 to 7, 2018. St. Louis, Missouri, USA

– S.M. Almeida, T. Faria, V. Martins, N. Canha, I. Cunha-Lopes, C. Correia, E. Diapouli, M. Manousakas, K. Eleftheriadis (2018) Indoor-to-outdoor particle concentration assessment for human exposure analysis.

The 15th Conference of the International Society of Indoor Air Quality & Climate (ISIAQ). July 22 to 27, 2018, Philadelphia, PA, USA.

- V. Martins, T. Faria, N. Canha, M. Almeida-Silva, E. Diapouli, M. Manousakas, K. Eleftheriadis, M. Viana, S.M. Almeida (2018) Distribuição granulométrica da massa de partículas amostradas no interior e exterior de casas e escolas de Lisboa. Conferência Internacional de Ambiente em Língua Portuguesa (CIALP). 8 a 10 de maio de 2018

2. Panel Communications (Poster)

2.1 Author and presenter

- S.M. Almeida, M. Almeida-Silva, N. Canha, T. Faria, K. Eleftheriadis, E. Diapouli, A. Miranda, J. Ferreira, O. Hänninen, M. Lazaridis, et al. LIFE Index-Air project: Development of an integrated exposure - dose management tool for reduction of particulate matter in air. 14th International Conference on Urban Health - Health Equity: The New Urban Agenda and Sustainable Development Goals. 26-29 September 2017, Coimbra, Portugal

2.2 Author

– E. Diapouli, T. Faria, V. Martins, S.M. Almeida, T. Maggos, K.A. Bairachtari, M. Dasopoulou, K. Eleftheriadis. Indoor and outdoor concentrations of polycyclic aromatic hydrocarbons (PAHs) at residences and schools, in Lisbon, Portugal. European Aerosol Conference. EAC 2020. 30 August - 4 September.

- H. Lehtomäki, S.M. Almeida, V. Martins, T. Faria, E. Diapouli, K. Eleftheriadis, O. Hänninen. Air pollution exposure and school absenteeism. 7th Iberian Meeting on Aerosol Science and Technology. RICTA 2019. Lisbon, Portugal. 9 - 11 July 2019.

- O. Hänninen., H. Lehtomäki, A. Korhonen, S.M. Almeida, V. Martins, T. Faria, N. Canha, A.I. Miranda, J. Ferreira, H. Relvas, D. Lopes, E. Diapouli, K. Eleftheriadis, E. Chalvatzakis, M. Lazaridis. Domains of air pollution health impact assessment in the LIFE Index-Air project. 7th Iberian Meeting on Aerosol Science and Technology. RICTA 2019. Lisbon, Portugal. 9 - 11 July 2019.

- E. Diapouli, T. Faria, V. Martins, S.M. Almeida, Th. Maggos, K.A. Bairachtari, M. Drosopoulou, K. Eleftheriadis. Indoor and outdoor concentrations of polycyclic aromatic hydrocarbons (PAHs) at residences and schools, in Lisbon, Portugal. 7th Iberian Meeting on Aerosol Science and Technology. RICTA 2019. Lisbon, Portugal. 9 - 11 July 2019.

– T. Faria, M. Almeida-Silva, V. Martins, I. Cunha-Lopes, C. Correia, C. Galinha, C. Alves S.M. Almeida (2018) Exposure of Children to Particulate Matter and Chemical Elements in Urban Environment. 10th International Aerosol Conference. September 2 to 7, 2018. St. Louis, Missouri, USA

- V. Martins, S.M. Almeida, T. Faria, C. Correia, I. Cunha-Lopes, N. Canha, E. Diapouli, M. Manousakas, K. Eleftheriadis (2018) Personal Exposure to Particulate Matter While Commuting. 10th International Aerosol Conference. September 2 to 7, 2018. St. Louis, Missouri, USA

- S.M. Almeida., M. Almeida-Silva, N. Canha, V. Martins, T. Faria, K. Eleftheriadis, E. Diapouli, V. Galifianakis, A. Miranda, J. Ferreira, O. Hänninen, M. Lazaridis. Development of an Integrated Exposure – Dose Management Tool for Reduction of Particulate Matter in Air: Overview of the LIFE Index-Air Project. European Aerosol Conference (EAC2017), 27th August-1st September, Zurich, Switzerland.

ANNEX II - Individual questionnaire on children's time-activity patterns

	Home	School - outdoor	School - indoor	Indoor physical activit (gym)	Indoor physical activit (pool)	Outdoor physical activity	Extracurricular activity in class	Public transport - Bus	Public transport - Train	Public transport - Metro	Private Transport - Car	Private transport - Motorcycle	Outdoor - street	Outdoor - garden/terrace/park	Beach	Indoor - supermarket/stores	Indoor - Movie theater	Indoor - Restaurant/ coffee shop	Other
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