LIFEINDEXAIR

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Technical report on PM chemical characterization in different microenvironments and sources identification

Deliverable B2.2

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TÉCNICO LISBOA · universidade de aveiro · Technical University of crete · DEMOKRITOS NATIONAL CENTRE FOR SCIENTIFIC RESEARCH · NATIONAL INSTITUTE FOR HEALTH AND WELFARE

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1. CONTENTS

2. EXECUTIVE SUMMARY

The main objective of the Action B2 of the LIFE Index-Air project is to build an available, accessible, comparable and interoperable database to incorporate data on time activity patterns for children and data on chemical characterization of particles from microenvironments (ME) that most contribute for children exposure - schools, homes, transports and outdoor. The Technical Report on PM chemical characterization in different microenvironments and sources identification (Deliverable B2.2), developed in the scope of Action B2, describes the work developed in:

- Action B2.2 – Chemical characterization of particles sampled in microenvironments in Lisbon;

- Action B2.3 - Chemical characterization of particles sampled in mobile microenvironments in Lisbon;

- Action B2.5 – Identification of sources.

This report presents the overall methodology used in the three actions, the results obtained in the different microenvironments and the respective discussion.

3. INTRODUCTION

The technical report on PM chemical characterization in different microenvironments and sources identification is a document of the LIFE Index-Air project, delivered in the context of the Action B2 – Air Quality Database Module, more specifically in Activity B2.2, B2.3 and B2.5.

IST performed a sampling campaign in different Lisbon micro-environments – 40 homes, 5 schools, 4 transport modes (car, bicycle, metro and bus) and in the respective outdoor environments. Gravimetry was assessed in IST and the chemical analysis of the particles was performed by NCSR-D.

This report presents 5 main chapters:

1) PM mass concentrations in houses and schools from Lisbon;
2) Chemical characterization of PM sampled in houses and schools from Lisbon;
3) Source Apportionment of PM in micro-environments frequented by children in Lisbon;
4) Size distribution of particles sampled in houses and schools from Lisbon;
5) Particle exposure and inhaled dose while commuting in Lisbon;
6) Children exposure assessment to particulate matter in Lisbon using portable equipment.

4. PM MASS CONCENTRATIONS IN HOUSES AND SCHOOLS FROM LISBON

INTRODUCTION

PM are a complex mixture of particles with different sizes and enriched with organic and inorganic compounds. PM is usually classified into coarse particles, with diameters between 2.5 µm and 10 µm (PM2.5-10), and fine particles with diameters lower than 2.5 µm (PM2.5). The coarse particles, which result from the processes of abrasion of surfaces, resuspension of industrial dust, road works and natural sources, such as ocean spray and events from the Sahara desert, reach the upper respiratory tract (trachea). The fine particles can reach the lower respiratory tract (lungs) and may be originated by 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 at low levels of exposure and there is no evidence of a threshold below which no adverse health effects occur (Jakovljevi et al. 2018; Lazaridis et al. 2012; Almeida et al. 2016).

Measuring of the outdoor air levels and trends of pollutants at fixed ambient air quality monitoring sites together with modelling outdoor air concentrations with dispersion and chemical transport models has been the traditional way of evaluating urban air quality and estimating the needs and effectiveness of air pollution abatement programs. The potential of harmful health effects of air pollution has been estimated by comparing these levels to air quality guidelines and with health outcomes. However, this logic has been changed by a number of recent developments in both air pollution and scientific knowledge. Poor correlations have been found between ambient PM concentrations and personal exposure and therefore this approach fails to account for all components of exposure. Since people spend 90-95% of their time indoors, individual's exposure to PM is dominated by indoor air pollution, which is partly outdoor air pollution that has penetrated indoors and partly pollution from indoor sources. However, data available for risk assessment of indoor air pollution are scarce and often insufficient. Information is available for the indoor air concentrations of some well-known pollutants, but is lacking for others whose effects are unclear such as the chemical components of indoor PM that are currently poorly characterized.

Since the time activity patterns performed for the children living Lisbon showed that the main micro-environments occupied by children are the homes and schools, the objective of this work was to characterize the indoor and outdoor concentrations of PM in these two micro-environments in the city of Lisbon.

METHODOLOGY

Aerosol particles were sampled in 5 schools and 40 houses, located in the city of Lisbon where traffic is the main source of atmospheric particles (Figure 1). In the 5 schools, samples were collected simultaneously in the indoor (classroom) and in the outdoor (playground). All schools were monitored for 5 days - Monday through Friday and during the occupied period. In the 40 houses the indoor sampling occurred in the living room while simultaneous measurements were taken on the outdoor (balcony). All homes were monitored for 5 days - 4 days during the week and one day during the weekend always in the occupied period - 15 hours during the week from 6 pm to 9 am and 24 hours during the weekend from 9 am on Saturday to 9 am on Sunday.
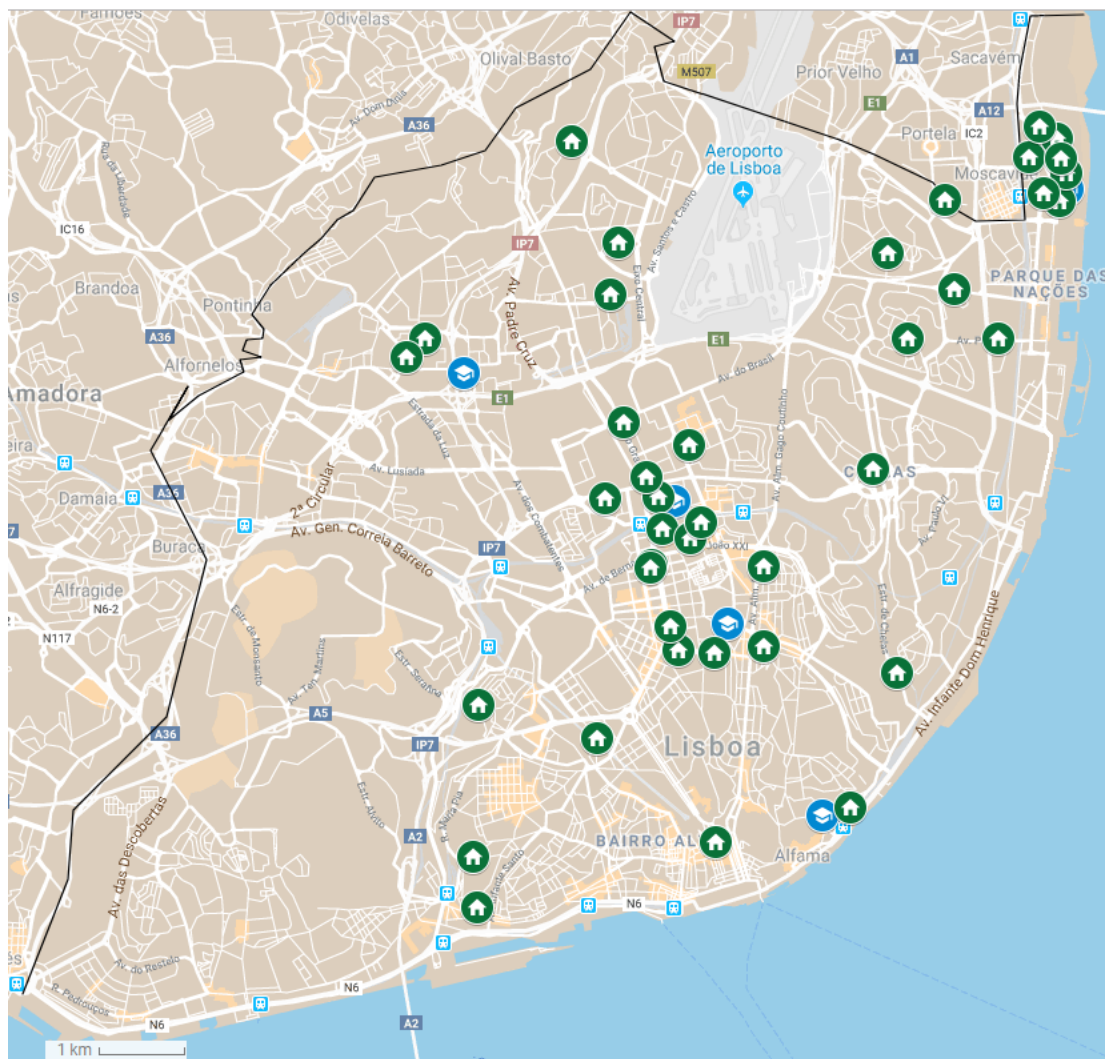
Figure 1 – Localization of the 5 schools and 40 houses

PM2.5 and PM2.5-10 samples were collected using 4 Leckel MVS6 who operated at a flow of 2.3m^3/h. The 4 samplers worked in parallel: 2 installed in the indoor and the other 2 installed in the outdoor (Figure 2 and Figure 3). PM2.5-10 was sampled in 25 mm filters and PM2.5 was sampled in 47 mm filters. Two samplers (one installed in the indoor and the other in the outdoor) worked with quartz filters. The other two samplers (one installed in the indoor and the other in the outdoor) worked with Nuclepore and PTFE filters. PM2.5-10 was sampled in 25 mm Nuclepore filters and PM2.5 was sampled in PTFE 47 mm filters. The filter loads were measured by gravimetry with an analytical microbalance (Sartorius R160P) in a controlled clean room (class 10,000) at 20 ˚C and relative humidity of 50 % according to EN 12341:1998.

Figure 2 – Matrix and dimension of the filters used in the sampling campaign.

Figure 3 – Equipment installed in the classroom and outside the school (upper graphs) and in the living room and in the balcony (lower graphs).

QUALITY ASSURANCE AND QUALITY CONTROL

The calibration and inter-comparison of the different equipment used during sampling campaign were carried out.

Measurements in both outdoor and indoor premises of IST were performed to test the samplers and the new sampling heads developed by NCSR-D. The results showed that the use of the new sampling heads yield equivalent results to those obtained by the use of commercial heads (referred as reference Leckel in the Figure 4), as results are within the expected uncertainty. A good correlation was obtained in the inter-comparison study (R^2=0.86 – 0.96, see Figure 4). Occasional outliers were flagged and removed from the statistical analysis (red point). With the development of the sampling heads, the sampling campaigns was less intrusive in the home and school environments, as the use of a single instrument for both PM2.5-10 and PM2.5 sampling allowed significant reduction in the noise emission and space usage. Moreover, all efforts were done to minimize artifacts and contamination in the samples. It must be noted

that several variables independent of the sampling head may affect the results, including variability in the sampled aerosol and weighting and handling of filters.

Notes:
L1 - Leckel sampler with sampling head developed by NCSR-D
L2 - Leckel sampler with sampling head developed by NCSR-D

L3 - Leckel sampler with PM10 commercial head
L4 - Leckel sampler with PM2.5 commercial head

Figure 4 - Results of the inter-comparison study.

RESULTS

PM2.5 AND PM10 LEVELS

Table 1 presents the PM2.5 and PM10 concentrations measured in the indoor and outdoor of the homes and schools during weekdays and weekend.

Table 1 - PM10 and PM2.5 concentrations measured in the indoor and outdoor of the homes and schools during weekdays and weekend.

			Weekdays		Weekend		Total	
			PM2.5	PM10	PM2.5	PM10	PM2.5	PM10
Homes	Indoor	$\bar{x}$	14.5	18.2	14.2	18.3	14.5	18.2
		Sd	12.3	13.3	11.8	12.8	12.2	13.2
		Min	2.1	2.5	4.2	5.1	2.1	2.5
		Max	91.9	97.6	66.6	75.5	91.9	97.6
	Outdoor	$\bar{x}$	13.8	22.5	11.8	19.5	13.4	21.9
		Sd	13.1	14.9	6.3	7.6	12.1	13.8
		Min	0.8	5.4	3.8	9.7	0.8	5.4
		Max	138.0	148.8	31.5	43.7	138.0	148.8
Schools	Indoor	$\bar{x}$	35.3	65.4	-	-	35.3	65.4
		Sd	24.9	38.9	-	-	24.9	38.9
		Min	10.0	22.2	-	-	10.0	22.2
		Max	112.2	164.5	-	-	112.2	164.5
	Outdoor	$\bar{x}$	20.9	31.7	-	-	20.9	31.7
		Sd	15.3	15.2	-	-	15.3	15.2
		Min	1.9	9.9	-	-	1.9	9.9
		Max	78.3	80.8	-	-	78.3	80.8

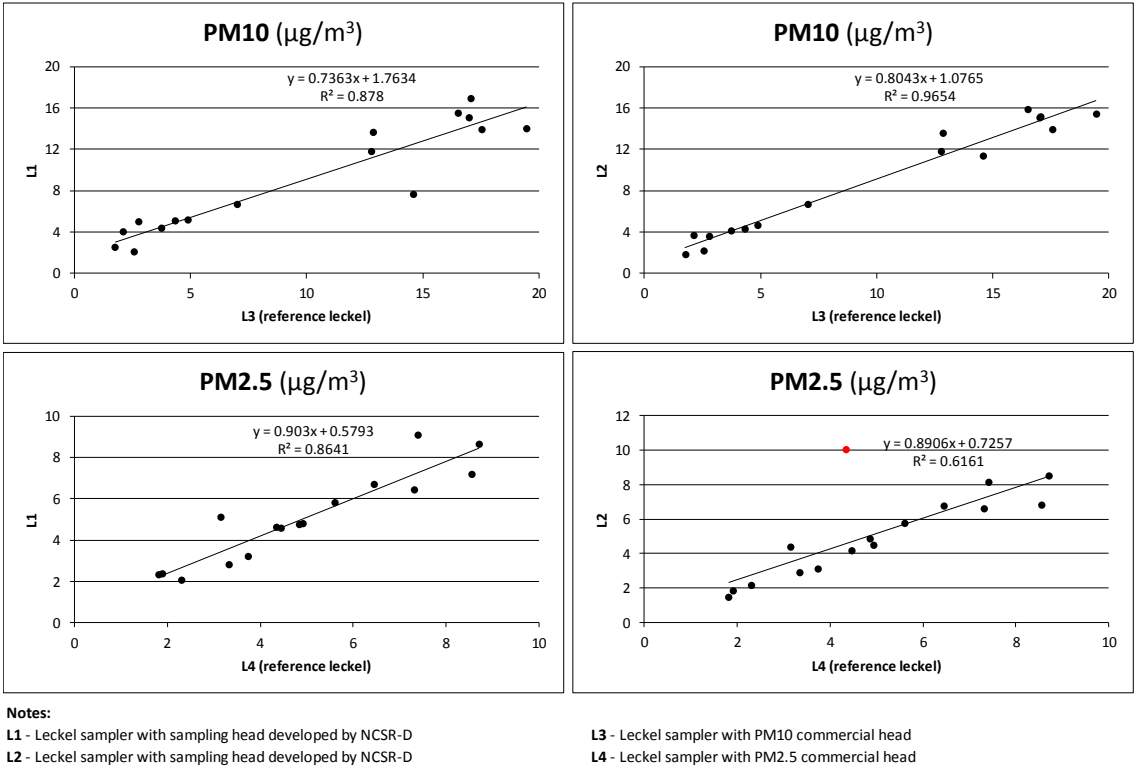The PM2.5 average concentration measured in the classrooms (35.3 µg/m^3) was higher than the limit value established by the Portuguese legislation (Portaria 353-A/2013) to the indoor PM2.5 concentrations (25 µg/m^3). An opposite behavior was observed for homes (14.5 µg/m^3) being the PM2.5 average concentration lower than 25 µg/m^3. The PM2.5 average concentrations measured in the outdoor of the schools (20.9 µg/m^3) and homes (13.4 µg/m^3) haven't exceeded the limit value of 25 µg/m^3 established by the Directive 2008/50/EC. However, the PM2.5 levels could not accomplish the ambitious goal proposed by the WHO guideline (10 µg/m^3).

The PM2.5 concentrations measured during the weekdays were more than double in schools (35.3 µg/m^3) than in homes (14.5 µg/m^3). The outdoor concentrations in schools (20.9 µg/m^3) and in homes (13.8 µg/m^3) were lower than those measured in the respective indoor spaces. At the weekend, the indoor concentrations measured in homes (14.2 µg/m^3) were lower than those measured during the weekdays and the same happened with outdoor concentrations (11.8 µg/m^3).

The PM10 average concentration measured in the classrooms (65.4 µg/m^3) was higher than the PM10 limit value stablished by Portaria 353-A/2013 (50 µg/m^3). As for the PM2.5, an opposite behavior was observed for homes (18.2 µg/m^3) that accomplished the limit value. The PM10 average concentrations, measured in the outdoor of the schools (31.7 µg/m^3) and homes (21.9 µg/m^3) haven't exceeded the limit value of 40 µg/m^3 established by the Directive 2008/50/EC. However, the PM10 levels were not able to accomplish the WHO guideline of 20 µg/m^3, indicating that Lisbon needs to adopt an increasingly more stringent set of standards and track progress through monitoring of emission reductions and air quality.

The average PM10 concentrations measured during the weekdays in schools and homes were 65.4 µg/m^3 and 18.2 µg/m^3, respectively. The outdoor concentrations were lower when compared with the schools levels (31.7 µg/m^3) and higher in case of the homes (22.5 µg/m^3).

It was not possible to observe significant differences between the PM10 concentrations measured in homes during the weekday (18.2 µg/m^3) and weekend (18.3 µg/m^3). However, results showed increased outdoor PM10 concentrations during the week.

The results obtained in our study were lower than those found in London for houses (PM2.5 = 23 µg/m^3 and PM10 = 50 µg/m^3), but higher for PM2.5 measured in schools (PM2.5 = 27 µg/m^3 and PM10 = 70 µg/m^3) (Wheeler et al, 2000). This study also registered large differences between these two MEs. Langer et al. (2016) measured PM2.5 and PM10 concentrations in 567 French dwellings, and reported higher levels than the ones measured in Lisbon both for PM2.5 (16 µg/m^3) and PM10 (26 µg/m^3). In a review paper from Morawska et al. (2013) also higher results were reported for homes (PM2.5 = 18 µg/m^3 and PM10= 35 µg/m^3). Canha et al. (2016) measured the IAQ in 17 schools/51 classrooms from France and registered lower PM2.5 values (22±8 µg/m^3).

Figure 5 and Figure 6 present the PM2.5 and PM10 concentrations discriminated by home and school. The lowest PM2.5 average concentration was measure in home H2 (4.6 µg/m^3) located in the residential area of Parque das Nações and the highest PM2.5 concentrations (68.0 µg/m^3) was registered in home H22, which is occupied by a smoker.

The 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 the schools SA (28.7 µg/m^3), SC (52 µg/m^3) and SD (52.9 µg/m^3) (representing 60% of the schools) exceeded the PM2.5 limit value established by the Portuguese legislation for IAQ.

The PM2.5 concentrations measured outside the homes H6 (33.4 µg/m^3) and H24 (49.1 µg/m^3) and outside the schools SA (25.9 µg/m^3) and SC (31.3 µg/m^3) exceeded the EU limit value for PM2.5.

The lowest PM10 average concentrations were measure in home H2 (9.9 µg/m^3) and H29 (9.1 µg/m^3), both located in residential areas from Lisbon with low traffic intensity. The highest average concentration (72.9 µg/m^3) was registered in home H22, whose one of the residents smoked in the living room during the measurements. To aggravate the situation the measurements were made during a week with rain that did not allow the opening of the windows. The influence of cigarette smoke on PM2.5 and PM10 in the indoor of homes was studied before. 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 et al. (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.

The PM10 concentrations measured in houses H12 (40.5 µg/m^3) and H22 (72.9 µg/m^3) (representing 5% of the homes) and in schools SB (51.6 µg/m^3), SC (95, 6 µg/m^3) and SD (109 µg/m^3) (representing 60% of the schools) were higher than the limit value established by the Portuguese legislation for IAQ.

PM10 concentrations measured outside the homes H6 (43 µg/m^3) and H24 (62.5 µg/m^3) and outside the school SC (47.2 µg/m^3) presented values above the PM10 limit value established by the EU.

The PM2.5 and PM10 concentrations were significantly higher in schools due to the poor ventilation conditions, activities developed by the students and to the dust resuspension caused by the children movement (Wheeler et al, 2000; Almeida et al, 2011; Canha et al, 2016).
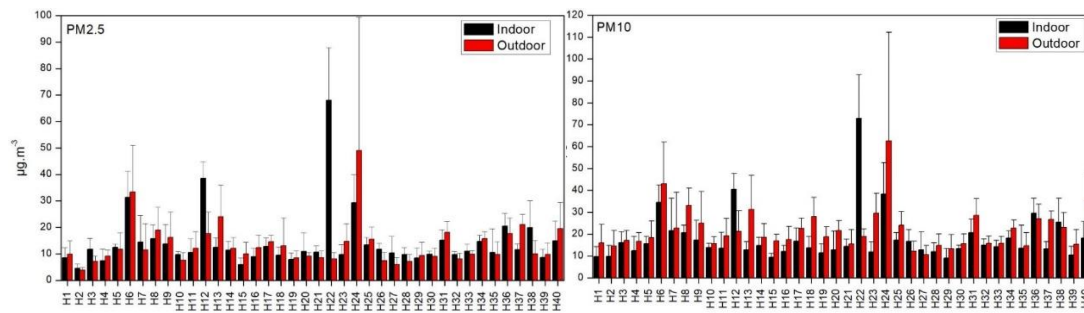
Figure 5 – PM2.5 and PM10 results in indoor and outdoor environments by houses.
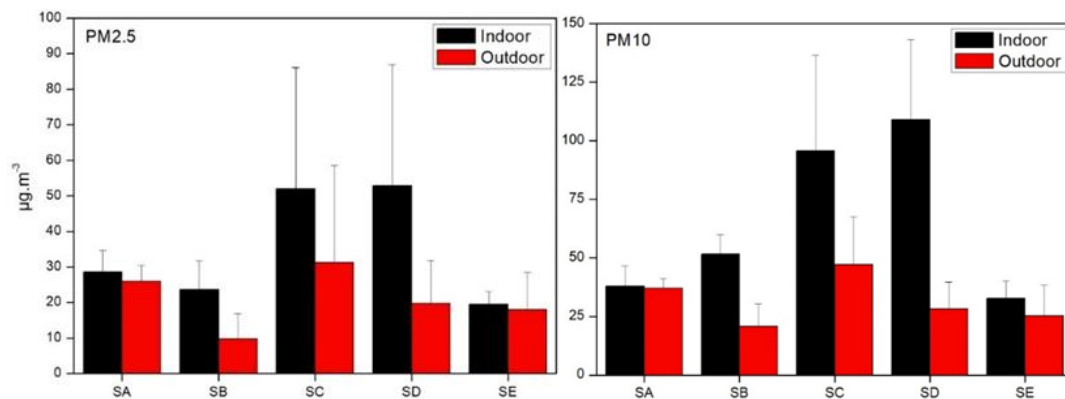
Figure 6 - PM2.5 and PM10 results in indoor and outdoor environments by schools.

In Figure 7 the PM2.5 and PM10 concentrations measured in the indoor and outdoor of the 40 houses and 5 schools are scattered throughout the city. The construction characteristics of the houses, the distance to important traffic emissions, the existence of green spaces, among others, vary from parish to parish, affecting the indoor and outdoor PM concentrations over the city. Results showed that in the parishes of Parque das Nações and Olivais (upper right corner of the graph) and in the parish of Lumiar (left side of the airport) the outdoor and indoor PM levels were below the WHO guidelines. The House H11 (located in the northernmost point in the Figure 7) was the only one in this parish with values of PM2.5 in the outdoor between 10 - 25 µg/m^3 that may be related to the proximity to the Vasco da Gama Bridge. The parishes previously described are the most recent ones in Lisbon, having recent buildings, and ample and green spaces. They also have less traffic than the city center.

In the city center, PM10 and PM2.5 concentrations increased considerably, especially the PM2.5 levels. Results showed that homes located near busy or narrow streets, where the emissions are higher and the dispersion conditions are lower, presented the highest levels of PM. A study from Massey et al. (2012) in North-Central India also registered higher PM concentrations homes near the roads with more traffic. The study reported PM10 and PM2.5 indoor concentrations of 247 ± 71 µg/m^3 and 161 ± 62 µg/m^3, respectively in roadside houses, and 181 ± 84 and 109 ± 48 in urban houses.
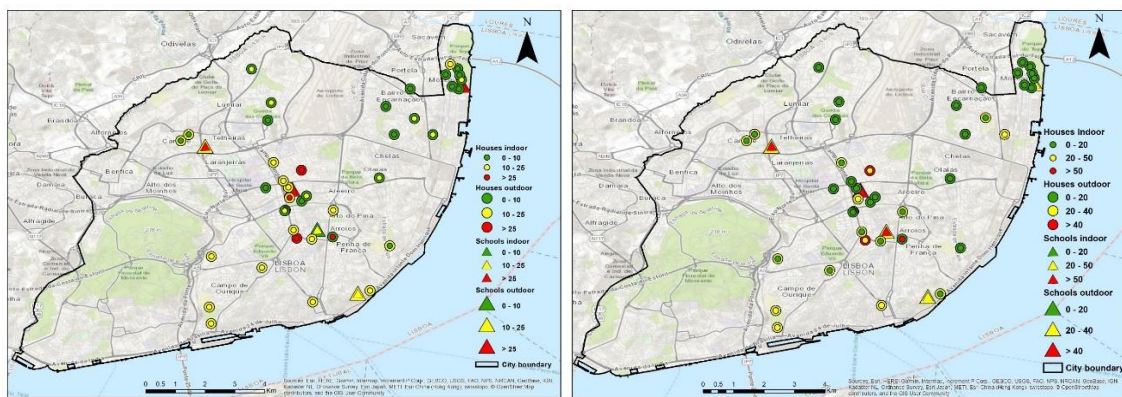
Figure 7 - PM2.5 and PM10 results in indoor and outdoor environments in houses and schools.
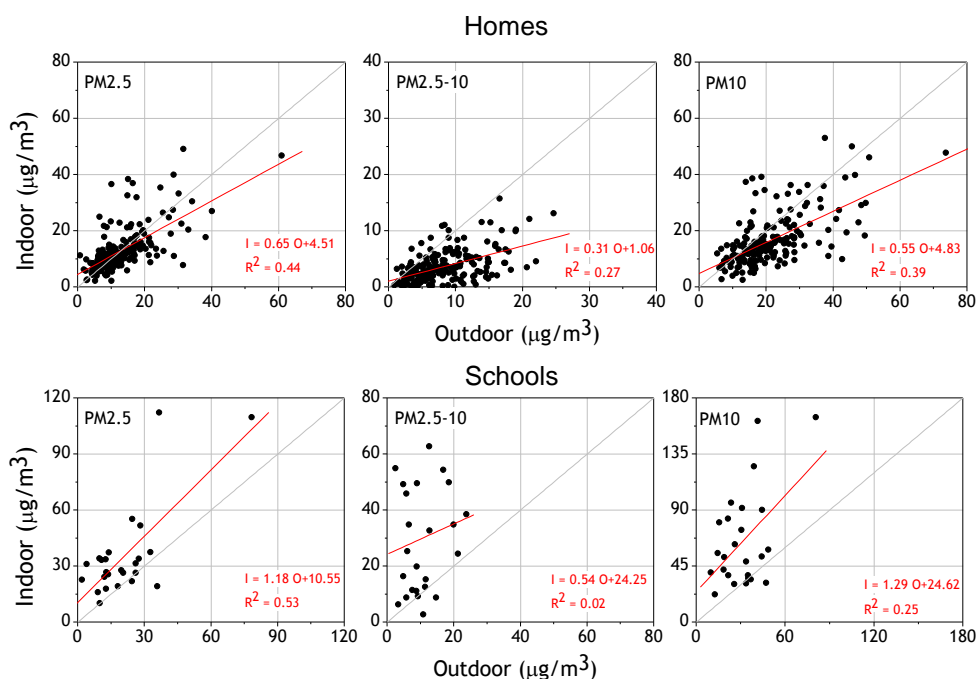
Figure 8 - Relation between the indoor and outdoor PM concentrations measured in homes and schools.

In the homes the PM2.5/PM10 ratios were always higher in indoor (0.77) than outdoor (0.61). The PM inside the homes is mainly allocated to the fine fraction (Figure 8). Similar outdoor PM2.5/PM10 ratio was observed among homes and schools. Statistical analysis showed significant similarities between PM2.5 and PM2.5–10 concentrations measured inside the schools ($p = 0.55$), representing on average a PM2.5/PM10 ratio around 0.5. The ratios both in homes and schools are within the WHO's normal range of 0.5-0.8 for developed countries. Moreover, the lower indoor PM2.5/PM10 ratio in schools was presumably a consequence of the increase in the contribution of coarse fraction, i.e. from their resuspension and generation due to the movement and different activities of the children in the classroom. The high I/O ratio for PM2.5 and PM10 mainly obtained in the schools suggests that a substantial fraction of both fine and coarse particles was generated by indoor sources, i.e. associated to the dust resuspension and generation of particles due to children activities.

CONCLUSIONS

Measurements of PM10 and PM2.5 for indoor and outdoor in 40 homes and 5 schools were successfully achieved. A quality assurance and quality control was done prior to the study to test samplers and the new sampling heads where good correlations were obtained (R2 = 0.86 - 0.96).

The results found for PM2.5 and PM10 show much higher values inside the schools, and above the legislated, in relation to the indoor of the houses. The weekends have the same values as the week in the indoor of houses, while the outdoor has lower values.

Some homes have indoor values higher than outdoor ones, which may be related to indoor sources. The house with higher indoor values in this study (H22) belonged to the only smoker in the study who smoked inside the room and kitchen.

It was possible to observe a pattern along the city, and the measurements in the more recent parishes, presented better results than the older parishes and especially than the center of the city, where the traffic is bigger and the houses are old. It was not possible to have houses in all the parishes of the city. The values of outdoor that exceeded the legislation, were found in streets with continuous traffic and with little dispersion of pollutants.

In most of the houses, the indoor concentrations follow the concentrations found in the outdoor. In the five schools, through the mass analysis, it was not possible to relate the values of outdoor with the environment where the school was located and with values of houses in its surroundings, which leads to wanting that is related to the activities in the school.

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5. CHEMICAL CARACTERIZATION OF PM SAMPLED IN HOUSES AND SCHOOLS FROM LISBON

INTRODUCTION

Ambient and indoor PM are comprised from a number of different chemical species, including carbonaceous particles (mainly in the form of organic compounds and elemental carbon), ionic species and major and trace elements (Diapouli et al., 2017). The detailed chemical composition of atmospheric PM may provide insight into their emission sources and formation mechanisms. PM components are generally grouped into the following source categories: (i) Organic matter and (ii) Elemental carbon, both categories associated with combustion activities, and particularly traffic, in the case of urban environments; (iii) Secondary inorganic aerosol, including mainly ammonium sulphate and nitrate; (iv) Sea salt aerosol, including mainly sodium (Na) and chloride (Cl); (v) Mineral dust, including all soil related elements; and (vi) Trace elements, which are associated with anthropogenic activities, such as industrial emissions (Amato et al., 2016). Detailed PM chemical composition data may be further used for the application of more sophisticated source apportionment techniques, such the Positive Matrix Factorization (PMF) technique, applied also in the framework of the LIFE Index-Air project.

While consistent associations between outdoor particulate air pollution and various health endpoints (mainly related to cardiovascular and respiratory diseases) have been reported by epidemiological studies (Samoli et al., 2013), the mechanisms through which PM affect the human organism have not been fully explained; nevertheless, it has been recognised that particle size and chemical composition play a crucial role. Recent review studies on the impact of PM exposure underline the need to identify the specific particle components which are linked to adverse health effects, in order to better understand exposure paths and mechanisms and develop more effective, targeted control strategies for the protection of public health (Guarnieri & Balmes, 2014; Wyzga &d Rohr, 2015). A number of studies have identified possible health-related components (such as transition metals, carbonaceous species, inorganic secondary aerosols) (Beelen et al. 2015). Still, a better understanding is needed regarding which PM components / sources are the most harmful for health.

Recognising the significant value of acquiring detailed PM chemical composition data, both for source identification and health impact assessment, the LIFE Index-Air project has performed a comprehensive characterisation of the ambient and indoor aerosol in Lisbon. For this reason, the PM samples collected at indoor and outdoor locations in homes and schools across the city of Lisbon, have been analysed for major PM components, thus creating a PM10 and PM2.5 chemical composition database, characteristic of the main exposure micro-environments for the population subgroup of children.

METHODOLOGY

All PM2.5-10 Nuclepore and PM2.5 PTFE samples were analysed by X-Ray Fluorescence (XRF) for 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. XRF is a non-destructive technique. Analysis was performed by the use of an Energy Dispersive X-ray spectrometer (ED-XRF) Laboratory Instrument (Epsilon 5, PANalytical, the Netherlands) (Manousakas et al., 2017). The instrument was calibrated for aerosol filters by means of 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 elements measured are provided in Table 2.

A subgroup of 20 PM2.5-10 Nuclepore and PM2.5 PTFE samples (including both indoor and outdoor locations) were also analysed by Electrothermal Atomic Absorption Spectroscopy (ET-AAS), for two heavy metals (As and Cd). These two metals are among the four heavy metals for which there are legislated limit values in EU (As, Ni, Cd and Pb). The additional analysis by AAS was decided in order to assess the levels of Cd in indoor and outdoor environments in Lisbon. As was also measured in these filters, since ET-AAS may achieve lower detection limits for this metal, in comparison to XRF. ET-AAS analysis was performed by a Varian 220 spectrometer equipped with a GTA 110 graphite furnace and a Varian auto sampler. Extraction of total metal content from the filters was accomplished through microwave digestion with 2 ml of concentrated HNO_3 65% and 1 ml of HF 40%. The analytical data were validated using the NIST 1 648 Standard Reference Material (Air particulate on filter media). The analytical uuncertainty was below 10%. The detection limit for As and Cd was 0.04 and 0.007 ng/cm^3, respectively. Details on the analytical procedure by ET-AAS are provided in Vasilatou et al. (2017).

All PM2.5-10 and PM2.5 Quartz samples were analysed by the Thermo-Optical Transmittance method (TOT) for the determination of the organic (OC) and elemental carbon (EC) in PM10 and PM2.5 (Popovicheva et., 2019). A punch of 1x1.5 cm was cut from all Quartz samples for the analysis. The TOT analysis was performed by the use of the Lab OC-EC Aerosol Analyzer (Sunset Laboratory, Inc.) and the EUSAAR2 protocol, following the QA/QC procedures described in EN 16909: 2017. The limit of detection was 0.02 $\mu g/m^3$. The analytical uncertainty was in the range 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.

Table 2– Detection limits (in ng/m^3) for all elements measured by XRF.

Element	Detection limit (ng/m^3)	Element	Detection limit (ng/m^3)
Na	10.3	Mn	0.6
Mg	3.1	Fe	0.6
Al	5.1	Ni	0.4
Si	10.3	Cu	0.2
S	1.6	Zn	0.6
Cl	0.6	As	0.8
K	0.4	Br	1.0
Ca	1.2	Sr	0.8
Ti	0.6	Ba	2.1
V	0.4	Pb	0.6
Cr	0.2		

A subgroup of 3000 PM2.5-10 and PM2.5 Quartz samples, including 5 schools and 10 homes, were also analysed by Gas Chromatography – Mass Spectrometry (GC-MS) for the determination of Polyaromatic Hydrocarbons (PAHs), following ISO 12884: 2000. Agilent Technologies 7890A GC System, 5975 C inertXL EI/CI MS Detector, provided with 7683B auto sampler, was used for the analysis (Pateraki et al., 2019). In total, 25 PAHs were determined, including

benzo[a]pyrene (B[a]P), which is among the PM components for which there are legislated limit values in EU.

A schematic representation of the use of PM samples for the different analyses performed is provided in Figure 9. A detailed description of the analytical methods applied is included in Deliverable A2.1 – Technical guide (submitted in January 2017).
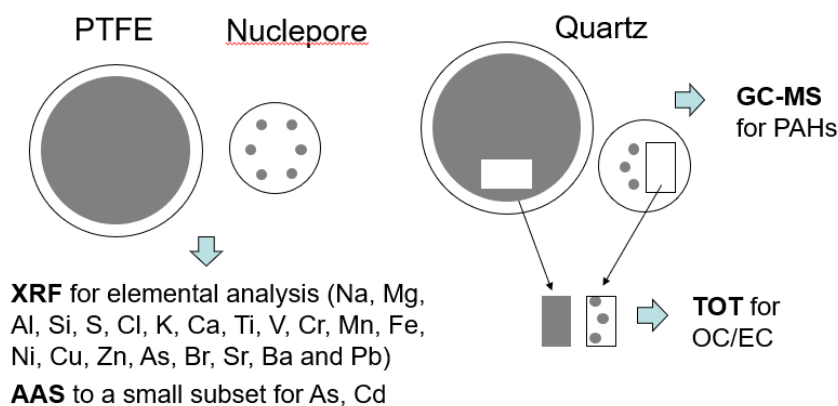
Figure 9 - Analysis of the PM2.5-10 (25-mm filters) and the PM2.5 (47-mm filters) samples by different techniques.

RESULTS

CARBONACEOUS COMPONENTS

Table 3 presents the OC and EC concentrations found in PM2.5 and PM10 in indoor and outdoor locations, at homes and schools. The ambient OC and EC levels were within the levels reported for urban background sites in other Southern European cities (Amato et al., 2016). The carbonaceous particle concentrations were higher at the school sites, probably due to the measurement period at these sites. Sampling at schools was conducted during the busy working hours (usually 9 am – 6 pm), while, the corresponding measurement period at homes, during most of the days, was 6 pm – 9 am. Outdoor carbonaceous aerosol was mostly found in the fine particle fraction; the PM2.5/PM10 concentration ratio was calculated equal to 0.78 ± 0.05 and 0.97 ± 0.02, for OC and EC, respectively. A moderate to good correlation was observed between ambient OC and EC levels for both size fractions (Figure 10). The presence of a non-negligible intercept in the linear regression equation suggests that there were other, non-combustion related, sources of OC, such as biogenic OC and secondary organic aerosol. The OC/EC concentration ratio was calculated equal to 4.1 ± 2.3 for PM10 and 3.3 ± 2.0 for PM2.5. These values of the ratio are typical of urban environments (Lonati et al., 2007).

Table 3 – OC and EC concentrations (in µg/m^3) measured in PM2.5 and PM10, in indoor and outdoor locations at homes and schools. The arithmetic mean, standard deviation, minimum and maximum values are provided.

			PM2.5		PM10	
			OC	EC	OC	EC
Homes	Indoor	Mean	6.1	1.0	7.4	1.10
		St. Dev.	6.6	0.9	6.8	0.9
		Min	1.2	0.1	1.5	0.1
		Max	54.4	5.2	56.0	5.3
	Outdoor	Mean	3.0	1.2	3.7	1.3
		St. Dev.	2.3	1.2	2.6	1.3
		Min	0.6	0.2	0.8	0.2
		Max	17.4	6.1	19.6	6.3
Schools	Indoor	Mean	12.6	1.3	20.9	1.7
		St. Dev.	9.6	0.8	11.4	0.9
		Min	7.0	0.4	10.6	0.4
		Max	56.5	3.2	68.1	3.8
	Outdoor	Mean	5.1	1.3	6.7	1.4
		St. Dev.	2.6	0.8	3.2	0.9
		Min	2.7	0.3	3.6	0.3
		Max	15.6	3.7	20.3	3.9
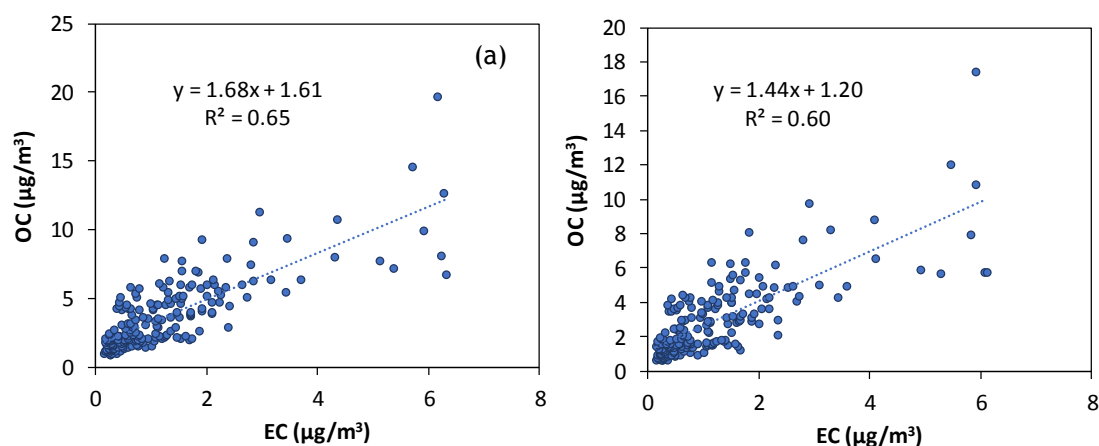
Figure 10 - Correlation analysis between ambient OC and EC for the PM10 (a) and PM2.5 (b) size fractions.

Indoor organic carbon (OC) concentrations were generally higher than the respective outdoor ones. One home (HX19) displayed very high indoor OC concentrations, resulting to indoor-to-outdoor (I/O) ratios of 24.5 ± 8.5 for PM2.5 and 19.6 ± 6.7 for PM10. These very high I/O ratios point towards a significant indoor source, also related to fine particle generation, such as some form of combustion activity. For the remaining homes, the I/O ratios for OC in PM2.5 and PM10 were found equal to 2.2 ± 1.8 and 2.2 ± 1.5, respectively. The corresponding ratios for schools were 2.7 ± 1.8 for PM2.5 and 3.4 ± 1.8 for PM10. The calculated I/O ratios for homes and schools suggest that indoor activities/conditions (such as cooking and presence of people) lead to OC generation. The condensation of semi-volatile organic compounds during the ambient air infiltration indoors and the formation of secondary organic aerosol indoors may also contribute to these higher than 1.0 I/O ratios (Amato et al., 2014; Waring et al., 2011). The slightly higher I/O ratios for PM10 in schools may be explained by a significant contribution from resuspension indoors, due to the presence and mobility of a high number of children. Very similar results are reported by Custodio et al. (2014) for residences in Aveiro and São João da Madeira, in northwestern Portugal and by Pegas et al. (2012) for schools in Aveiro, Portugal. Slightly lower

I/O ratios in comparison to our study (1.0 – 1.5, on average) have been reported for residences in Athens, Greece (Assimakopoulos et al., 2018; Saraga et al., 2015; Seleventi et al., 2012).

Elemental carbon (EC) concentrations indoors were generally very close to the outdoor ones, in both homes and schools. The calculated I/O ratios were 0.9 ± 0.3 for both PM2.5 and PM10 at homes and 1.0 ± 0.2 for PM2.5 and 1.3 ± 0.3 for PM10 at schools. Very similar I/O ratios have been reported for schools by Pegas et al. (2012) and for homes by Custodio et al. (2014). The results indicate that EC in indoor microenvironments is mainly of ambient origin (Assimakopoulos et al., 2018; 2014; Diapouli et al., 2010).

It is interesting to note that indoor aerosol at homes was significantly enriched in carbonaceous components. Total carbon (TC), that is the sum of OC and EC, constituted on average 0.50 ± 0.12 of PM10 and 0.54 ± 0.15 of PM2.5 indoors and only 0.23 ± 0.08 of PM10 and 0.34 ± 0.12 of PM2.5 outdoors. Apart from the presence of indoor carbon-emitting sources (such as combustion processes), this result may be also related to the fine size distribution of carbonaceous particles, which leads to their very effective infiltration indoors. Coarser PM components (such as soil dust) may not enter that effectively, due to their larger size. This enrichment of indoor PM with carbonaceous aerosol was not apparent at schools, where the presence and intense movement of children in and out of classes caused the intrusion of soil dust and the resuspension of coarse particles indoors. This is further supported by the PM2.5/PM10 ratios found for EC and OC concentrations indoors and outdoors. At homes, these ratios were very similar indoors and outdoors, supporting the fine nature of carbonaceous aerosol. At schools, the indoor PM2.5/PM10 ratios were much lower (0.59 ± 0.06 and 0.79 ± 0.10, for OC and EC, respectively), pointing towards a significant contribution from coarse particles, especially in the case of OC (such as skin flakes, clothes fibers etc) (Amato et al., 2014).

A very good correlation was observed between indoor and outdoor EC concentrations at both micro-environments (Figure 11 and Figure 12); PM10 and PM2.5 data followed the same patters. The high correlation coefficients (R^2 = 0.79 for both size fractions and both micro-environments) and the low values of the intercepts of the respective linear regression equations, fully agree with the ambient origin of EC in indoor microenvironments, as commented also above. OC indoor concentrations were moderately correlated with the outdoor concentrations, suggesting that both indoor and outdoor sources affect indoor levels. Houses HX9, HX19 and HX21 displayed very different indoor-outdoor relationships, pointing towards one or more indoors sources with significant impact on indoor OC concentration levels. This/these sources do not seem to affect the EC levels though, which seem to be mainly of ambient origin in these homes as well. At schools, indoor and outdoor OC concentrations were not correlated, demonstrating the effect of children's and teaching activities on the indoor levels (Pegas et al., 2012).
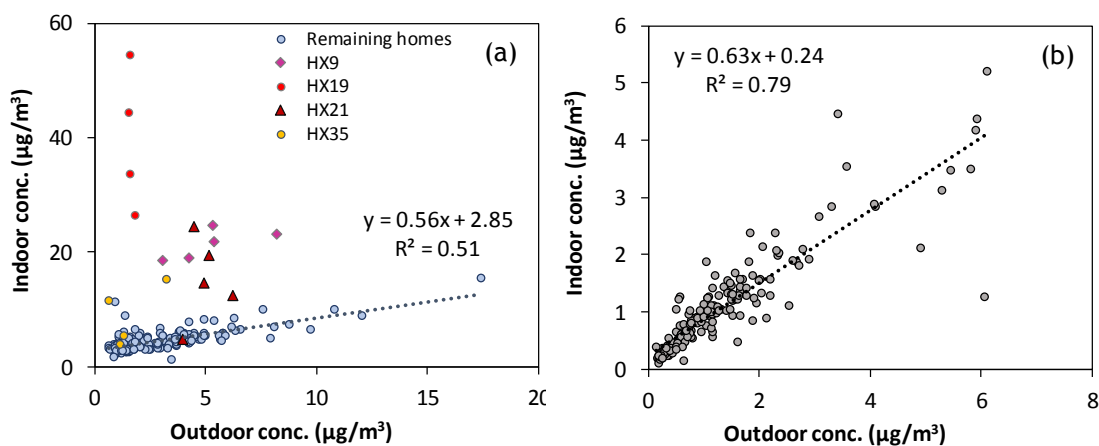
Figure 11 - Correlation analysis between indoor and outdoor concentrations of (a) OC and (b) EC in PM2.5 at homes.
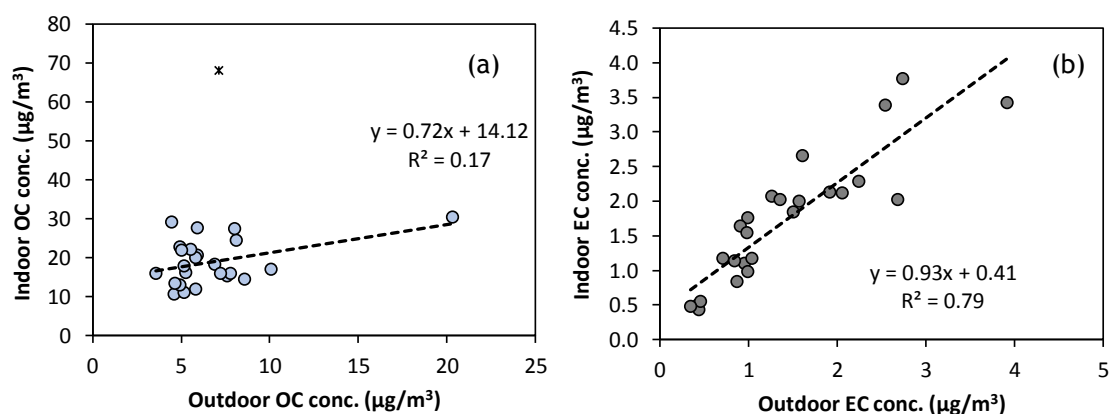
Figure 12 - Correlation analysis between indoor and outdoor concentrations of (a) OC and (b) EC in PM10 at schools.

MAJOR AND TRACE ELEMENTS

The measured concentrations of major and trace elements inside and outside homes and schools are provided in Figure 13 - Figure 14 and Figure 15 - Figure 16, respectively. Arsenic (As) concentrations were always below the detection limit of the XRF method. The As and Cd concentrations reported in Figure 13 - Figure 14 were obtained by AAS and correspond to 20 samples from home indoor and outdoor locations. In Figure 15 - Figure 16, the As concentrations reported correspond to ½ of the detection limit of the XRF method, since all the measurements were below the detection limit. This value is similar to the concentrations measured by ASS both indoors and outdoors.
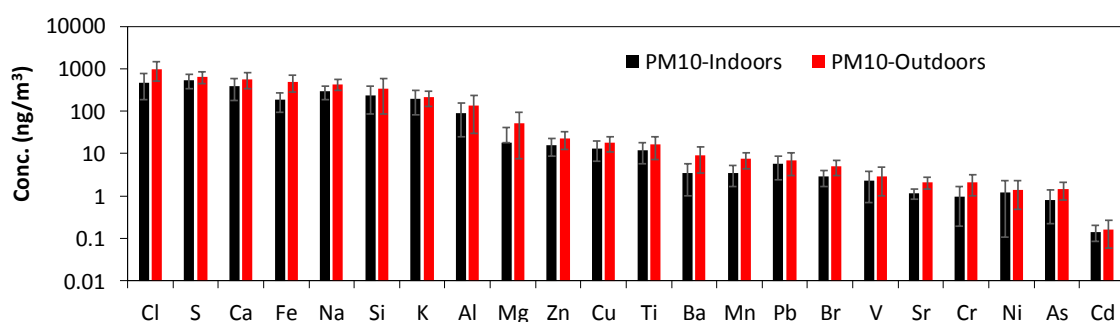
Figure 13 - Mean concentrations (± Standard Deviation) of major and trace elements in PM10, inside and outside homes.
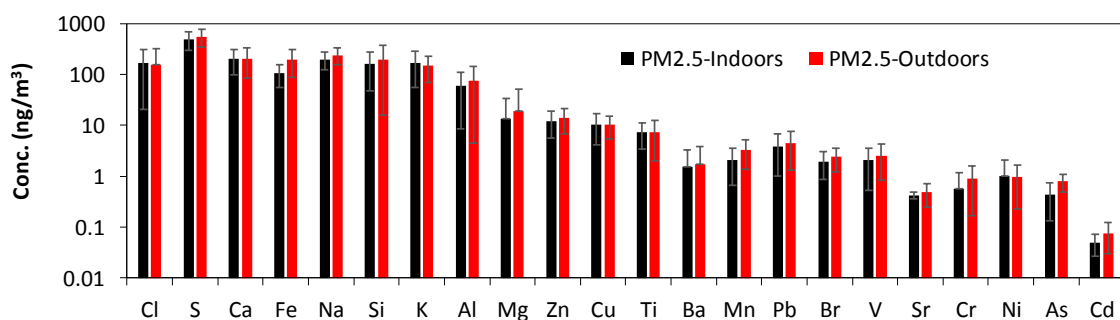
Figure 14 - Mean concentrations (± Standard Deviation) of major and trace elements in PM2.5, inside and outside homes.

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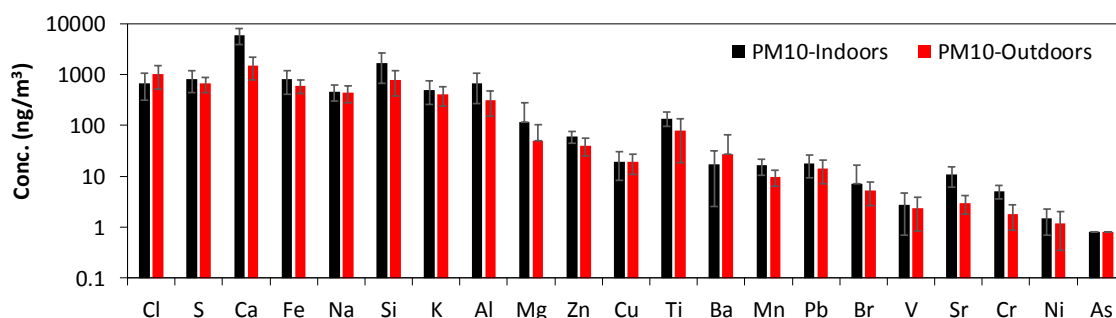
Figure 15 - Mean concentrations (± Standard Deviation) of major and trace elements in PM10, inside and outside schools.
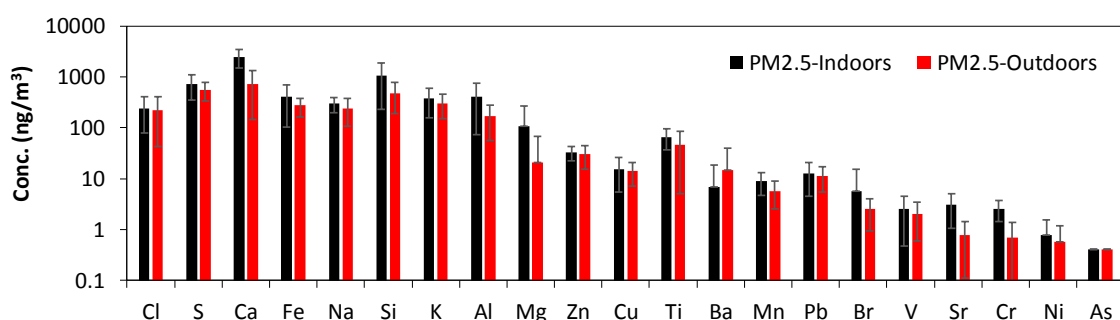
Figure 16 - Mean concentrations (± Standard Deviation) of major and trace elements in PM2.5, inside and outside schools.

The average concentrations in PM10 of the four heavy metals for which there are legislated limit values in EU, along with the respective limit values for the ambient atmosphere, are presented in Table 4. The mean outdoor concentrations were calculated by both home and school samples. The levels of all heavy metals, both indoors and outdoors, were much lower than the ambient annual limit values set by EU. The higher Pb concentrations inside schools (which are still much lower than the Pb limit value) are related to higher ambient levels at the school locations; the outdoor concentrations of Pb at schools were found equal to 14.1 ± 13.7 ng/m^3, while at homes they were 6.8 ± 7.5 ng/m^3.

Table 4 – Mean concentrations (in ng/m^3) of heavy metals in PM10, at indoor and outdoor locations in Lisbon. The respective annual limit values set by EU for the ambient atmosphere are also reported (in ng/m^3).

	Annual limit value	Outdoors	Indoors-Homes	Indoors-Schools
As [1]	6	1.4	0.8	< 0.8
Cd [1]	5	0.2	0.1	na [3]
Ni [1]	20	1.4	1.2	1.5
Pb [2]	500	7.7	5.6	17.6

[1] Directive 2004/107/EC   [2] Directive 2008/50/EC   [3] not available

The main elements contributing to PM mass outdoors were Cl, S, Ca, Fe, Na, Si K and Al. Na and Cl are related to sea salt aerosol. S is mainly found in aerosol in the form of SO_4^{2-} and is produced through the conversion of gaseous SO_2 to particulate sulphate salts. The remaining elements are major components of soil dust, while K is also related to biomass burning. The ambient concentrations of soil and road dust related elements (such as Ca, Ti, Si, Al, and Ba

and Pb, respectively) were elevated at the school sites in comparison to homes. This could be indicative of higher contribution from road traffic at the areas where the schools are located.

A number of anthropogenic elements, such as S, V, Cu, Zn, Pb and As, displayed PM2.5/PM10 concentration ratios outdoors above 0.6, suggesting that these aerosol components are mainly found in the fine size fractions (Figure 17). K also displayed high PM2.5/PM10 ratio, indicating an impact from biomass burning to the measured K levels (since soil-related K is mainly found in the coarse mode). The PM2.5/PM10 ratios were in generally higher indoors, especially in the case of PM components found mainly in the coarse size fraction, pointing towards an enrichment of indoor aerosol with smaller particles, due to their more effective penetration indoors. This result has significant implications for personal exposure and health impact assessment, since particles' size greatly affects their transport and deposition in the respiratory tract and lungs (Zwozdziak et al., 2017).
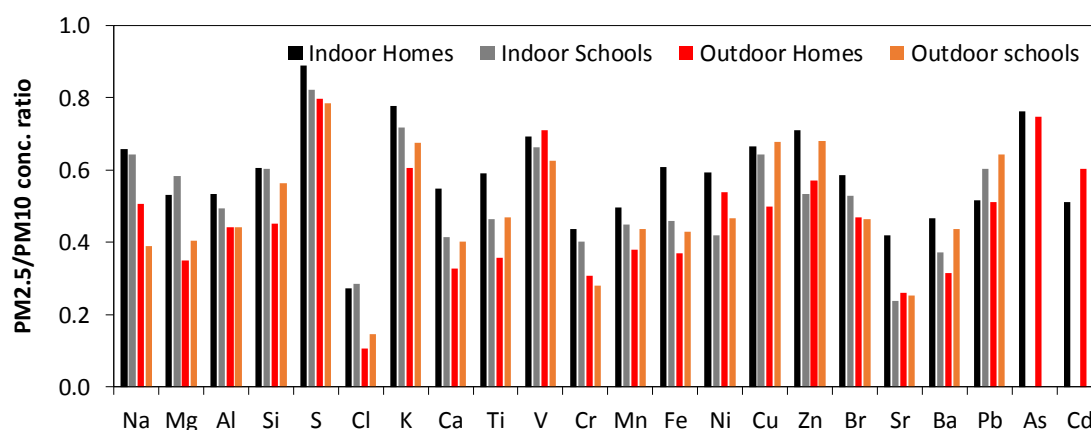
Figure 17 - Mean PM2.5/PM10 concentration ratios for major and trace elements measured in indoor and outdoor locations of homes and schools.

Indoor-to-outdoor concentration (I/O) ratios were below or close to 1.0 for all elements at the home micro-environment. At schools, a few elements (mainly of crustal origin, such as Ca, Si, Al, Mg, Ti and Sr) displayed I/O ratios much higher than 1.0, reaching up to 5.0. This may be attributed to the resuspension of these PM components (included in the coarse size fraction) due to children's intense movement, as well as to the entrapment and transfer of soil dust from students entering the school buildings.

The indoor and outdoor concentrations of S were highly correlated, at both homes and schools, indicating the outdoor origin of this species as well as its efficient penetration indoors, due to its size (mostly found in the fine fraction). The regression between indoor and outdoor concentrations of Sulphur in PM2.5 is depicted in Figure 18(a). Home and school concentrations followed the same pattern, except for some days with higher I/O ratios (marked with an asterisk in the Figure), all corresponding to one school (SE). The respective regression analysis for PM10 produced again a very high correlation coefficient (R^2 = 0.92) and a slightly lower slope (0.87), in agreement with the lower penetration of PM10 in comparison to PM2.5 (Diapouli et al., 2013).

A good correlation was also observed between the indoor and outdoor K concentrations, especially at homes. The regression between indoor and outdoor concentrations of Potassium in PM10 is depicted in Figure 18(b); the respective linear regression equation for PM2.5 displayed again good correlation (R^2 = 0.71) and a slightly higher slope (0.81). The school concentrations followed a similar pattern to the home concentration; nevertheless, some school data were related to somewhat higher I/O ratios, probably due to the presence and

movement of students. Regarding the home data, home HX19 displayed again a very different indoor-outdoor relationship, with very high indoor concentrations, similar to the OC data presented above. This result further supports the presence of a significant indoor source in this house (such as smoking or use of heating appliance) (Koutrakis et al., 1992).
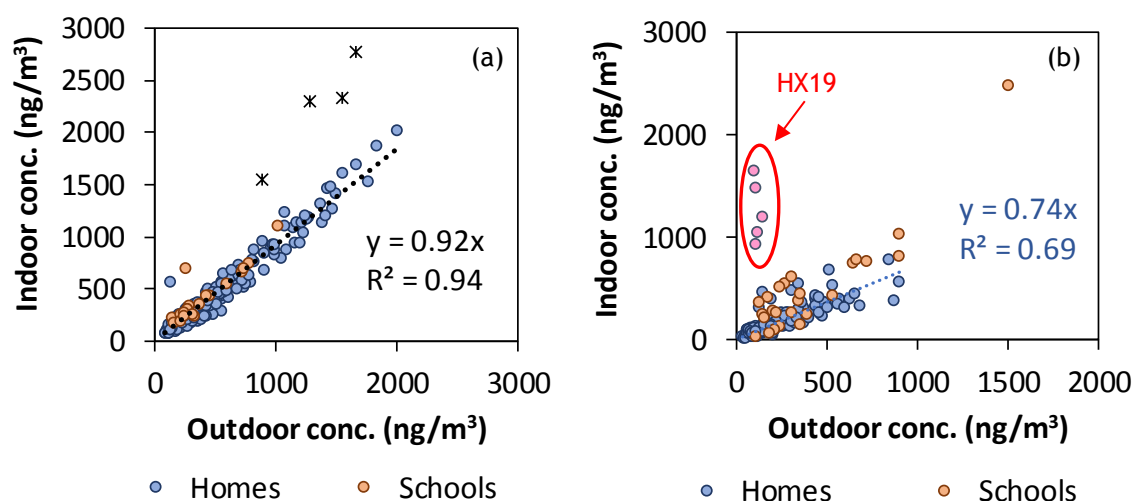
Figure 18 - Linear regression analysis between indoor and outdoor concentrations of (a) Sulphur (S) in PM2.5 and (b Potassium (K) in PM10, at homes and schools.

Moderate correlations between indoor and outdoor concentrations were observed for the sea-salt and soil-related components, probably due to their large size, which hinders their penetration inside the buildings, while favors particle deposition and subsequent resuspension indoors (especially in schools). Regarding the remaining metals of anthropogenic origin, again moderate to poor correlations were observed, which may be attributed also to their very low concentrations and the associated increased uncertainty.

POLYAROMATIC HYDROCARBONS

The mean concentrations of the 25 polyaromatic hydrocarbon (PAHs) measured in indoor and outdoor locations are presented in Table 5. The observed concentration levels were comparable to other Southern European cities and urban background sites (Alves et al., 2017; Martelliniet al., 2012; Mantis et al., 2005). Very low levels of benzo(a)pyrene (BaP) were recorded in the ambient atmosphere, being for several days below the detection limit of the method (bdl). The ambient benzo(a)pyrene (BaP) concentrations were calculated in the range bdl-0.87 ng/m³. The mean ambient concentration in PM10 (0.18 ng/m³) was much lower than 1 ng/m³, which the respective annual limit value set by EU (Directive 2004/107/EC). BaP was mainly found in the fine size fraction. Similar levels have been reported for a suburban site in Athens and an urban background site in Florence (during the warm season) (Alves et al., 2017). The relative concentrations of BaP and benzo(e)pyrene(BeP) may be an indication of the distance of the sampling site from emissions, since BaP is photodegraded faster than its isomer BeP. The BaP/(BaP+BeP) ratio was found on average equal to 0.52, suggesting impact from fresh emissions.

Indoor concentrations were always lower than the respective outdoor levels. The indoor-to-outdoor (I/O) ratios for the different PAHs were in the range 0.15 – 0.95 (mean value equal to 0.59 ±0.27). The I/O ratio for BaP was calculated equal to 0.9, demonstrating that a major fraction of ambient generated BaP is infiltrated in indoor microenvironments.

Table 5 – Mean concentrations and related standard deviations (in ng/m^3) of PAHs in PM10 and PM2.5, at indoor and outdoor locations in Lisbon.

	PM2.5		PM10	
	Indoors	Outdoors	Indoors	Outdoors
naphthalene	0.11	0.15	0.38	0.55
2-methylnaphthalene	0.25	0.31	0.49	0.61
1-methylnaphthalene	0.09	0.13	0.25	0.31
acenaphthylene	0.01	0.01	0.01	0.02
1,2-dimethylnaphthalene	0.02	0.03	0.04	0.05
2,6- dimethylnaphthalene	0.00	0.00	0.01	0.01
acenaphthene	0.01	0.05	0.02	0.08
2,3,5- trimethylnaphthalene	0.01	0.01	0.01	0.02
fluorene	0.01	0.07	0.02	0.13
phenanthrene	0.18	0.38	0.28	0.53
1-methylphenanthrene	0.02	0.03	0.03	0.05
3,6 -dimethyl phenanthrene	0.01	0.02	0.02	0.02
anthracene	0.01	0.02	0.01	0.03
fluoranthrene	0.10	0.30	0.11	0.32
pyrene	0.12	0.26	0.13	0.28
benz(a)anthracene	0.08	0.13	0.08	0.13
chrysene	0.13	0.25	0.14	0.26
benzo(b)fluoranthene	0.16	0.21	0.16	0.22
benzo(k)fluoranthene	0.15	0.21	0.15	0.22
benzo(e)pyrene	0.12	0.16	0.12	0.16
benzo(a)pyrene	0.15	0.18	0.15	0.18
perylene	0.02	0.03	0.02	0.03
indeno(1,2,3-c,d)pyrene	0.16	0.20	0.16	0.21
dibenzo(a,h)anthracene	0.02	0.02	0.02	0.02
benzo(ghi)perylene	0.19	0.24	0.19	0.25

CONCLUSIONS

The PM2.5-10 and PM10 samples collected in indoor and outdoor sites in Lisbon have been analysed for carbonaceous components, major and trace elements and polyaromatic hydrocarbons.

The ambient OC and EC levels were within the levels reported for urban background sites in other Southern European cities. The OC/EC concentration ratio was calculated equal to 4.1 ± 2.3 for PM10 and 3.3 ± 2.0 for PM2.5, which are typical values of urban environments. Outdoor carbonaceous aerosol was mostly found in the fine particle fraction (PM2.5/PM10 concentration ratio equal to 0.78 ± 0.05 and 0.97 ± 0.02, for OC and EC, respectively). Similar ratios were calculated for indoor home concentrations, while at schools, the indoor PM2.5/PM10 ratios were much lower (0.59 ± 0.06 and 0.79 ± 0.10, for OC and EC, respectively), pointing towards a significant contribution from coarse particles, especially in the case of OC (such as skin flakes, clothes fibers etc). Except for one home with very high indoor concentration, at the remaining homes the I/O ratios for OC in PM2.5 and PM10 were found equal to 2.2 ± 1.8 and 2.2 ± 1.5, respectively. The corresponding ratios for schools were 2.7 ± 1.8 for PM2.5 and 3.4 ± 1.8 for PM10. The calculated I/O ratios for EC were 0.9 ± 0.3 for both PM2.5 and PM10 at homes and 1.0 ± 0.2 for PM2.5 and 1.3 ± 0.3 for PM10 at schools. Indoor aerosol at homes was significantly enriched in carbonaceous components; total carbon (TC) constituted on average 0.50 ± 0.12 of PM10 and 0.54 ± 0.15 of PM2.5 indoors and only 0.23 ± 0.08 of PM10 and 0.34 ± 0.12 of PM2.5 outdoors. OC indoor concentrations were moderately correlated with the outdoor concentrations, suggesting that both indoor and outdoor sources affect indoor levels. On the

other hand, a very good correlation was observed between indoor and outdoor EC concentrations, demonstrating the ambient origin of EC in indoor microenvironments.

The main elements contributing to PM mass outdoors were Cl, S, Ca, Fe, Na, Si K and Al. The ambient concentrations of soil and road dust related elements (such as Ca, Ti, Si, Al, and Ba and Pb, respectively) were elevated at the school sites in comparison to homes. This could be indicative of higher contribution from road traffic at the areas where the schools are located. The PM10 concentrations of the four heavy metals for which there are legislated limit values in EU (As, Ni, Cd and Pb) were lower than the respective ambient annual limit values set by EU, both indoors and outdoors. The PM2.5/PM10 ratios were in generally higher indoors, especially in the case of PM components found mainly in the coarse size fraction, pointing towards an enrichment of indoor aerosol with smaller particles, due to their more effective penetration indoors. Indoor-to-outdoor concentration (I/O) ratios were below or close to 1.0 for all elements at the home micro-environment. At schools, a few elements, mainly of crustal origin, displayed I/O ratios much higher than 1.0, reaching up to 5.0. This may be attributed to the resuspension of these PM components (included in the coarse size fraction) due to children's intense movement, as well as to the entrapment and transfer of soil dust from students entering the school buildings.

The observed concentration levels of PAHs were comparable to other Southern European cities and urban background sites. The mean ambient concentration of BaP in PM10 (0.18 ng/m^3) was much lower than 1 ng/m^3, which the respective annual limit value set by EU. BaP was mainly found in the fine size fraction. Indoor concentrations of PAHs were always lower than the respective outdoor levels. The indoor-to-outdoor (I/O) ratios were in the range 0.15 – 0.95 (mean value equal to 0.59 ±0.27). The I/O ratio for BaP was calculated equal to 0.9, demonstrating that a major fraction of ambient generated BaP is infiltrated in indoor microenvironments.

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6. SOURCE APPORTIONMENT OF PM IN MICRO-ENVIRONMENTS FREQUENTED BY CHILDREN IN LISBON

INTRODUCTION

Particulate matter (PM) is a key air pollutant in terms of adverse health effects. According to the document "Air Quality in Europe – 2017 report", published by the European Environment Agency (EEA), in 2015 75% of the stations located in 27 of the 32 countries reporting PM2.5 data exceeded the World Health Organization (WHO) guideline for PM2.5 annual mean (10 µg/m^3) (EEA, 2017). The 2018 edition of the same report states that in 2015, 422000 premature deaths in Europe were attributed to PM2.5 (EEA, 2018). These numbers indicate that despite the great deal of improvement as a result of emission control strategies in European urban areas, PM2.5 is still a major problem regarding its detrimental impact on human health.

Several anthropogenic and natural sources emit PM. Particles can be released directly from primary sources or indirectly through the conversion of gaseous emissions in the atmosphere (Sienfeld and Pandis, 2006). Depending on the location, many different sources may contribute to PM levels such as traffic, dust resuspension, biomass burning, industrial emissions, power plants, sea salt, ship emissions, etc (Viana et al., 2008, Belis et al., 2013). PM sources and components also vary by the microenvironments (MEs) in which children live, learn and play. The home and school classroom are the MEs were children spend the major part of their day. Therefore, these MEs have been identified as the most relevant for the daily PM exposure.

Several source apportionment methods have been developed to identify sources of PM and their contribution to air quality: exploratory methods, emission inventories, inverse modelling, artificial neural networks, Lagrangian models, Gaussian models, Eulerian models and receptor models (Belis et al., 2014). Receptor models identify PM sources and quantify their contribution using aerosol chemical composition data at a given receptor, in contrast to source-oriented dispersion models, which account for transport, dilution, and other processes that take place between the source and the receptor site. Positive Matrix Factorization (PMF) was developed to overcome the weaknesses points of previous receptor models. It introduces a weighting scheme taking into account the uncertainties of the measurement results, which are used as point-by-point weights. Adjustment of the corresponding uncertainty estimates also allows it to handle missing and below detection limit data. Additionally, non-negative constraints are applied in order to obtain more physically explainable factors (Manousakas et al., 2015).

MATERIALS AND METHODS

PM SAMPLING AND CHEMICAL ANALYSIS

Aerosol particles were sampled in 5 schools and 40 houses, located in the city of Lisbon. Samples were collected simultaneously in the indoor and in the outdoor with Leckel MVS6 samplers. Before and after sampling filters were weighed by means of a microbalance using the procedure described in EN12341. PM mass concentrations were determined by dividing filter loads by the volume of air filtered. Afterwards, filters were analyzed by XRF (X-Ray Fluorescence) for the determination of major and trace elements and thermal-optical analysis for the measurement of elemental and organic carbon. Details about the sampling and chemical analysis were given before in this report.

SOURCE APPORTIONMENT

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

$$x_{ij} = \sum_{k=1}^{p} g_{ik} f_{ik} + e_{ij} \qquad i = 1, 2, \ldots m \quad j = 1, 2, \ldots n \qquad (1)$$

where x_{ij} is the concentration of the species j in the ith sample, g_{ik} is the contribution of the kth source in the ith sample, f_{ik} is the concentration of the species j in the source k, and e_{ij} is the uncertainty of each individual measurement result.

In this study PMF (Paatero and Tapper, 1994) was used to solve Eq. (1) and the software US EPA PMF version 5 was applied to the data sets obtained in the 16 cities. Factor contributions and profiles were derived in the PMF model by minimizing an objective function Q, without detailed prior knowledge on sources inventories (Paatero, 1999).

Prior to applying PMF, the data was screened to eliminate values that could detract the quality of the analysis. Data validation tests to identify values that appeared abnormal as compared to the overall data were performed using the scatter plot and time series analysis.

Data below the limit of quantification (LOQ) were replaced by half of the LOQ and the uncertainties were set to 5/6 of the LOQ. Missing data were replaced by the geometric mean of the measured values and their accompanying uncertainties were set as four times these geometric mean values (Polissar et al., 2001).

In order to reduce the influence of poor variables on the PMF analysis, chemical components with high noise were down-weighted based on their signal-to-noise (S/N) ratio. Species with S/N <0.5 were generally defined as bad variables and removed from the analysis, and species with 0.5<S/N<1 were generally defined as weak variables and down-weighted (increasing uncertainty by a factor of 3) (US-EPA, 2014).

Some tests were carried out to assess rotational ambiguity in the PMF solutions. The Base Model Displacement Error Method was used to explore the rotational ambiguity in the PMF final solutions. This model assesses the largest range of source profile values without an appreciable increase in the Q value. To assess the rotational ambiguity, the factor profile values are adjusted to the maximum allowable level, with the constraint that the difference between the Q values associated with the original and the modified solutions (dQ) is not greater than a predefined by the model value (dQmax). No factor swaps occurred for the smallest dQmax considered, which indicated that there was not significant rotational ambiguity and that the solution was sufficiently robust to be used (US-EPA, 2014). Additionally, to assess the stability of the solutions the Bootstrap (BS) method was used in order to assess the uncertainty that originates from random errors in the dataset and partially from rotational ambiguity. According to BS results all the factors were reproduced at a level of a least 75%, while no unmapped factors were recorded.

RESULTS AND DISCUSSION

The PMF analysis was conducted to resolve the sources and quantify their contribution to PM in homes, schools and ambient environment.

The PMF identified six source factors that contributed to PM2.5. 51% of PM2.5 was attributed to vehicles exhaust, 19% to secondary sulfates, 12% to soil, 9.9% to a Pb source, 6.3% to sea salt and 0.36% to road dust (Figure 19).
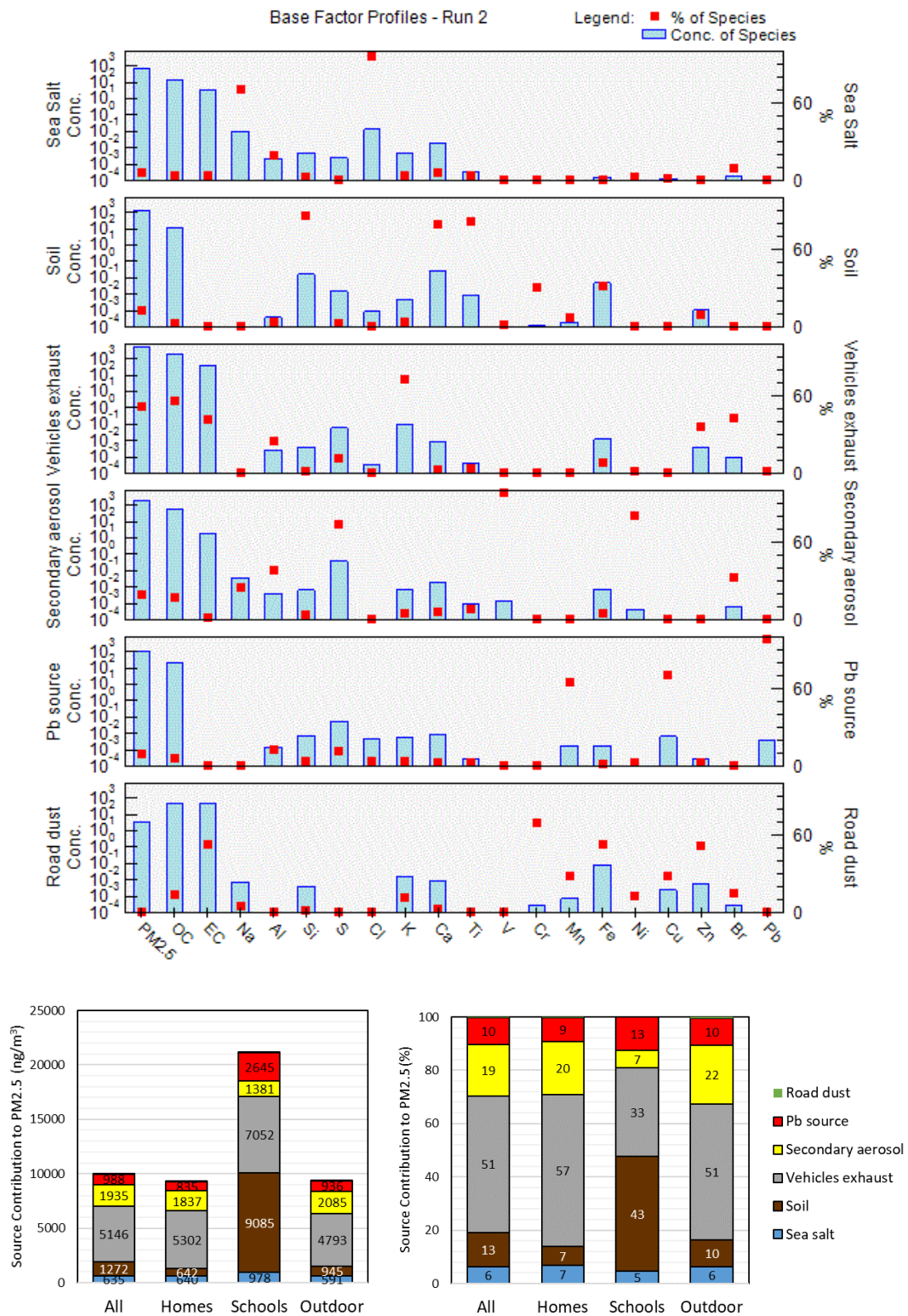
Figure 19 - Source profile and source contribution to PM2.5 sampled in homes, schools and outdoor.

PMF also identified 6 source factors for PM10. Vehicles exhaust, soil and secondary aerosols contributed on average, with 29%, 21% and 20%, respectively, while sea spray, a Pb source and road dust represented, respectively, 17%, 5.4% and 7.8% (Figure 20).
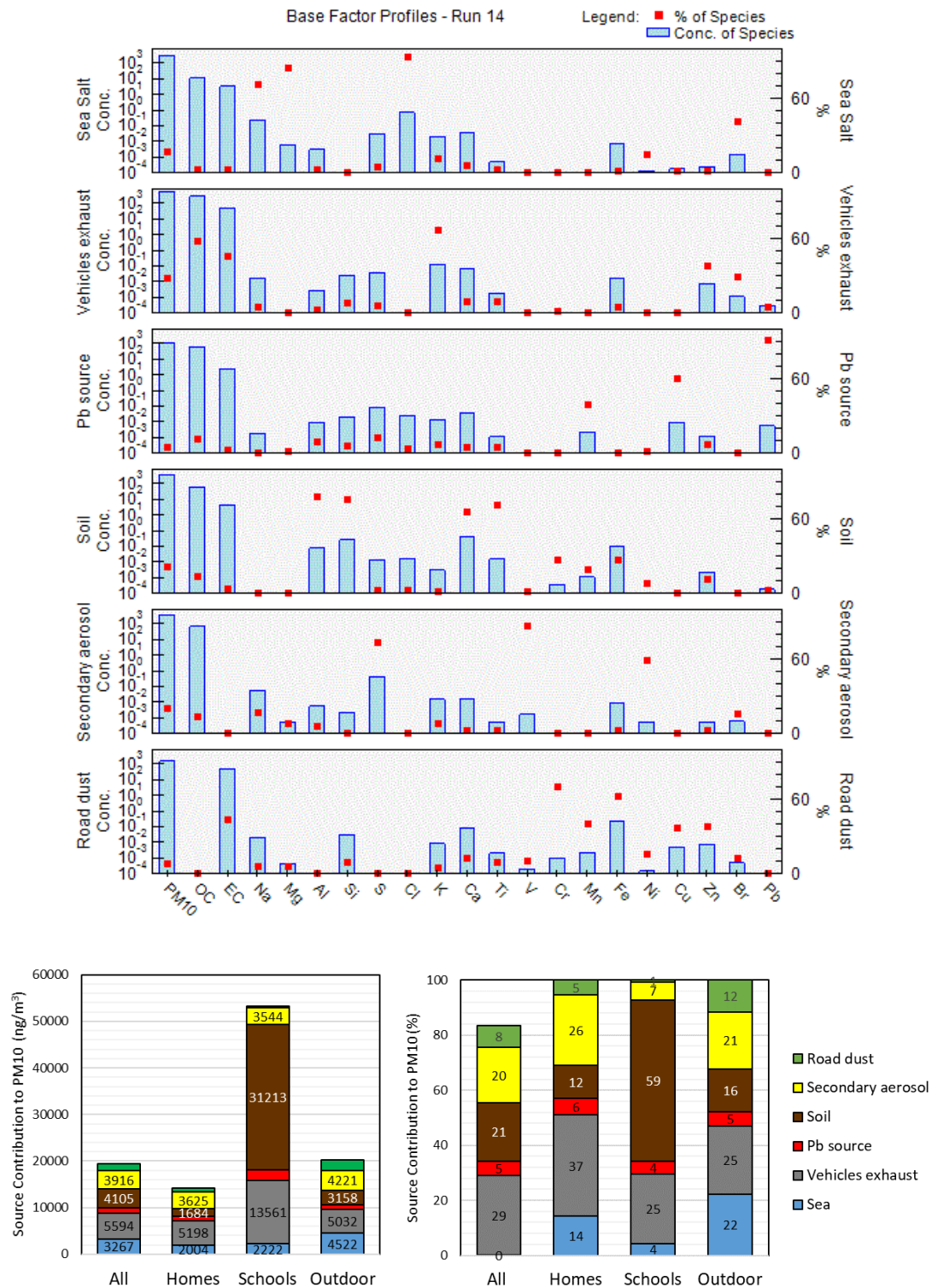
Figure 20 - Source profile and source contribution to PM10 sampled in homes, schools and outdoor.

The vehicles exhaust source was characterized by high contributions of OC, EC, K, Zn and Br both in PM2.5 and PM10. The contribution of the vehicles exhaust for PM was higher in schools than in homes and outdoor. The contribution of this source for PM2.5 was 5.3 μg/m^3 in homes, 7.1 μg/m^3 in schools and 4.8 μg/m^3 in the outdoor. For PM10, the contribution of the vehicles exhaust was 5.2 μg/m^3 in homes, 13.6 μg/m^3 in schools and 5.0 μg/m^3 in the outdoor. Figure

21 shows a good correlation between the vehicles contribution to indoor and outdoor indicating that traffic pollutants highly influence the indoor air quality.
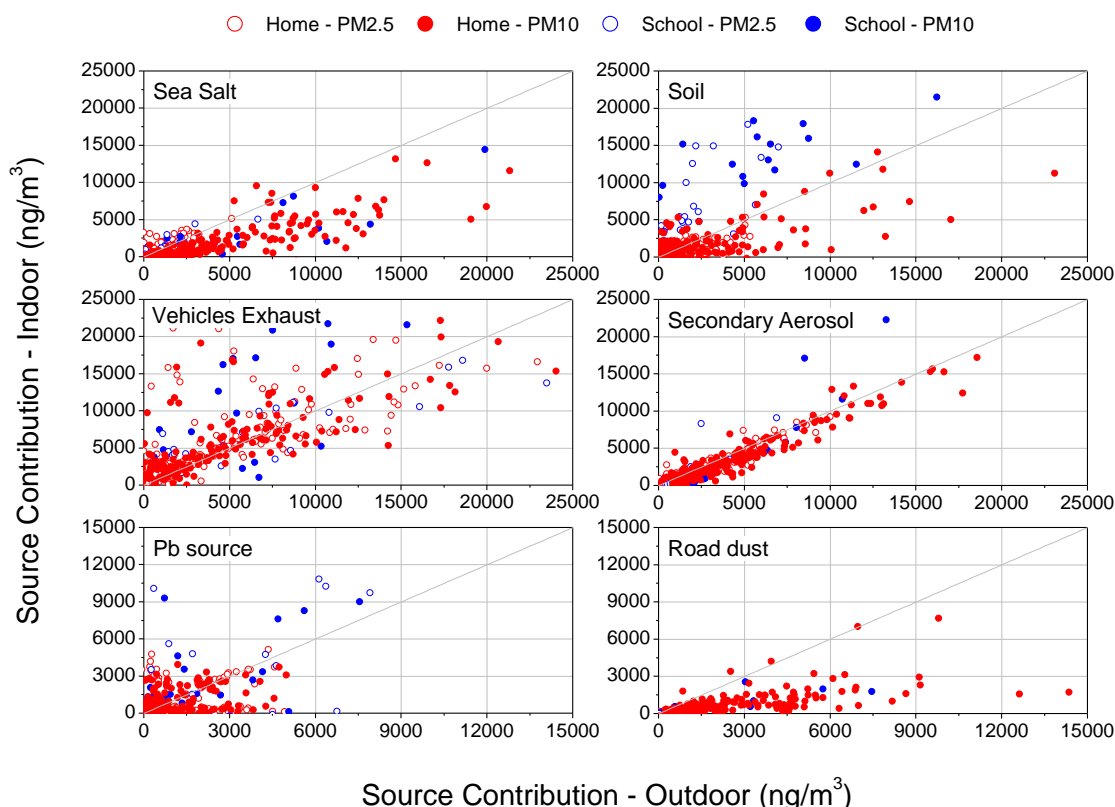
Figure 21 - Sources contribution to indoor and outdoor PM2.5 and PM10.

Figure 21 also presents a very good correlation for the contribution of the secondary aerosols to the indoor and outdoor PM, showing the importance of the outdoor sources for the indoor MEs. Ideally, the secondary sulfate factor contains only the secondary inorganic species but in this study this factor was also associated with Ni and V. Secondary aerosols are by definition not emitted directly into the atmosphere by a single source, they are usually the result of atmospheric chemical transformations of gaseous precursors derived from combustion to PM at shorter or longer timescales, often involving heterogeneous processes and therefore they share the same marker species with anthropogenic emissions on the local- and meso-scale (Viana et al., 2008). Secondary sulfates are in many cases attributed to long-range transport events and are frequently associated with "aged air masses" due to the slow oxidation of SO_2 to SO_4^{2-} (Lazaridis et al., 2006, Manousakas et al., 2017). Consequently, 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 contribution of the secondary aerosol to PM was similar for all MEs (1.8 $\mu g/m^3$ in homes, 1.4 $\mu g/m^3$ in schools and 2.1 $\mu g/m^3$ in the outdoor for PM2.5, and 3.6 $\mu g/m^3$ in homes, 3.5 $\mu g/m^3$ in schools and 4.2 $\mu g/m^3$ in the outdoor for PM10).

The soil was characterized by high contributions of Al, Si, Ca, Ti, Fe, Cr. In schools the contribution of this source was significantly higher (9.1 $\mu g/m^3$ in PM2.5 and 31.2 $\mu g/m^3$ in PM10) than in homes (0.64 $\mu g/m^3$ in PM2.5 and 0.17 $\mu g/m^3$ in PM10) and outdoor (0.95 $\mu g/m^3$ in PM2.5 and 0.32 $\mu g/m^3$ in PM10). These results are consistent with previous studies that showed the importance of the high activity of the students from the primary schools in the re-suspension of dust.

The sea factor was characterized by high contributions of Na and Cl in PM2.5 and Na, Cl, Mg and Br in PM10. The contribution of this emission source for PM2.5 was 0.64 $\mu g/m^3$ in homes, 0.98 $\mu g/m^3$ in schools and 0.59 $\mu g/m^3$ in the outdoor. For PM10 the sea contribution was higher in the outdoor (4.5 $\mu g/m^3$) than in homes (2.0 $\mu g/m^3$) and schools (2.2 $\mu g/m^3$).

A source of Pb, also correlated with Mn and Cu, was identified both for PM2.5 and PM10. The contribution of this source for PM2.5 was 0.84 $\mu g/m^3$ in homes, 2.6 $\mu g/m^3$ in schools and 0.94 $\mu g/m^3$ in the outdoor, and for PM10 was 0.87 $\mu g/m^3$ in homes, 2.4 $\mu g/m^3$ in schools and 1.0 $\mu g/m^3$ in the outdoor. Figure 21 shows a poor correlation between indoor and outdoor for this source indicating an indoor generation of these pollutants.

Road dust characterized by high contributions of EC, Cr, Fe, Cu and Zn, presented the lowest contribution for PM2.5 (0.024 $\mu g/m^3$ in homes, 0.004 $\mu g/m^3$ in schools and 0.050 $\mu g/m^3$ in the outdoor) and PM10 (0.75 $\mu g/m^3$ in homes, 0.33 $\mu g/m^3$ in schools and 2.3 $\mu g/m^3$ in the outdoor). Figure 21 shows that the contribution of this source in the outdoor was higher than in the indoor MEs.

CONCLUSIONS

This work provides information on the sources contributing to indoor and outdoor PM2.5 and PM10 concentration.

Six sources contributing to PM concentrations were identified. 51% of PM2.5 was attributed to vehicles exhaust, 19% to secondary sulfates, 12% to soil, 9.9% to a Pb source, 6.3% to sea salt and 0.36% to road dust. For PM10, vehicles exhaust, soil and secondary aerosols contributed on average, with 29%, 21% and 20%, respectively, while sea spray, the Pb source and road dust represented, respectively, 17%, 5.4% and 7.8%.

Indoor concentration levels were comparable to those found outdoors for traffic emissions, secondary aerosol and sea salt, demonstrating penetration of outdoor pollution to indoors. The contribution of the soil and of a Pb source was significantly larger in schools.

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7. SIZE DISTRIBUTION OF PARTICLES SAMPLED IN HOUSES AND SCHOOLS FROM LISBON

INTRODUCTION

Particulate matter is an issue of increasing importance in pollution studies due to its noticeable effects on human health (e.g. Dominici et al., 2006; Katsouyanni et al., 2001; Lepeule et al., 2012; Pope and Dockery, 2006; Russell and Brunekreef, 2009; Schikowski et al., 2007; Shaughnessy et al., 2015; Valavanidis et al., 2008; Zhou et al., 2015), including decreased lung function, increased respiratory symptoms such as cough, shortness of breath, wheezing, and asthma attacks, as well as chronic obstructive pulmonary disease, cardiovascular diseases, and lung cancer (e.g. Anderson et al., 2012; Dockery, 2009; Kim et al., 2015; Rückerl et al., 2011; and references therein). Particular attention is being paid to the fine-sized particles (PM2.5) due to their ability of being inhaled and reaching the gas exchange region of the lungs. There is strong evidence that PM2.5 plays a significant role in the observed health effects even at very low levels of exposure (Dominici et al., 2006; Pope and Dockery, 2006). PM composition may better predict health effects than PM mass or size (Rohr and Wyzga, 2012; Stanek et al., 2011; and references therein). Indeed, the harmful potential of particles is related to their ability in crossing human respiratory system, depositing in the deepest and most defenceless regions of the lung and carrying with them a number of toxic compounds. Airborne ultrafine particles (defined as particles with aerodynamic diameters < 0.1 μm) have been linked more strongly to adverse health effects, because of the ability to penetrate deeper into the respiratory tract and to translocate to other organs (WHO, 2013).

Toxicological studies suggest that several elements, including Al, Si, V, Pb, Ni and Zn, are most closely associated with health impacts, although many other components, such as elemental carbon and organic carbon, have also been implicated (Chen and Lippmann, 2009; Rohr and Wyzga, 2012). The adverse health effects are related to both short-term (acute) and long-term (chronic) exposures to PM, and can range from relatively minor, such as increased symptoms, to very severe effects, including increased risk of premature mortality and decreased life expectancy from long-term exposure (Bentayeb et al., 2015; Cesaroni et al., 2013; Rückerl et al., 2011; Thurston and Lippmann, 2015).

The partitioning of elements among various sizes depends on their sources and affects their chemical composition and therefore will impact the potential toxicity induced on different regions of the body (Cassee et al., 2013). Because literature results evidence that health effects from airborne particles depend on their chemical composition but also on physical properties, it is essential to assess the link between the two by evaluating the concentration of major and trace aerosol components across particle size fractions (Cassee et al., 2013). This assessment could be used as input data for the assessment of health effects of particles reaching different regions of the body.

Assessment of individual exposures to particles can be significantly improved by using personal monitors, as these samplers incorporate the effects of factors like indoor pollutant sources and human time-activity patterns. The need to better understand and characterize personal exposure led to the development of portable, light-weight impactors such as the personal cascade impactor sampler (PCIS; Misra et al., 2002) The impactors collect airborne aerosols and segregate them into a number of aerodynamic sizes for subsequent determination of mass size distribution, chemical and/or physical properties (Seinfeld and Pandis, 2006).

Finally, understanding the way in which elements partition across particle size fractions also helps to interpret changes in such particle size distributions, especially those induced by

physical and/or chemical processes, such as particle infiltration from outdoor to indoor air. In the present study, the chemical size distribution data of aerosol components affecting child exposure will be provided, which to the authors' knowledge is very scarce in the literature.

METHOD

STUDY DESCRIPTION

The study was conducted in homes and schools located in the city of Lisbon. A map depicting the children' house and schools location is given in Figure 1. The measurements were conducted between October 2017 and January 2018.

At each site, the sampling was performed concurrently in an indoor and an outdoor place. In the schools a classroom and a playground location, which were assumed to give the best overall exposure from the indoor and the outdoor of the school, respectively, were chosen to conduct the measurements. The selected schools are public and are not near any major pollution sources apart from traffic emissions. At 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 manual recorded by the teachers and home' inhabitants, respectively. This included the condition of the buildings, the size of the room and, where necessary, potentially significant influences and disruptive factors.

INSTRUMENTATION AND MEASUREMENTS

At 4 homes and 4 schools was obtained the size distribution of particles by using a Personal Cascade Impactor Sampler (PCIS) connected to a SKC Leland Legacy pump, operating at 9.0 L/min. The PCIS is a miniaturized cascade impactor, consisting of four impaction stages followed by an after-filter. 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. The collection substrates were 37 mm polytetrafluoroethylene (PTFE) filters for the < 0.25 μm stage and 25 mm PTFE filters for the remaining stages. In order to facilitate interpretation of the data, a lower cut diameter of 30 nm was assumed for the last filter stage of particles < 0.25 μm. Two PCIS were placed simultaneously (1 indoor and 1 outdoor).

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, USA). The flow was always set to within ±0.05 L/min of the desired flow rate.

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.

The particle collection was performed during a week at each sampling place. At schools the samples were collected during school hours (about 8 h/day, depending on the schools), from Monday to Friday, and at homes the sampling period was 24 h during weekends (from 09:00 until 09:00 of the next day) and 15 h (18:00-9:00h) 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.

SAMPLE ANALYSIS

Mass concentrations were gravimetrically determined by pre- and post-weighing the PCIS 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. Afterwards, the filters collected indoors and outdoors were analyzed by XRF (X-Ray Fluorescence) for the determination of major and trace elements. The elemental (EC) and organic carbon (OC) concentrations were determined by thermal-optical method. Details about the sampling and chemical analysis were given before in this report.

RESULTS

AEROSOL MASS SIZE DISTRIBUTION

The pattern of the particles mass size distribution was found to be heterogeneous not only among locations but also between indoor and outdoor microenvironments (Figure 22). Previous studies have also stated that the particle mass size distributions change over the time and are different depending on the season and sampling location (Fonseca et al., 2016; Pant et al., 2016).

In the homes, the indoor 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, Abt et al. (2000b) found that the relative contribution of outdoor PM to indoor levels varied by particle size, with outdoor air generally contributing a majority of the smaller particles (less than 0.5 μm) measured indoors, while indoor sources contributed more to the larger size fraction (2–10 μm). A unimodal size distribution was observed inside the home H9 with the mode in the range between 0.03 and 0.25 μm.

In the schools the indoor concentrations tended to be higher than that for the corresponding outdoor for the size range between 2.5 and 10 μm, reflecting the contribution of indoor sources such as the resuspension and generation of particles associated with the student's activities. Contrarily, in the school SA the size distributions among the different size ranges (0.03–0.25, 0.25-0.5, 0.5–1, 1–2.5 and 2.5-10 μm) are not considerably variable.

In general, in the outdoor of both homes and schools the highest mass concentrations of PM were observed in the coarse fraction. This might be related to the high mineral and marine aerosol contributions in the study area.

From the mass size distribution was applied the statistical Spearman test. The PM concentrations of the size ranges 0.03–0.25, 0.25-0.5 and 2.5–10 μm were strongly correlated with their outdoor levels, with Spearman correlation coefficients of 0.79, 0.93 and 0.86 ($p < 0.05$), respectively. The lower correlation coefficients obtained for ultrafine (0.03-0.25 μm) and coarse particles (2.5–10 μm) may be related to particle losses indoors from deposition as well as the generation of particles indoors from activities, as also referred by (Abt et al., 2000a).

The size-fractionated PM levels obtained in this study provide essential data for determining particle dose.
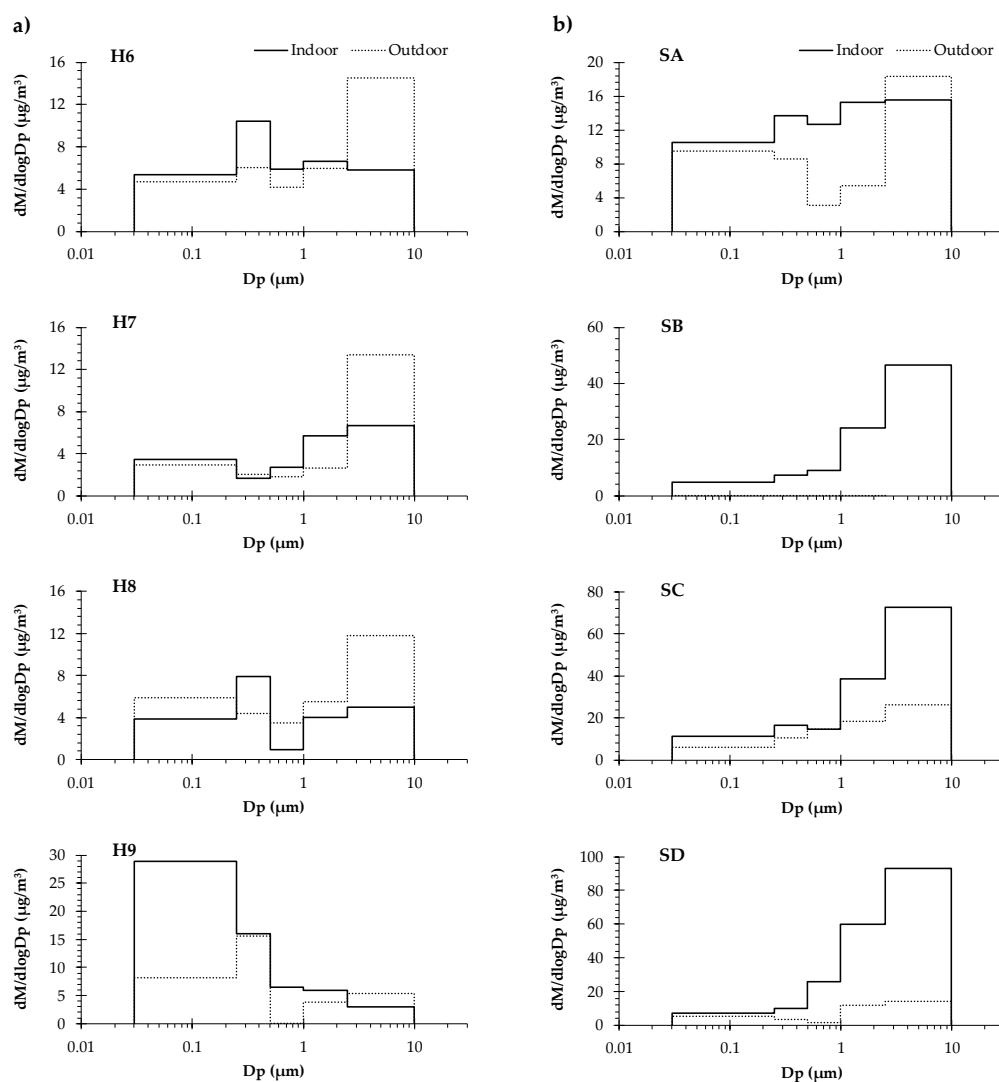
Figure 22 - Average mass size distribution for PM at the a) homes and at the b) schools. Note that the scales are different.

SIZE DISTRIBUTION OF CHEMICAL CONSTITUENTS

Figure 23 depicts the average mass closure for PM (in µg/m3 and %) 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 of the home H6 and the school SC. The major and trace chemical constituents were grouped into five different categories: marine aerosol (sum of Na and Cl), mineral matter (calculated as the sum of Mg, Al, Si, K, Ca and Fe), OC, EC and trace elements.

It is evident that organic carbon is the major contributor to particles with aerodynamic diameter <0.25 and 0.25–0.5, representing around 30% of the mass in the indoor of both home H6 and school SC. Despite its usually large grain size distribution, the elemental carbon is the second major constituent in the particles with aerodynamic diameter <0.25, accounting for 15 and 8% of the mass collected in the home and school, respectively. As expected, EC contributions (1-2%) decrease with increasing particle size (>0.25 µm).

In the home H6 was also observed a considerable fraction of mineral matter in the particles with aerodynamic diameter <0.25 (8%) and 0.25–0.5 (6%). It should be taken into account that anthropogenic sources such as combustion, lubricant oils or industry may also contribute to

these elements in these size fractions (Cernuschi et al., 2012; Lin et al., 2005; Miller et al., 2007). Levels of mineral matter for particles with aerodynamic diameter <0.25; 0.25–0.5 and 0.5–1.0 are similar between the indoor of the home and the school. In the outdoors the levels varied between 0.10-0.20 and 0.16-0.30 in the homes and schools, respectively. As expected, the highest contributions of mineral matter were observed for the particles > 0.5 μm, since that these species are mostly present in this size fraction. The highest difference between the levels of mineral matter was observed for PM2.5–10, accounting for 0.62 μg/m^3 in home and 7.06 μg/m^3 in school, evidencing that the high mineral matter contents may enter from playground dust. Apart from playground dust resuspension and entrainment towards the classroom by children, one additional source of mineral matter is suggested in indoor air by the slightly higher ratio of Ca/Al (9.12) obtained in comparison to outdoor (4.89). 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.

The marine aerosol contribution was relatively small for particles < 0.5 μm, accounting for 0.04-0.31% of the mass indoors. An indoor source of fine Cl particles such as cleaning products may influence this contribution. Moreover, as the marine aerosol is dominantly in the coarse mode its contribution (2-9%) is higher for particles > 0.5 μm, as expected.

The presence of trace elements was more evident in the home environment.

Finally, the undetermined fraction varied between 36 and 58% in the home H6 and between 51 and 73% in the school SC. These undetermined fractions can be explained by the presence of oxide species, heteroatoms from the carbonaceous compounds, secondary inorganic aerosols, some water molecules (moisture, formation and crystallization water) and mineral components such as carbonates that have not been determined.
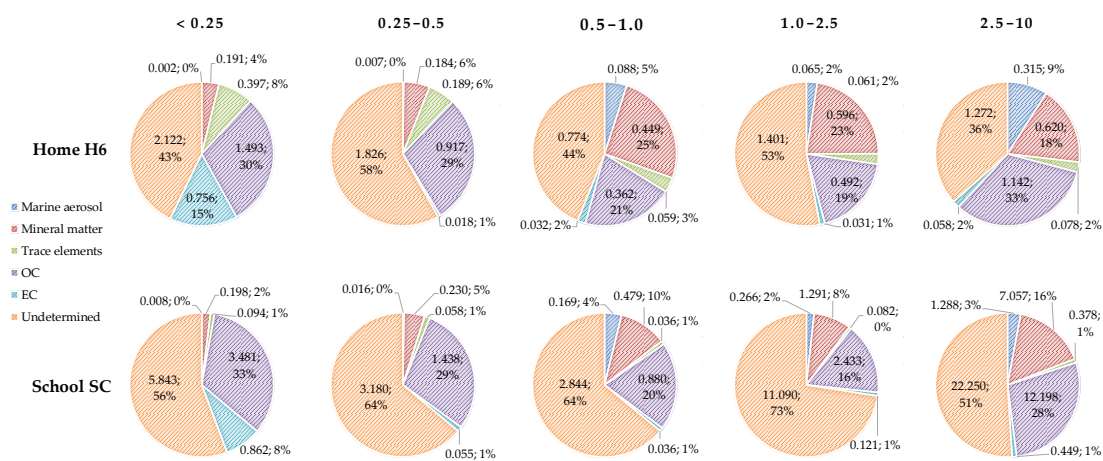
Figure 23 - Average mass closure of PM (in μg/m3 and %) in 5 aerodynamic diameter ranges (<0.25; 0.25 to 0.5; 0.5 to 1.0; 1.0 to 2.5; and 2.5 to 10 μm) in the indoor of the home H6 and the school SC.

Figure 24 and Figure 25 show the particle mass size distributions of aerosol chemical constituents for the home H6 and school SC, respectively. Similarly to the mass size distribution of PM, the size distribution of its chemical constituents was very heterogeneous, not only among locations (home vs. school) but also between indoor and outdoor microenvironments.
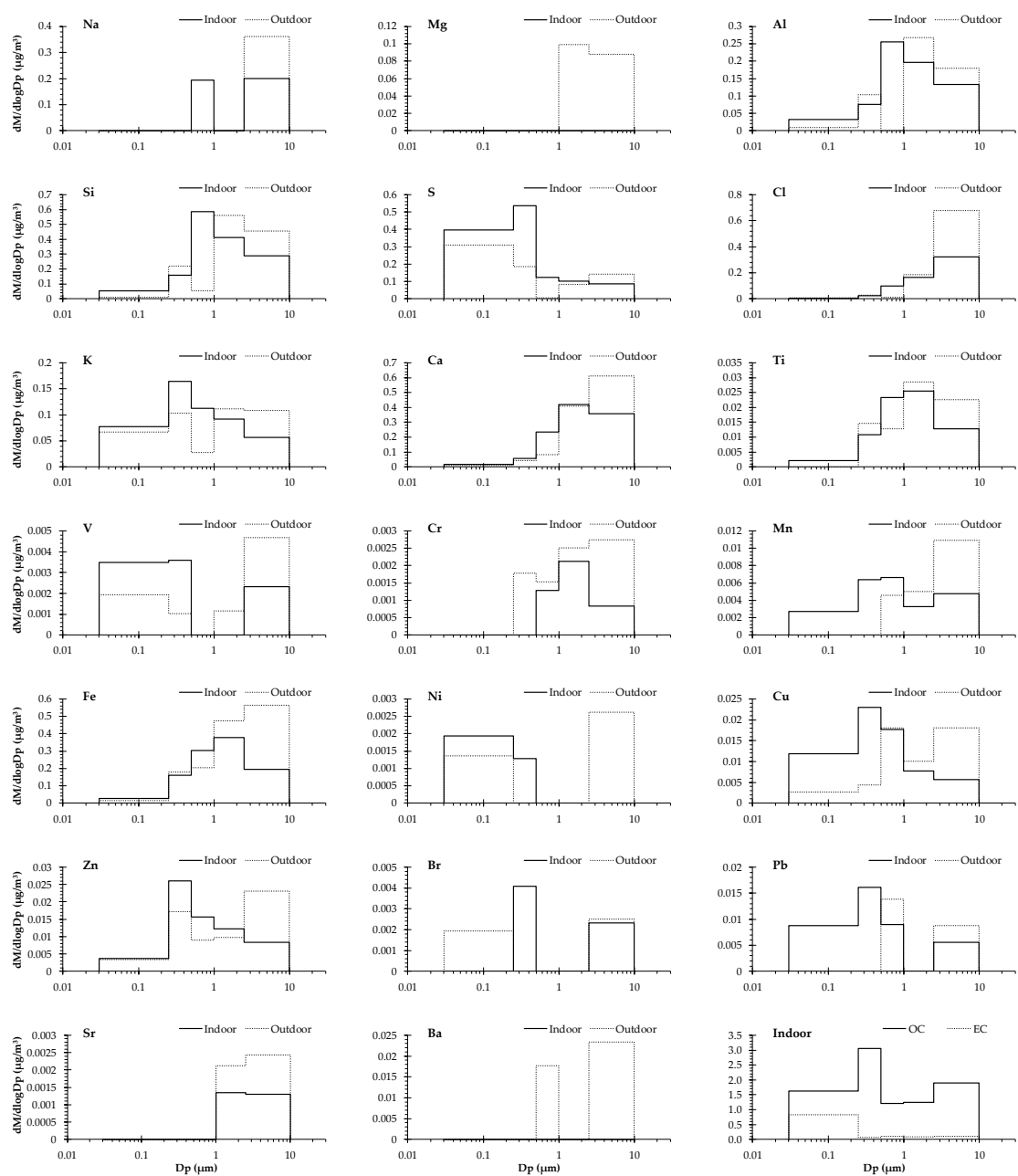
Figure 24 - Average mass size distributions for different chemical constituents at the home H6. Note that the scales are different.
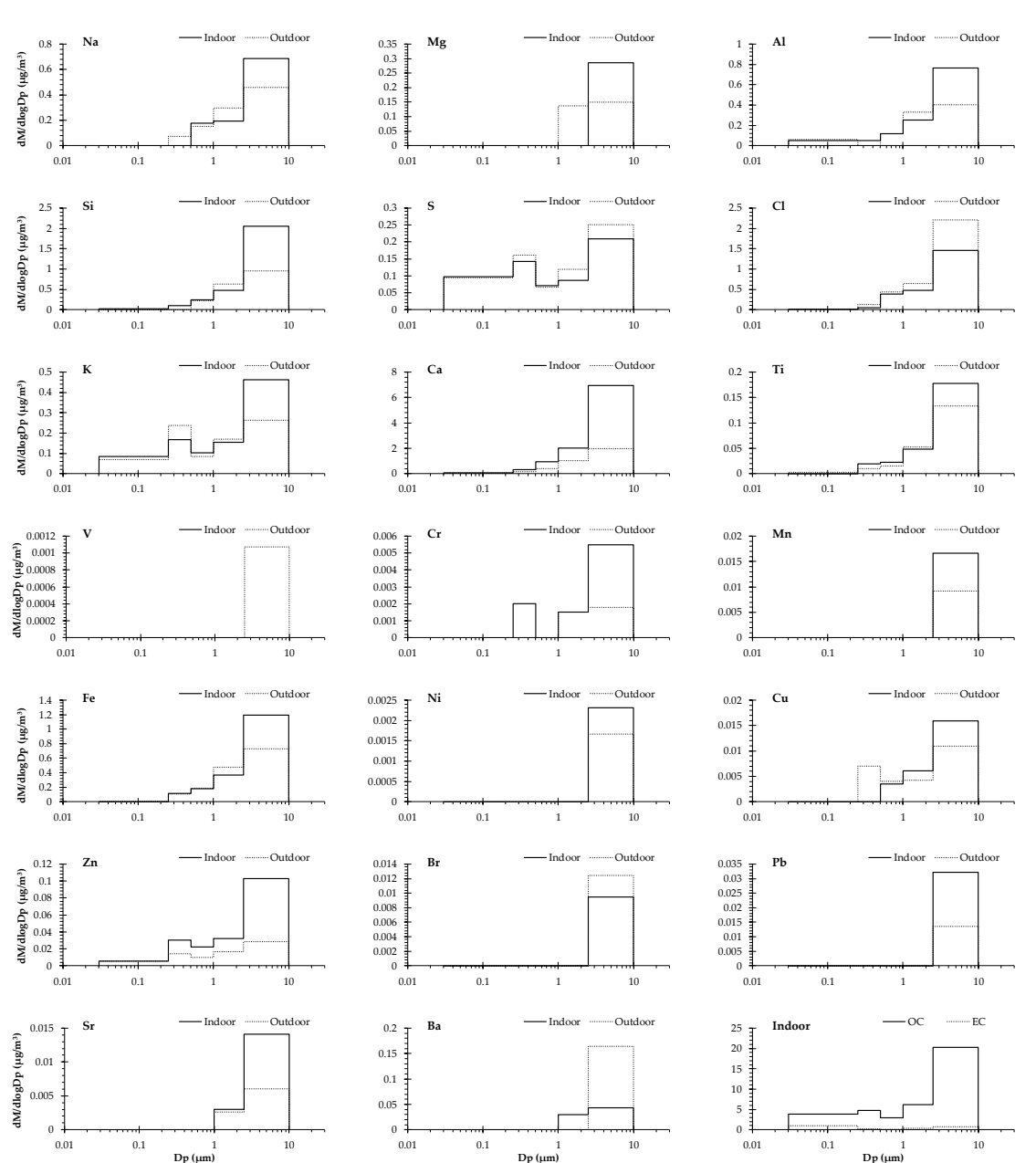
Figure 25 - Average mass size distributions for different chemical constituents at the school SC. Note that the scales are different.

CONCLUSIONS

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

– The pattern of the particles mass size distribution and its chemical constituents was very heterogeneous, not only among locations (home vs. school) but also between indoor and outdoor microenvironments.
– The particle mass size distribution depends on the contribution of both indoor and outdoor sources.
– OC and EC were the main contributors of the mass of particles with aerodynamic diameter <0.25 in the indoors.
– EC contributions decrease with increasing particle size.

- The highest contributions of mineral matter were observed for PM2.5-10 in the indoor of the school, associated to the outdoor infiltration and also to the presence of an indoor source (use of chalk on blackboards).

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8. PARTICLE EXPOSURE AND INHALED DOSE WHILE COMMUTING IN LISBON

INTRODUCTION

Air pollution is a major concern around the world since exposure to air pollutants leads to an increase in mortality and morbidity owing to respiratory and cardiovascular diseases, cancer, and increased risk of reproductive problems (Kampa and Castanas, 2008; WHO, 2013; Almeida et al., 2014; Steinle et al., 2015; Pinault et al., 2017). Some authors (Favarato et al., 2014; Aggarwal and Jain, 2015; Brønnum-Hansen et al., 2018) have also found associations between exposure to traffic and adverse health effects, such as mortality, heart disease, myocardial infarction, hypertension, stroke and atherosclerosis.

The basis of the human daily exposure estimation involves the microenvironment concept, since each microenvironment contributes differently to the exposure, considering the pollutants concentration in the microenvironment and the time that individuals spend in this environment. While commuting, individuals are inevitably exposed to high concentrations of traffic air pollutants that usually exceed the limits set by the air quality guidelines (EEA, 2017). This fact together with the considerable amount of time that people spend on their daily commutes in urban areas, lead to an important contribution of commuting to the human daily exposure to air pollutants.

Therefore, it is essential to assess the exposure while commuting in the modes of transport frequently used by the urban population. Over the last few years, the number of studies addressing this subject has increased, and all of them concluded that the transports microenvironment, where the population moves daily, is associated to high concentrations of air pollutants (Adams et al., 2001; Asmi et al., 2009; Berghmans et al., 2009; Kaur and Nieuwenhuijsen, 2009; de Nazelle et al., 2012; Huang et al., 2012; Goel et al., 2015; Ramos et al., 2015; Ramos et al., 2016; Alameddine et al., 2016).

The assessment of exposure in transports is not trivial since there are several factors that may influence it, such as, mode of transport (Adams et al., 2001; de Nazelle et al., 2012; Goel et al., 2015; Ham et al., 2017), route (Adams et al., 2001; Tan et al., 2017), time of the day (Asmi et al., 2009; Berghmans et al., 2009; Betancourt et al., 2017), traffic intensity (Adams et al., 2001; Kaur and Nieuwenhuijsen, 2009; Hatzopoulou et al., 2013; Li et al., 2017), meteorological conditions (Adams et al., 2001; Kaur and Nieuwenhuijsen, 2009; de Nazelle et al., 2012; Alameddine et al., 2016), street configuration (Kaur et al., 2005; Hatzopoulou et al., 2013; Betancourt et al., 2017), type of ventilation (Wu et al., 2013; Alameddine et al., 2016; Ham et al., 2017), among others. For this reason, exposure of each individual, which results from a variety of interactions between environment and human systems, has a wide spatial and temporal variability (Steinle et al., 2013).

Consequently, real-time and empirical assessment of human exposure is difficult. For this reason, human exposure to air pollutants and respective dose can be estimated combining modelled outdoor air concentrations, time activity patterns, indoor-outdoor ratios for each micro-environment frequented by the individuals and inhalation rate. This study aims to assess commuters' exposure to $PM_{2.5}$, PM_{10}, BC and $PN_{0.01-1}$ in the most used modes of transport in Lisbon (car, bicycle, metro and bus) and determine indoor-outdoor ratios for cars and buses. This work will generate base information that will be further used in studies that aim to assess the human exposure to air pollutants through the methodology described before.

METHOD

STUDY DESIGN

This study was performed in the Lisbon Municipality that, in 2017, had 505 526 inhabitants (Pordata, 2017). The field measurements were conducted in the four most used modes of transport in Lisbon (car, bicycle, metro and bus) in a route that is representative of the commutes performed by the Lisbon citizens. The selected route has 6.7 km, starts in Telheiras, a residential area, and ends in Praça dos Restauradores located in the city center (Figure 26).
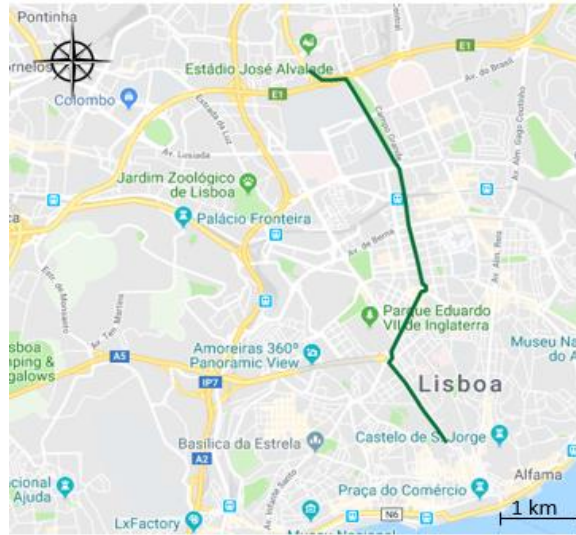

Figure 26. Route selected for this study (green line).

Measurements were perfomed 5 times a day (at 8h, 10h30, 13h, 18h and 20h) during 18 weekdays. In order to increase the representativeness of the work, measurements were performed in cars powered by different types of fuel: 3 Diesel cars, 2 gasoline cars and 1 electric car. Moreover, 3 types of ventilation were tested: middle ventilation, without ventilation and with air conditioning.

The levels of exposure to $PM_{2.5}$, PM_{10}, BC and $PN_{0.01-1}$ were measured for each transport mode. Besides that, in cars and buses the concentrations of $PM_{2.5}$, PM_{10} and BC were measured in the indoor and outdoor simultaneously to determine the ratio between indoor and outdoor concentrations.

The inhaled doses of each pollutant under study were determined according to the Equation 1:

$$P_{inhaled\ dose} = [P] \times IR \times T \tag{1}$$

where [P] is the pollutant concentration ($PM_{2.5}$, PM_{10} and BC in µg m^{-3} and $PN_{0.01-1}$ in # cm^{-3}), IR is the inhalation rate (m^3 h^{-1}) and T is the time spent travelling (h). The inhalation rates are equal to 0.6 m^3 h^{-1} for passive modes of transport (car, metro and bus) and 1.7 m^3 h^{-1} for active modes of transport (bicycle) (Buonanno et al., 2011).

MEASUREMENTS AND SAMPLING EQUIPMENT

Measurements were performed with the equipment described in Table 6. $PM_{2.5}$ and PM_{10} sampling was carried out in Polytetrafluoroethylene (PTFE) filters using a Personal Environmental Monitor (PEM) that consists of a compact personal sampling device that has a single stage impactor (Válio, 2015). The PEM was connected to an air suction pump SKC Leland Legacy whose flow rate (10 L min^{-1}) was verified with a flow meter Defender TM 510. Before

and after sampling filters were weighed by means of a microbalance using the procedure described in EN12341. $PM_{2.5}$ and PM_{10} mass concentrations were determined by dividing filter loads by the volume of air filtered.

Two microAeth AE51 measured BC mass concentrations through light absorption. $PN_{0.01-1}$ number concentrations were measured with a Condensation Particle Counter (CPC 3007) that uses isopropyl alcohol as the condensing liquid. Finally, a GPS was used to record position as a function of time.

Table 6 - Measurement devices.

EQUIPMENT	MEASURES	CAR	BYCICLE	METRO	BUS
PEM	$PM_{2.5}$ and PM_{10}	X (IN and OUT)	X	X	X (IN and OUT)
microAeth AE51	BC	X (IN and OUT)	X	X	X (IN and OUT)
CPC 3007	$PN_{0.01-1}$	X	X	X	X
GPS Garmin eTreck 20	Location and time	X	X	X	X

The equipment was placed as near as possible from the respiration area. The PEMs and the microAeth AE51, that measured outdoor concentrations in cars, were fixed to a sponge, immobilized by the window of the vehicle, which prevented air intakes to the interior of the vehicle.

The data obtained with the microAeth AE51 was corrected with the Optimized Noise-Reduction Algorithm (ONA) software (Hagler et al., 2011).

STATISTICAL ANALYSIS

Statistical tests were carried out in STATISTICA software. Mann-Whitney U test was used for samples that are non-parametric and independent (as, for example, concentrations of a pollutant in two different modes of transport). This test compares medians to suggest if two samples are from the same population. The tests were considered significant for $p < 0.05$.

RESULTS AND DISCUSSION

$PM_{2.5}$ AND PM_{10}

AVERAGE PM MASS CONCENTRATION

$PM_{2.5}$ mass concentration ranged from 20.7 to 61.6 µg m^{-3} for the commuting using all transport modes. The $PM_{2.5}$ average concentrations were 37.8$\pm$20.8 µg m^{-3}, 33.7$\pm$8.6 µg m^{-3}, 30.5$\pm$9.0 µg m^{-3}, and 28.4$\pm$5.3 µg m^{-3} for metro, car, bicycle, and bus, respectively. For all the transport modes, concentrations tended to exceed the 25 µg m^{-3} guideline established by the World Health Organization (WHO) (Krzyzanowski and Cohen, 2008). Boogaard et al. (2009) reported that in 11 Dutch cities overall mean $PM_{2.5}$ concentrations were 49.3 µg m^{-3} for car and 44.5 µg m^{-3} for bicycle. Besides that, Moreno et al. (2015) found that the average $PM_{2.5}$ concentration inside the Barcelona metro was equal to 43.0 µg m^{-3}. These values of concentrations were higher than the ones found in Lisbon commutes. Finally, Rivas et al. (2017) reported that, in London, $PM_{2.5}$ concentrations were 34.5 µg m^{-3}, 13.9 µg m^{-3}, and 7.3 µg m^{-3} for metro, bus and car, respectively. In this case, concentrations were lower than the ones measured in Lisbon.

PM_{10} concentrations varied between 39.4 to 120.6 µg m^{-3} for the commuting using all transport modes. For PM_{10} the number of exceedances of the WHO guideline (50 µg m^{-3}) was lower than for $PM_{2.5}$. Concentrations were 84.1±34.0 µg m^{-3}, 42.2±10.3 µg m^{-3}, 41.5±10.1 µg m^{-3} and 39.6±0.3 µg m^{-3} for metro, bicycle, car and bus, respectively. Hwang et al. (2017) reported that, inside the metro, the mean PM_{10} concentrations were 41.5±10.1 µg m^{-3}, a value much smaller than the one found in Lisbon.

As it is shown in Figure 27, the PM_{10} average mass concentration was higher for the metro due to the elevated levels registered in the coarse fraction, which is similar to what was found in Barcelona by Moreno et al. (2015). This can be caused by the absence of incomplete combustion sources in the metro (Wu et al., 2013) as it happens in the other modes of transport under study. Besides that, the sources in the metro contribute significantly to the coarser fraction. According to Martins et al. (2015), emission sources like abrasion of rails, wheels and brakes and also the resuspension of particles due to turbulence led to higher PM concentrations in the metro system. In spite of the high concentrations found in the metro mode, these could not represent a major risk to human health due to the different nature of particles that are mainly iron oxides (Seaton et al., 2005). The greatest variability in $PM_{2.5}$ and PM_{10} concentrations was found in the metro because of the conditions in this environment, such as variations in the type of ventilation and in the influx of people.
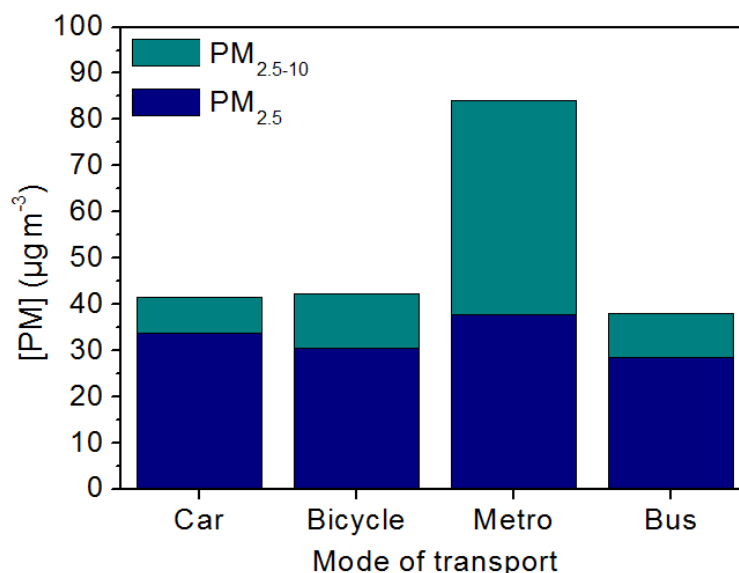
Figure 27 - Average $PM_{2.5}$ and $PM_{2.5-10}$ concentrations (µg m^{-3}) for car, bicycle, metro and bus modes.

$PM_{2.5}$ concentrations were slightly smaller in bicycle mode than in car mode. This may be due to the fact that, in parts of the route, the bicycle pathway is far from the road and, therefore far from the motorized vehicles (EEA, 2014; Karagulian et al., 2015). Considering the road modes of transport, the coarser fraction was more significant in bicycle mode, which means that the infiltration, to the interior of cars and buses, of particles resulting from processes of resuspension is less significant than the infiltration of smaller particles. Besides that, the bicycle pathway crosses a green area and a construction zone. According to Berghmans et al. (2009), peaks of PM_{10} can be attributed to construction activity.

The lowest average $PM_{2.5}$ concentration was registered in the bus mode. Buses run on dedicated lanes being less time and in a smaller frequency in start and stop moments which could lead to a reduction in exposure levels. Moreover, the buses air filters could have been more efficient in the removal of particles from the air that enters in the cabin. The coarser fraction is significantly higher in bus mode than in car mode. A reason for this is the fact that the opening

of bus doors and the entry of passengers can promote the entrance and resuspension of particles of larger dimensions.

INDOOR TO OUTDOOR PM CONCENTRATION

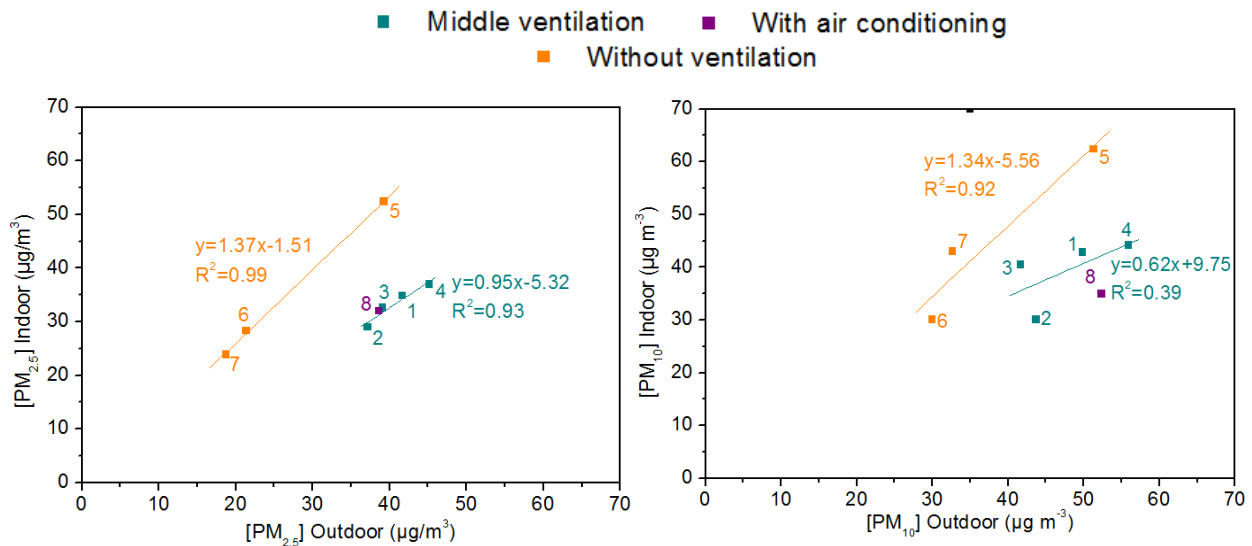Figure 28 presents the indoor concentrations as a function of the outdoor concentrations for cars.

Figure 28 - Indoor to outdoor concentrations ($\mu g\ m^{-3}$) for $PM_{2.5}$ and PM_{10} for cars.

When sorting the samples by the type of ventilation used in cars it became clear that there was a high correlation between the indoor and outdoor concentrations both for $PM_{2.5}$ and PM_{10}, being the same verified by Alameddine et al. (2016).

The use of ventilation (in middle intensity or with air conditioning) led to lower concentrations of $PM_{2.5}$ and PM_{10} inside the vehicles because the air filters of the car prevented the penetration of particles to the interior, as it was also reported by Alameddine et al. (2016). The same did not happen when it was not used any kind of ventilation. In fact, the disuse of ventilation led probably to the accumulation of particles and thus to higher PM concentrations inside the vehicle. In conclusion, while the use of ventilation led to ratios I/O higher than one the reverse occurred when no ventilation was used. The use of air conditioning had apparently a reducing effect of PM concentrations even though the small sample collected does not allow reaching accurate conclusions about this fact. In any case, Wu et al. (2013) reported that the use of air conditioning had a reducing effect on PM concentrations.

Regarding the buses, on each sampling day concentrations were measured in a variety of buses, which introduced a large variability regarding the buses used and most likely the types of ventilation. Results indicate that the concentrations in the indoor were higher than the ones in the outdoor resulting in an average I/O ratio equal to 0.72 for $PM_{2.5}$. Unlike the results obtained in Lisbon, in Bogotá, Columbia, Betancourt et al. (2017) reported that concentrations were higher inside buses, maybe due to bad ventilation. Adams et al. (2001) also reported that the bus shell did not act as a protection for passengers since it did not allow a significant reduction in $PM_{2.5}$ concentrations.

BLACK CARBON

AVERAGE BC MASS CONCENTRATION

Figure 29 shows that the average BC concentrations were higher in car (5.5 ± 5.9 µg m^{-3}) mode followed by metro (4.6 ± 3.6 µg m^{-3}), bicycle (3.8 ± 5.7 µg m^{-3}) and, finally, bus (1.6 ± 5.2 µg m^{-3}) mode. This is in line with previous studies, such as Dons et al. (2012) that reported, in Flanders (Belgium), BC concentrations equal to 5.6 µg m^{-3} in car, 5.1 µg m^{-3} in metro and 3.2 µg m^{-3} in bicycle mode. Rivas et al. (2017b) reported that, in London, BC concentrations were 5.4 µg m^{-3} for bus mode and 4.4 µg m^{-3} for car mode. Williams and Knibbs (2016) made measurements in different transport modes and found BC concentrations equal to 2.4 ± 2.8 µg m^{-3} for bus, 1.7 ± 4.0 µg m^{-3} for car, and 1.0 ± 1.2 µg m^{-3} for bicycle mode. Excluding the values measured in cars, the concentrations obtained by these studies were lower than those recorded in Lisbon, which could mean that there is a higher traffic intensity in the study area, in Lisbon, since BC is a primary pollutant and a specific marker of motor vehicles emissions (Cai et al., 2013). Furthermore, Dons et al. (2012) reported that BC concentrations were equal to 6.6 µg m^{-3} for bus, 6.4 µg m^{3} for car, 5.1 µg m^{-3} for metro and 3.2 µg m^{-3} for bicycle mode, which are similar to the concentrations measured in Lisbon, except for the bus.
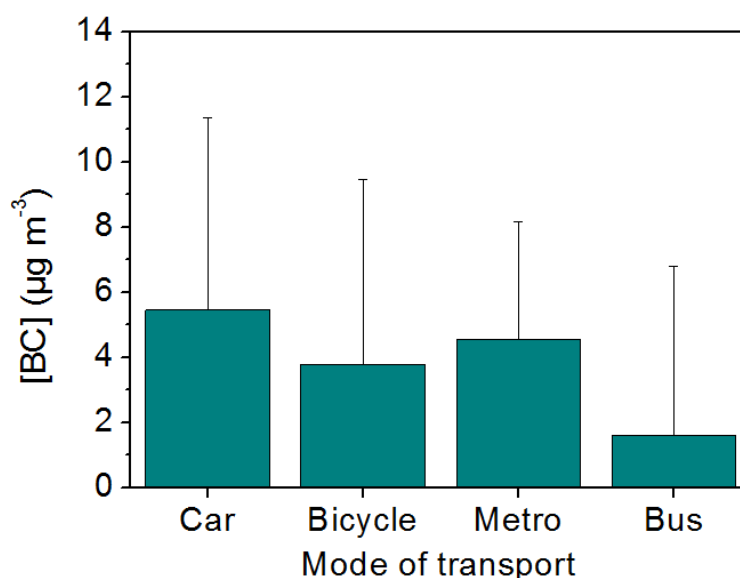
Figure 29 - Average BC concentrations (µg m^{-3}) for car, bicycle, metro and bus modes.

Considering the road modes of transport, concentrations were higher in car followed by bicycle and bus modes. Concentrations in cars and buses may depend significantly on the type of ventilation used, as it will be discussed in the next chapter. In any case, it was verified that the fact that concentrations were lower inside buses than inside cars might indicate a better efficiency of the ventilation system in the removal of BC from the outside air in buses. Besides that, buses run in a separated bus line allowing less moments of stop and go and the opening of bus doors at each stop on the side of the sidewalk may have allowed the dilution of BC concentrations.

In the metro, the absence of combustion sources such as vehicular emissions would lead to smaller concentrations of BC. Despite this fact, BC from the outside can be transported into the metro through the ventilation system (often the air inlet is located near the road). Particles associated to BC have small diameters and, therefore, could not be efficiently removed by the filters in the ventilation system.

Furthermore, the main sources of PM in the metro that are the mechanical abrasion between rails, wheels and brakes results in high concentrations of particulate iron (Moreno et al., 2015a; Rivas et al., 2017b). This could result in a BC overestimation by the microAeth AE51, since iron absorbs light at wavelengths similar to BC (Chow et al., 2004; Karanasiou et al., 2015).

INDOOR TO OUTDOOR BC CONCENTRATION

In order to attest if different ventilation settings would bring differences in BC concentrations inside cars, a test was conducted being the results presented in Figure 30.
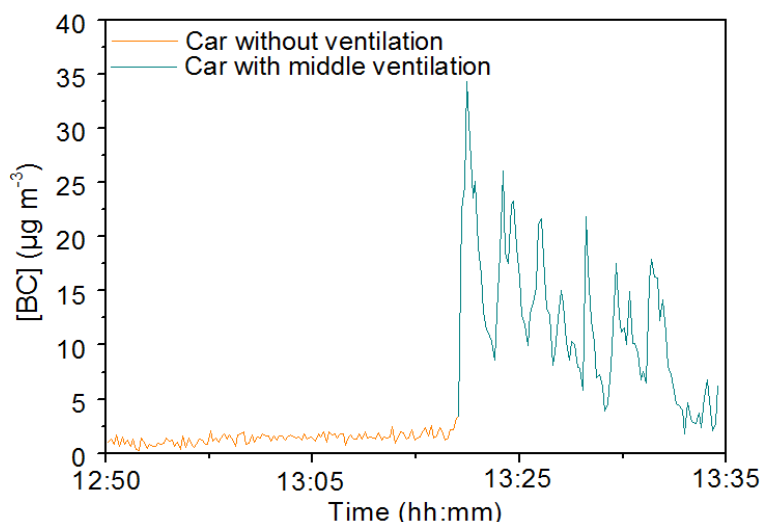

Figure 30 - Influence of ventilation on BC concentrations ($\mu g\ m^{-3}$) inside a car.

When ventilation was switched off, BC concentrations were significantly lower ($p<0.0001$) than when ventilation was on. This attests the huge influence of ventilation on levels of BC inside cars. The low efficiency of filters in BC removal from the air that enters in the car cabins, lead to an accumulation of BC inside cars. However, when ventilation was switched off the reduced entrance of air in the cabin led to low BC concentrations.

The samples were segregated according to the type of ventilation used in each day of measurements to assess the influence of the ventilation in the BC concentrations inside cars. The results are presented in Figure 31.

Unlike what happened for $PM_{2.5}$ and PM_{10}, BC concentrations increased with the use of ventilation. However, this effect did not happen for all the cars. In fact, vehicle 4, which is a Diesel vehicle (Ford Mondeo 2016) was equipped with a high efficiency active carbon filter which, according to results obtained, was more efficient in the removal of BC from the air that entered in the cabin.

BC is often associated to small particles (Ning et al., 2013) that are hardly removed by common air filters, resulting in higher concentrations when ventilation is on. On the contrary, when ventilation was not used, the effect of outside concentrations was not so relevant because the entrance of fresh air was minimized. Ham et al. (2017) also verified that the prevention of intake of fresh air provided lower in-vehicle concentrations.

Regarding the buses, results indicate that the BC concentrations in the indoor were higher than the ones in the outdoor resulting in an average I/O ratio equal to 0.31.
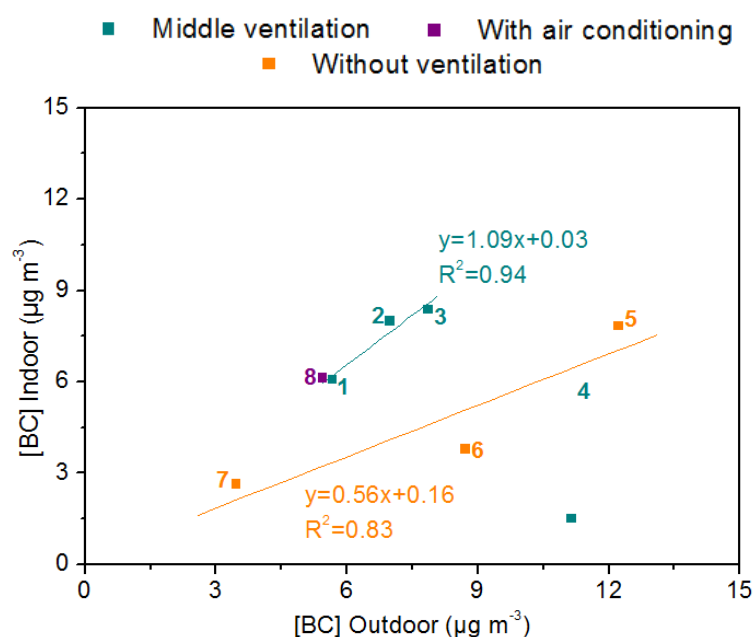
Figure 31 - Indoor to outdoor concentrations (µg m^{-3}) for BC.

SPATIAL DISTRIBUTION OF CONCENTRATIONS

According to de Nazelle et al. (2012), street morphology is a potential explanation for contrasts in concentrations and small physical separations can cause significantly lower exposures. Having this in consideration, the route under study was divided in several zones in which was expected to happen different traffic intensities and streets configuration (Figure 32 (a)). Being BC a proxy for traffic pollution (Moreno et al., 2015b), the BC average concentration was calculated for each zone and presented in Figure 32 (b).
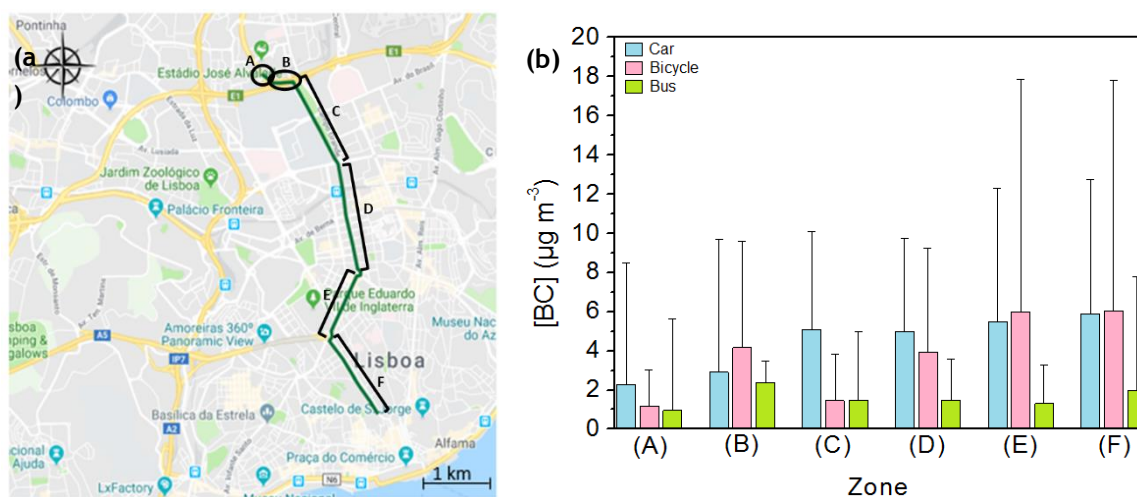
Figure 32 - Zones of the route from A to F (a) and average BC concentrations (µg m^{-3}) in each sub-route (b).
A - Residential area; B - Big crossing road and interface of modes of transport; C - Avenue with a garden located between the two street directions where the bicycle lane is located; D - Long avenue with good dispersion conditions; E - Avenue with high traffic intensity and low dispersion conditions and F – Largest avenue with high traffic intensity and low dispersion conditions.

The lowest BC concentrations were registered in the residential area of Telheiras (A) were traffic intensity is the lowest from all the routes. The highest BC levels were measured in Avenida da Liberdade (F) for all the modes of transport. This avenue has high traffic intensity,

which together with the bad dispersion conditions of pollutants, caused by the high trees and buildings that surround the avenue, led to the highest BC concentrations.

In zone C, Campo Grande, the two directions of the street are separated by a garden where the cycle path is located. As the cycle path has a physical separation from the road, BC concentrations in bicycle mode presented low values in this zone.

Avenida da República (C) has an open street configuration that could have allowed a better ventilation and led to lower BC concentrations (Betancourt et al., 2017) than in Avenida Fontes Pereira de Melo (E) in which the buildings are higher and closer to the road.

$PN_{0.01-1}$

AVERAGE $PN_{0.01-1}$ MASS CONCENTRATIONS

The highest $PN_{0.0-1}$ concentrations were measured for bus mode (28363 ± 20939 cm^{-3}), followed by bicycle (23213 ± 18715 cm^{-3}), car (18512 ± 14740 cm^{-3}) and metro mode (15775 ± 10209 cm^{-3}) (Figure 33).
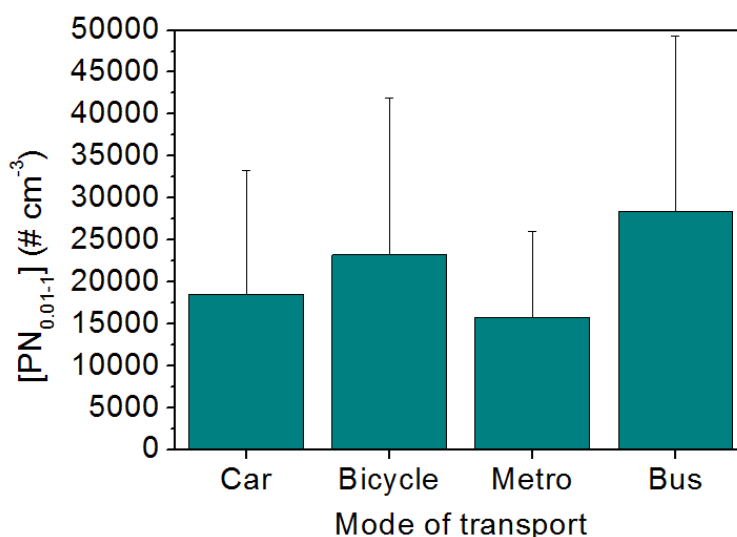
Figure 33 - Average $PN_{0.01-1}$ concentrations (# cm^{-3}) for car, bicycle, metro and bus modes.

de Nazelle et al. (2012) reported that, in Barcelona, concentrations were equal to 117600 cm^{-3} for car, 75300 cm^{-3} for bicycle and, 52300 cm^{-3} for bus mode. These results were higher than the ones obtained in Lisbon which could be related to different conditions experienced in each one of the two cities.

Unlike what happens for BC that is a primary pollutant proxy for traffic pollution, $PN_{0.01-1}$ can result from photoquemical reactions (Seinfeld and Pandis, 2006; Berghmans et al., 2009; Dall'Osto et al., 2012). These reactions depend on different meteorological variables, such as, temperature, relative humidity and the intensity of solar radiation. In fact, the photoquemical process occurs most likely when the intensity of solar radiation is higher than 100 W m^{-2}, what happened in all the days of measurements (Ma and Birmili, 2015). However, as Ma and Birmili (2015) reported, there has been an incidence of days in which the intensity of solar radiation was high and the photochemical phenomena did not occur. This added a difficulty in understanding the behavior of $PN_{0.01-1}$ concentrations.

Concentrations in bus mode were on average higher than the ones recorded in car mode. According to Westerdahl et al. (2005) vehicle motors where complete combustion happens (associated to less moments of stop and go) emmit more ultrafine particle. This is the case of

the buses once they run in a dedicated line that usually puts them in contact with less moments of stop and go. Bicycle mode is associated to higher concentrations of $PN_{0.01-1}$ which could be caused by the passage of the bicycle lanes in areas where there is the tendency to happen ressuspension of particles and thus increased concentrations of $PN_{0.01-1}$ (Westerdahl et al., 2005). In the metro, Mendes et al. (2018) reported that concentrations of smaller particles, such as $PN_{0.01-1}$, are the result of not only the friction from the movement of the metro but also the influence of the outside environment. Furthermore, there are not sources of combustion and, therefore, concentrations in the metro mode were smaller than the ones verified in other modes of transport. However, concentrations inside the metro could also be influenced by the outdoor concentrations since $PN_{0.01-1}$ are particles with small diameter that might not be efficiently retained by the metro ventilation system.

INFLUENCE OF THE TYPE OF VENTILATION IN $PN_{0.01-1}$ CONCENTRATIONS

The influence of the type of ventilation in $PN_{0.01-1}$ concentrations inside cars was tested, and Figure 34 shows the concentrations measured when ventilation was not in use and then when ventilation was switched on and set at middle intensity.
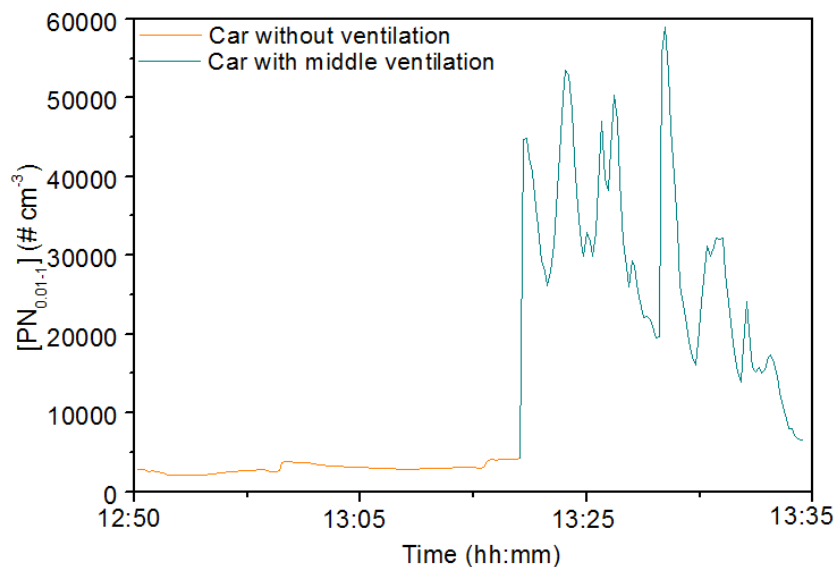
Figure 34. Influence of ventilation on $PN_{0.01-1}$ exposure concentrations (# cm^{-3}) inside a car.

$PN_{0.0-1}$ concentrations were strongly influenced by the type of ventilation used. When ventilation was not used concentrations (2993 ± 571 cm^{-3}) were significantly lower (p<0.0001) than those obtained when ventilation was used (28665 ± 12642 cm^{-3}). Moreover, the fact that standard deviation was higher when ventilation was used evidences the greater influence of the outdoor environment on concentrations recorded inside the car.

SPATIAL DISTRIBUTION OF THE $PN_{0.01-1}$ CONCENTRATIONS

Figure 35 presents the $PN_{0.01-1}$ average concentration calculated for each zone defined in Figure 32a.
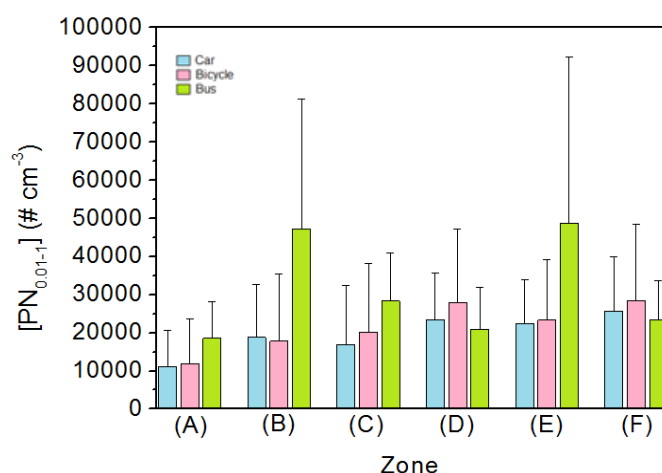
Figure 35 - Average $PN_{0.01-1}$ concentrations (# cm^{-3}) in each route.
A - Residential area; B - Big crossing road and interface of modes of transport; C - Avenue with a garden located between the two street directions where the bicycle lane is located; D - Long avenue with good dispersion conditions; E - Avenue with high traffic intensity and low dispersion conditions and F – Largest avenue with high traffic intensity and low dispersion conditions.

Primary emissions from motorized vehicles are predominantly smaller than 0.02 µm (Westerdahl et al. 2005; Zhu et al. 2006) and, because of that, measurements next to the emission sources and further away could present greater contrasts. The lowest $PN_{0.0-1}$ concentrations were measured in the residential area, which could be associated to the lower traffic intensity that occurs in that zone. For bicycle and car mode concentrations the highest $PN_{0.0-1}$ levels were registered in Avenida da Liberdade. However, the same did not happen for bus, which could be explained by the fact that the bus line allowed a rapid passage of the bus through this avenue. In other avenues, even though the bus runs in the bus line, there are several traffic lights and so the bus has more moments of stop and go.

INHALED DOSES

The inhaled doses for all the studied pollutants ($PM_{2.5}$, PM_{10}, BC and $PN_{0.01-1}$) do not follow the trend verified for the concentrations, unlike what was verified by Tan et al. (2017). The average inhaled doses for each pollutant and modes of transport are represented in Figure 36.

Figure 36 - Inhaled doses of $PM_{2.5}$ and $PM_{2.5-10}$ (a), BC (b), $PN_{0.01-1}$ (c).

Regardless the concentrations measured in each one of the modes of transport under study, the inhaled dose was always higher in bicycle journeys. This in accordance to what was reported

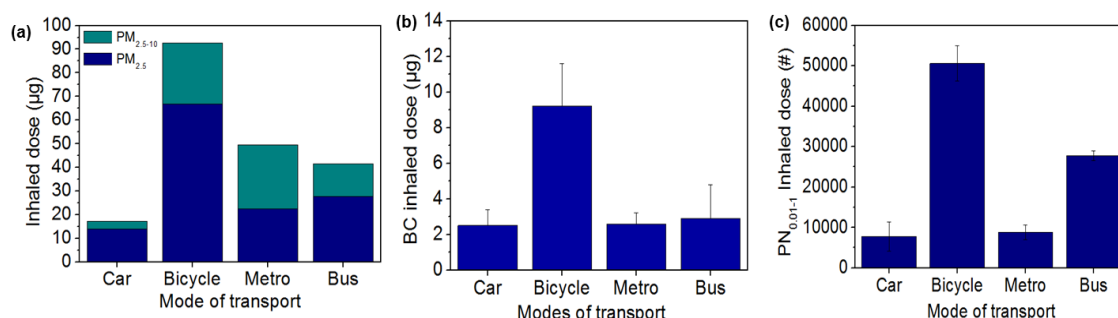by Zuurbier et al. (2010) that concluded that active travel (such as bicycle mode) has frequently been associated to higher inhaled doses of particles. This happens because the bicycle mode was always associated to higher travel times and, besides that, to a higher physical effort, which is expressed in higher inhalation rates.

The highest inhaled dose associated to bicycle commutes represents an extra risk for human health because of the nature of these particles. In fact, unlike what happens inside the metro (Seaton et al. 2005), surface particles, which are mainly generated from the combustion that happens in motorized vehicles in the transports microenvironment, pose a major risk for human health (Kelly and Fussell, 2012).

CONCLUSIONS

Exposure levels to $PM_{2.5}$, PM_{10}, BC and $PN_{0.01-1}$ were evaluated in a representative route of the daily commutes in Lisbon in four of the most used modes of transport in the city: car, bicycle, metro and bus. Measurements were made during 18 weekdays in five trips per day (8h, 10h30, 13h, 18h, 20h).

High concentrations of $PM_{2.5}$, PM_{10}, BC and $PN_{0.01-1}$ were observed for all commute modes. Concentrations of $PM_{2.5}$ and PM_{10} were higher in the metro mode which can be caused by the common emission sources in the metro such as the abrasion of rails, wheels and brakes and also the resuspension of particles due to turbulence. The difference between concentrations inside cars and in the bicycles can be explained by the distance to PM sources such as the combustion that happens in the motors of cars. The ratio between the indoor and the outdoor concentrations in cars depended heavily on the ventilation system. The common air filters were efficient for the $PM_{2.5}$ and PM_{10} and, because of that, the indoor/outdoor ratio was lower than 1.0. Moreover, the disuse of ventilation led to higher particles concentrations in the indoor than in the outdoor. For buses the I/O ratio was 0.72 for $PM_{2.5}$.

The highest BC concentrations was measured in cars and the lowest was registered in bus, which could be associated to the fact that, buses run in a separated bus line. Besides that, a dilution of BC concentrations inside the buses can happen when the bus opened its doors. BC is associated to smaller particles that were not so efficiently removed by common air filters in cars. For this reason, concentrations in the indoor of cars tended to be higher than in the outside and therefore the BC indoor/outdoor ratio was higher than 1.0. On the contrary, the disuse of ventilation led to ratios indoor/outdoor ratios smaller than 1.0. The filter with activated carbon was efficient in BC removal from the air that enters in the cabin. For buses the I/O ratio was 0.31 for BC.

For $PN_{0.01-1}$ the highest concentrations were measured in the bus mode.

For all the pollutants, the highest concentrations were measured in the streets where the traffic intensity was higher and where the morphology of the streets did not allow the dispersion of pollutants.

The highest inhaled doses were measured in bicycle journeys due to the greater inhalation rates and travel times associated to this transport mode.

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9. CHILDREN EXPOSURE ASSESSMENT TO PARTICULATE MATTER IN LISBON USING PORTABLE EQUIPMENT

INTRODUCTION

Adverse health effects of particulate matter with an aerodynamic diameter (AD) less than 2.5 μm (PM2.5) have been reported in tens of scientific studies (Kelly and Fussell, 2011; Guarieiro and Guarieiro, 2013; Sax, Zu and Goodman, 2013; Almeida, Silva and Sarmento, 2014). PM2.5 can enter in the respiratory tract, reach deeper parts of the lung and be deposited in the alveoli (Hinds, 1999). The main source of PM2.5 in the urban areas is the vehicles exhaust, which is composed by heterogeneous mixtures of compounds known to be allergenic, toxic, and carcinogenic. Black Carbon (BC) represents about 23% of the mass of PM2.5 (Islam *et al.*, 2014) and is emitted from incomplete combustion from mobile sources (Moreno *et al.*, 2015), burning of biomass (Seinfeld and Pandis, 2006; EEA, 2013) and cooking activities (Buonanno *et al.*, 2013; Jeong and Park, 2017b). According to the United Nations (2012), BC can be considered a better indicator of harmful particulate substances emmited by combustion sources than PM2.5 and PM10.

Human exposure was defined by Ott (1982) as 'the event when a person comes into contact with a pollutant of a certain concentration during a certain period of time', however the exposure to air pollutants has traditionally been assessed based on data from fixed-site monitoring networks. This monitoring networks usually provides a large quantity of data for a wide range of pollutants; nevertheless, it provides information for a few points in space (Steinle, Reis and Eric, 2013) that may be not representative for the entire population living in one city. Moreover, people spend around 90% of their time indoors (Klepeis *et al.*, 2001), so indoor air quality (IAQ) is a dominant factor for the daily exposure (Sundell, 2004). Therefore, an accurate personal exposure assessment should consider the different places in which time is spent (Steinle, Reis and Eric, 2013; Almeida, Ramos and Almeida-Silva, 2016) and the direct personal exposure measurements are the most representative method to evaluate it.

Adults have been the main target of personal exposure monitoring but children have different time-activity patterns and are more vulnerable to the harmful effects of ambient air pollutants. Children have higher breathing rates, since they are generally more physically active, they inhale a higher volume of air per body weight and, their defense mechanisms are still evolving (Mendell and Heath, 2005; Trasande and Thurston, 2005; Salvi, 2007). Moreover, BC personal measurements are scarce in the literature and to our knowledge, personal exposure to sized-fractioned PM among children has not yet been assessed.

The present study was designed to quantify the children's daily exposure to sized-fractioned PM and BC and to assess the contribution of each activity and ME to the children daily BC exposure and dose. This study provides valuable information that can contribute for the development of measures and policies focusing on the reduction of the exposure to PM and BC and, consequently, for the improvement of the children health and wellbeing.

MATERIALS AND METHODS

STUDY DESIGN

Nine children (7-10 years old) living and studying in nine different schools from Lisbon metropolitan area (Figure 37) were selected to carry personal monitors during all their daily

activities. The personal measurements were conducted for 72 h representing 27 sampling days. Measurements were carried out on weekdays from May 2 to June 22, 2018.
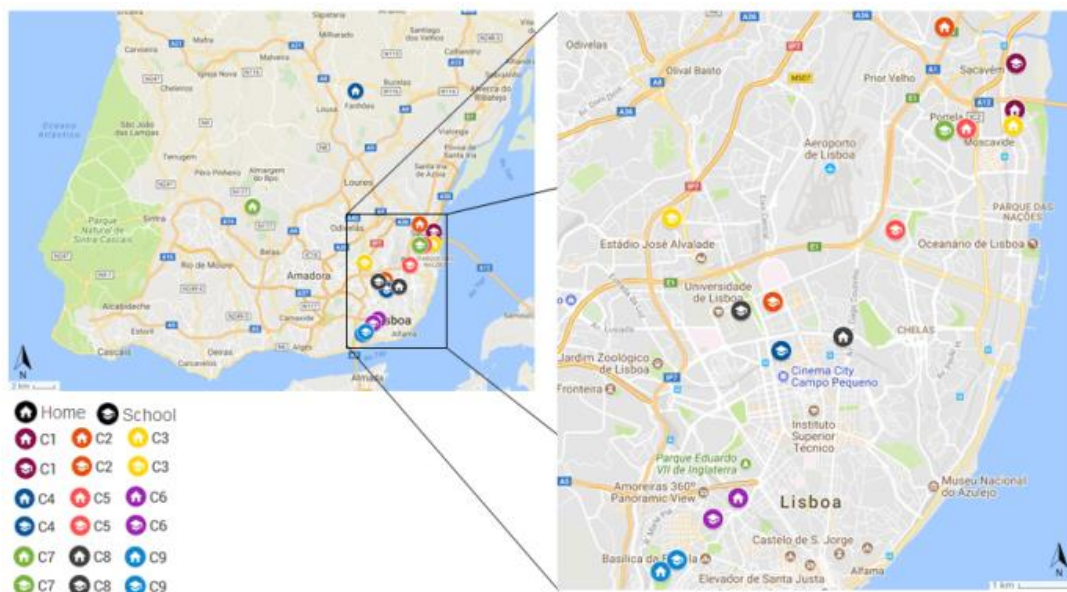

Figure 37 - Geographical distribution of the homes and schools of the 9 selected children.

MEASUREMENTS AND SAMPLING EQUIPMENT

Each child carried a trolley with three portable equipment with the air inlet tube placed in the breathing zone (Figure 38). Children were given detailed instructions to carry the trolley as much as possible throughout the day while performing their regular activities. However, the children were allowed to place the trolley aside but close to them while they were playing sports, swimming, bathing or sleeping to avoid discomfort and to protect the instrument from moisture and vibration.

Figure 38 - Trolley with the three portable equipment.

Measurement of particle mass size distribution was conducted using an SKC Sioutas Cascade Impactor (SKC Inc.) connected to a Leland Legacy® sampler pump at a constant flow rate of 9 L/min. The flow rate was calibrated with a DryCal primary flowmeter (Bios Defender 510, MesaLabs, USA) and the difference was under 10% in the post-sampling period. The Cascade Impactor separated and collected airborne particles in five 50% size-cut point ranges: > 2.5 µm, 1.0 to 2.5 µm, 0.50 to 1.0 µm, 0.25 to 0.50 µm, and < 0.25 µm. In order to facilitate

interpretation of the data, a lower cut diameter of 0.03 μm was assumed for the last filter stage of particles < 0.25 μm.

The collection substrates were polytetrafluoroethylene (PTFE) filters that were weighed before and after sampling by means of a microbalance using the procedure described in EN12341. PM mass concentrations were determined by dividing filter loads by the volume of air filtered.

A MicroAeth AE51 (AethLabs, USA) was used to assess BC concentrations by measuring changes in absorption of transmitted light at 880 nm with continuous collection of light-absorbing BC particles deposited on a small Teflon-coated borosilicate glass fiber filter. The filter strips were replaced to prevent the filter saturation and to maintain measurement integrity. The pump speed was set at a rate of 100 mL/min and logging was made at a 60 seconds basis. The data obtained was corrected using the "Optimized Noise-Reduction" (ONA) software to reduce the noise (Hagler *et al.*, 2011).

A GPS Garmin eTreck 20 was used to register the coordinates of the routes.

The children filled a time-activity diary, under the supervision of their parents, to record their location and the main indoor and outdoor activities (such as sleeping, eating, studying, commuting, etc.). The accuracy of the recorded locations was checked by consulting the GPS logs and in case of inconsistency the participants were contacted immediately after the measurement period to clarify the situation. After all sampling day, follow-up interviews were made with the children and parents personally to gain more accurate information on activities and MEs. In addition, a questionnaire was developed and applied in order to register the characteristics of the home and the classroom of each child.

DATA ANALYSIS

The daily exposure for each child was assessed by integrating the results from the time-activity pattern with the BC concentrations measured in the different MEs. The dose was calculated through the product between the exposure and a dosimetry factor as presented in Equation 1:

$$BC_{inhaled\ dose} = \sum_{j=1}^{m} C_{ij} \times t_{ij} \times IR_{ij} \qquad \text{(Equation 1)}$$

where,
C_{ij} – Arithmetic mean BC concentration by ME (j) and individual (i) (μg/m^3)
t_{ij} – Time spent by individual (i) in ME (j) (hours)
m – Total number of MEs, $\sum_{j=1}^{m} t_{ij} = 24$ h

IR is the inhalation rate (m^3/h)

Table 7 presents the IR used for the different activities (Buonanno et al., 2011). For home, dose determinations used an IR equal to 0.31 m^3/h for the sleeping period, and equal to 0.42 m^3/h for the resting period.

Table 7 - Inhalation rate (m3/h) as a function of age group and activity performed. Based on (Buonanno et al., 2011).

Activity		IR (m^3/h) for 6-10 age group
Sleeping and rest		0.31
Sedentary activities		0.42
Studying		0.42
Transportation	Vehicle	0.58
	Walking	0.91
Playing outside		1.27
Non-sedentary activities (ex.: leisure)		0.91
Indoor sport		1.27
Outdoor sport		1.44

The contribution of different MEs for the daily exposure and daily inhaled dose was calculated by the Equations 2 and 3.

Daily BC exposure contribution (%) = $\dfrac{C_{ij} \times t_{ij}}{\sum_{j=1}^{m} C_{ij} \times t_{ij}}$ (Equation 2)

Daily BC inhaled dose contribution (%) = $\dfrac{C_{ij} \times t_{ij} \times IR_{ij}}{\sum_{j=1}^{m} C_{ij} \times t_{ij} \times IR_{ij}}$ (Equation 3)

In order to deeply understand the contribution of each ME to the total daily exposure or dose, the intensity of exposure and dose to BC, was also calculated by the Equation 4:

BC exposure (inhaled dose) intensity = $\dfrac{\textbf{Daily exposure (inhaled dose) contribution (\%)}}{\textbf{Daily time contribution (\%)}}$

(Equation 4)

The intensity permits to compare the exposure (dose) in different ME by linking the daily exposure fraction with the daily time fraction.

STATISTICAL ANALYSIS

Statistical tests were carried out in STATISTICA software. Mann – Whitney U test was used for samples that are independent (differences between microenvironments and children). This test is non-parametric, hence it does not consider any assumptions related to the distribution. This test compares medians to suggest if two samples are from the same population. Statistical significance refers to $p < 0.05$.

RESULTS AND DISCUSSION

DAILY TIME – ACTIVITY PATTERNS

Daily time-activity patterns were obtained from the time-activity diary filled by each child. Figure 39 shows that children spent more than 80% of their time indoors indicating that risk assessment should focus on indoor MEs. The greatest amount of time was spent at home (55%) (40% sleeping and 15% in general activities), followed by school (22% in classroom, and 8.3% in playground) and transports (5.0%).

These results were quite similar to those found in previous studies. In the framework of the LIFE Index-Air (2017) project a questionnaire about time-activity patterns was developed and applied to 1189 children (5 - 10 years old) living in Lisbon. This study revealed that during the week children spent 89% of their time indoors – 55% in home, 27% in classrooms, 3.5% in vehicles and 2.7% practicing indoor physical activities. Jeong and Park (2017a) assessed the time activity pattern of 10-12 years old Korean children and showed that they also spent the greatest amount of time at home (59%).
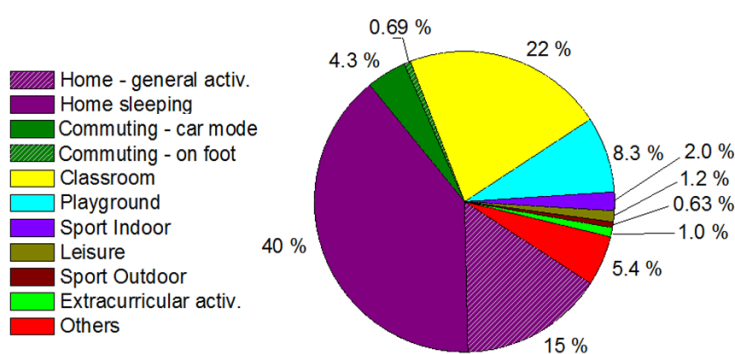

Figure 39 - Percentage of time spent on each ME/activity.

MASS SIZE DISTRIBUTION PATTERN OF PM2.5

Figure 40 shows the PM2.5 concentration to which children were exposed and the respective size distribution patterns.
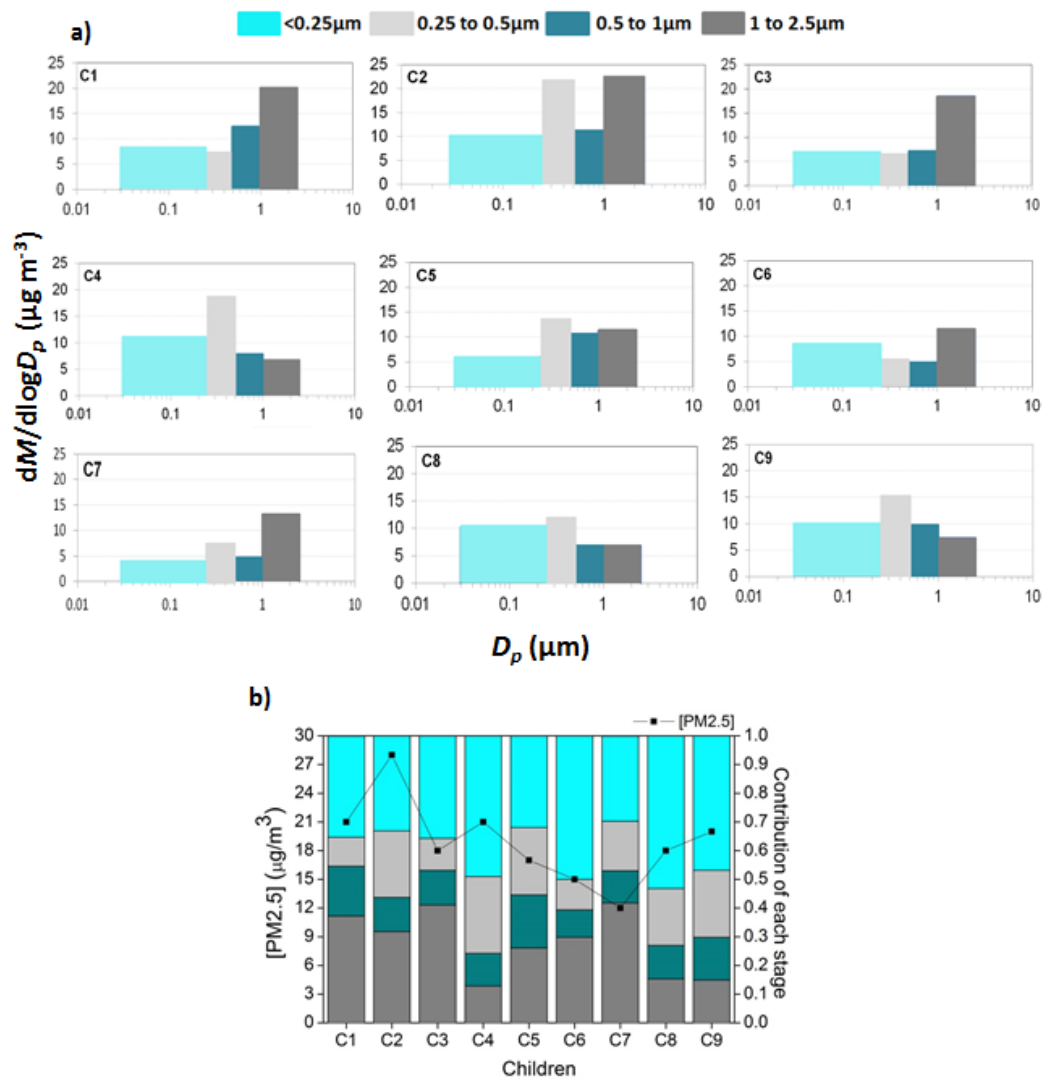
Figure 40 - a) Size distribution pattern of PM2.5; b) PM2.5 concentration to which each child was exposed and the respective size distribution.

The children exposure to PM2.5 varied between 12 and 28 µg/m^3, complying the World Health Organization (WHO) daily reference value of 25 µg/m^3, except in the case of the child C2 (Figure 4b). The average PM2.5 exposure (19 µg/m^3) was higher than those obtained in the nearest fixed urban background station (11 µg/m^3), indicating the importance of assessing the personal daily exposure. The average exposure to PM1, PM0.5 and PM0.25 was 14 (7.2-19 µg/m^3), 11 (5.8-16) µg/m^3, and 7.7 (3.7-10) µg/m^3, respectively.

No trend was found in the particles mass distribution by the different sizes among the 9 children (Figure 4a), probably due to the home and school location, which is influenced by different emission sources and traffic intensities and to the different time-activity patterns. The stages with the greatest contribution to the PM2.5 concentrations were 1<AD<2.5 µm and AD<0.25 µm. For children C2, C4, C5, C6, C8, and C9 the particles with an AD<0.25 µm were those that presented the greatest contribution to the PM2.5 concentration. This stage includes the inhaled and ultrafine particles, capable of depositing in the pulmonary alveoli, get into the bloodstream and reach different organs (Guarieiro and Guarieiro, 2013), thus these children may be more likely to present greater health problems.

The child C7 was exposed to the lowest PM2.5 concentration and about 42% of the mass of PM2.5 was in the fraction 1.0 to 2.5 μm. This child lives in a private condominium in Sintra, surrounded by trees and restricted traffic.

BC CONCENTRATIONS

Table 8 shows the BC concentrations measured in the different ME where children reported to be, in the diary. The lowest BC concentrations from the personal monitoring were measured at home (0.89 μg/m^3) and the highest were registered in the daily commuting. These results were consistent with those of two studies, one carried out with children in Seoul (Jeong and Park, 2017b) and the other in Barcelona (Rivas et al., 2016), which also measured the highest BC concentration in transport and the lowest during the periods that the children were at home. BC results from the incomplete combustion of fossil fuels, being the vehicles the most important BC source in urban areas (Buonanno *et al.*, 2013; Jeong and Park, 2017b; Climate and Clean Air Coalition, 2018). During commuting children were closer to traffic and at night when the traffic emissions were lower the children were at home. For commuting, children used the transport modes car and walking. The highest concentration was registered for car mode (5.1 μg/m^3) following by the commuting on foot (2.5 μg/m^3). Dons et al. (2012) and Jeong and Park (2017b) also showed that the average BC concentration in motorized transports was higher than in active mode.

At home, BC concentration was influenced by indoor sources (example: cooking and heating) and by infiltration from outdoor sources. The highest BC concentration was measured in the home from child C9 (2.2 μg/m^3). This home has an open kitchen, so the BC emitted from cooking disperse easily to the living room. Furthermore, this child lives with a large family composed by nine members. Jeong and Park (2017a) concluded that children with large families faced higher BC exposures than those with small families, due to the fact that a greater number of family members generally require longer times spent on cooking. The home of the child C7 presented the lowest BC concentration (0.36 μg/m^3). As described before this child had also the lowest exposure to PM2.5 due to the lowest volume of traffic near home.

Table 8 - Black carbon (BC) concentrations (average, standard deviation, minimum and maximum) by each children, activity and microenvironment.

Microenvironment			Children									Total
			C1	C2	C3	C4	C5	C6	C7	C8	C9	
Home		Average	0.93	0.47	0.59	0.91	1.1	0.77	0.36	0.73	2.2	0.89
		SD	0.71	0.51	0.29	0.54	0.94	0.61	0.30	0.59	1.0	0.82
		Minimum	0.008	0.013	0.14	0.24	0.017	0.0050	0.0062	0.0040	0.22	0.0040
		Maximum	6.3	4.6	4.5	5.1	8.7	4.7	4.3	3.0	8.8	8.8
Commuting	Car	Average	3.4	3.1	8.3	8.6	6.0	1.8	7.1	4.8	3.1	5.1
		SD	4.7	4.0	8.5	6.6	5.0	3.6	9.1	9.4	3.2	7.3
		Minimum	0.049	0.087	0.40	0.24	0.18	0.045	0.011	0.11	0.0044	0.0044
		Maximum	31	26	38	51	27	29	63	63	13	63
	On foot	Average	NA	1.8	NA	NA	NA	4.6	NA	1.0	NA	2.5
		SD	NA	2.1	NA	NA	NA	5.2	NA	1.4	NA	4.0
		Minimum	NA	0.020	NA	NA	NA	0.37	NA	0.12	NA	0.020
		Maximum	NA	7.9	NA	NA	NA	28	NA	7.6	NA	28
Classroom		Average	0.86	1.1	1.2	1.6	0.87	1.3	0.8	1.2	1.7	1.2
		SD	0.43	0.76	0.54	0.68	0.82	0.46	0.60	0.64	0.79	0.73
		Minimum	0.0020	0.041	0.014	0.25	0.0033	0.063	0.014	0.079	0.0044	0.0020
		Maximum	4.7	5.1	3.1	5.4	4.7	3.7	6.4	4.9	6.9	6.9
Playground at school		Average	0.93	0.91	0.68	2.1	0.73	1.1	0.93	1.3	1.5	1.1
		SD	0.56	0.87	0.48	1.84	0.84	0.78	1.1	1.28	1.7	1.0
		Minimum	0.010	0.020	0.014	0.25	0.0033	0.0041	0.016	0.054	0.12	0.0033
		Maximum	5.4	4.6	3.9	8.4	6.7	7.0	12	8.9	8.2	12
Sport Indoor		Average	0.71	NA	0.80	1.9	NA	1.0	1.0	NA	NA	1.1
		SD	0.36	NA	0.42	1.1	NA	0.95	0.40	NA	NA	0.86
		Minimum	0.2	NA	0.26	0.42	NA	0.036	0.31	NA	NA	0.036
		Maximum	2.8	NA	3.1	6.1	NA	3.2	2.4	NA	NA	6.1
Sport Outdoor		Average	NA	1.1	1.5	2.5	NA	NA	0.83	NA	NA	1.5
		SD	NA	1.0	0.43	1.9	NA	NA	0.28	NA	NA	0.48
		Minimum	NA	0.24	0.014	0.49	NA	NA	0.17	NA	NA	0.014
		Maximum	NA	5.7	3.0	6.9	NA	NA	1.9	NA	NA	6.9
Leisure		Average	2.6	NA	NA	NA	NA	1.0	3.1	1.4	3.0	2.2
		SD	0.53	NA	NA	NA	NA	0.39	2.6	4.9	5.5	4.3
		Minimum	2.3	NA	NA	NA	NA	0.38	0.62	0.032	0.5	0.032
		Maximum	4.2	NA	NA	NA	NA	2.1	10	53	25	53
Extracurricular activities		Average	1.8	2.6	1.7	NA	NA	NA	NA	NA	NA	2.0
		SD	0.53	0.48	1.2	NA	NA	NA	NA	NA	NA	0.99
		Minimum	0.36	1.2	0.16	NA	NA	NA	NA	NA	NA	0.16
		Maximum	2.5	3.7	5.4	NA	NA	NA	NA	NA	NA	5.4

Abbreviations: SD, Standard deviation; NA, Not Applicable

BC levels measured in classrooms (1.2 µg/m^3) and in the playground (1.1 µg/m^3) were very similar and correlated (R^2=0.72), as presented in **Figure 41**. Rivas et al. (2016) analyzed the relation among personal monitoring, fixed stations (school indoor and outdoor) and urban stations and concluded that generally indoor and outdoor school levels follow the urban trends. This confirms the importance of the BC infiltration and influence of the traffic emissions in classrooms.
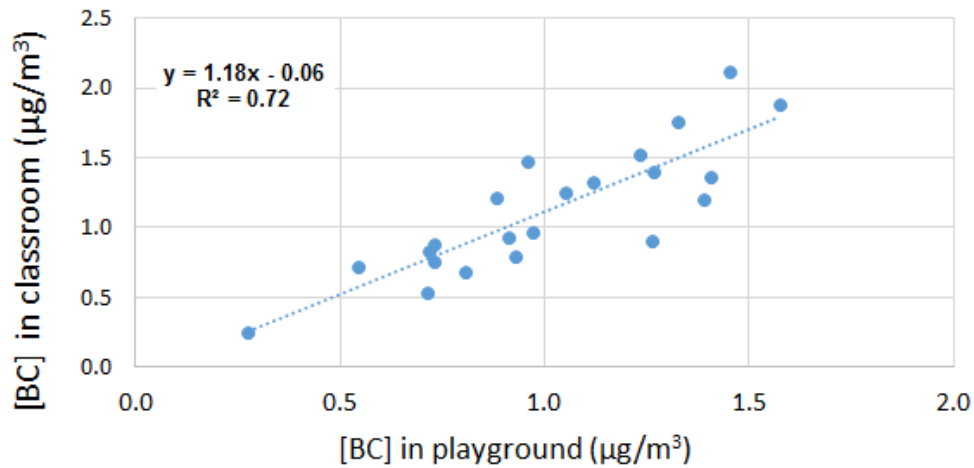

Figure 41 - Correlation of BC concentrations between the playground and the classroom.

The BC concentrations measured during the practice of the sport were very similar for outdoor sport (1.5 µg/m^3) and for indoor (1.1 µg/m^3).

The analysis of time series of the BC concentration allowed the identification of events and their relation with activities identified in the time-activity diary filled by each child. **Figure 42** shows the 24h BC time series of the three children who were exposed to the highest BC peaks. From 00h00 to 7h30 the BC concentrations were constant and low, being associated with the home environment, especially to the sleeping period and, consequently, to the lowest traffic emissions. Very high BC concentrations were measured during rush hours that coincide with the children commuting (peaks identified as A and A$_1$ in Figure 42). The mean BC concentration during commuting by car was 6.3 times higher than average concentrations measured at home. Rivas et al. (2016) also observed very high BC peaks during the rush hours when children commute to school.
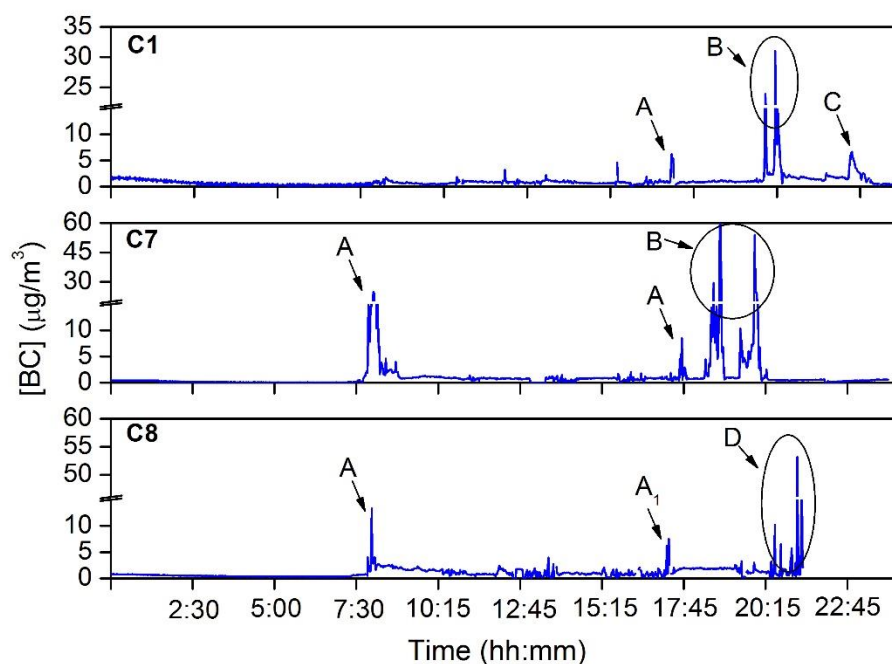
Figure 42 - BC time series corresponding to three children. A – Commuting – car mode; A1 – Commuting – on foot; B – Underground parking lot; C – Birthday party; D – Charcoal grills.

Children C1 and C7 were exposed to a high BC concentration (31 µg/m^3 and 63 µg/m^3, respectively) in the underground parking lot (peaks identified as B in Figure 6). The underground parking lots are completely or partially enclosed, so the pollutants emitted by the vehicles can have difficulty to disperse, depending on the efficiency of the exhaust system of the building. The peak identified by C, in Figure 42, ([BC] = 6.6 µg/m^3) resulted from burning candles in a birthday party. In accordance with Stabile, Fuoco, and Buonanno (2012) the combustion of candles produces carbonaceous particles with a ratio BC/PM10 greater than 0.80. This result suggests the negative impact that the candles can have for the indoor air quality. The child C8 presented a BC peak concentration (peak identified as D in Figure 42) at night during an outdoor party with charcoal grills, which is a substantial source of BC as stated by (Buonanno, Morawska and Stabile, 2009; Jeong and Park, 2017b).

BC EXPOSURE AND RESPECTIVE INHALED DOSES

The relative contributions from each activity/ME to children's daily BC exposure and inhaled dose is presented in **Figure 43**. The daily average BC exposure was equal to 1.3 µg/m^3, which is similar to the BC background concentrations ranging from 1.7 and 1.8 in European cities (Reche *et al.*, 2011) and with elemental carbon concentrations measured in an urban background station in Lisbon (1.5 µg/m^3) (Almeida *et al.*, 2005). The daily average BC inhaled dose was equal to 15 µg. These values were found to be lower when compared to the data reported by Buonanno et al. (2013) from Casino (5.1 µg/m^3 for daily exposure and 39 µg for the daily inhaled dose) and by Jeong and Park (2017b) from Seoul (1.9 µg/m^3 for daily exposure and 24 µg for the daily inhaled dose). A possible reason for the higher values of Buonanno et al. (2013) is the fact that the study was carried out in the winter and 83% of the houses had a fireplace which can release BC from the incomplete biomass combustion (Savolahti *et al.*, 2016; Climate and Clean Air Coalition, 2018; Mousavi *et al.*, 2018). In Seoul the cooking activities have different characteristics that can lead to higher BC concentrations.
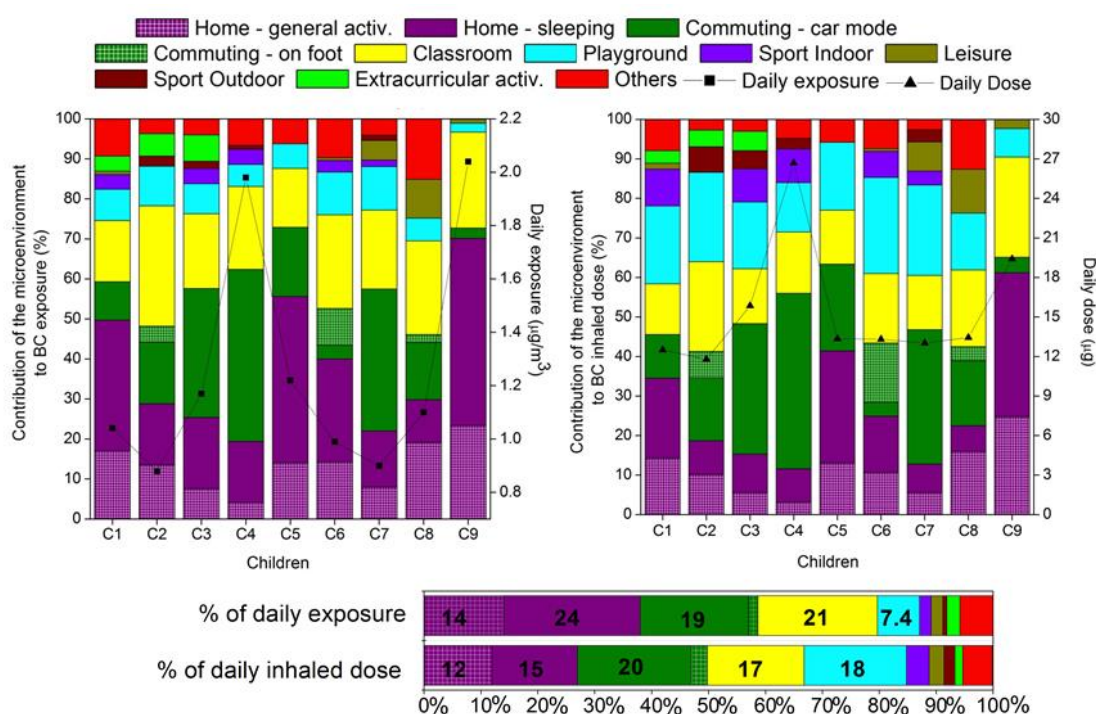
Figure 43 - Contribution of microenvironment to BC exposure and dose and respective total daily exposure and dose of each child.

Home, commuting and school were the MEs that more contributed to the daily exposure to BC and respective inhaled dose.

Besides the lowest BC concentrations measured in homes, this ME contributed 38% for the daily exposure, due to the large amount of time spent there by the children (55%). The contribution for BC exposure was higher while children were sleeping (24%) than awake (14%), because the time spent sleeping (40%) was higher than when they were awake (15%). Similarly, in Seoul (Jeong and Park, 2017b) and Casino (Buonanno et al. 2013) home was the place where children received the greatest daily exposure (52% in both). Considering that the activities carried out at home are sedentary, the home contribution to the inhaled dose decreased to 27%. For the dose, the contribution during sleeping (15%) and awake (12%) is similar due to the fact that the IR is higher while child is awake than when is sleeping. The intensity of BC average exposure and dose was higher while the child was awake (0.88 and 0.73 respectively) than while sleeping (0.60 and 0.38 respectively), because the fraction of the daily time at home was greater to sleep than awake (Figure 8).

Schools contributed for 28% of the daily integrated exposure. The contribution was higher in the classroom (21%) than in the playground (7.4%), due to the great percentage of time spent by children in the classroom (22%). School contributed 35% for the daily inhaled dose. The classroom and the playground presented similar contributions (17% and 18%, respectively) due to the higher inhalation rate of the children while they are in playground that compensates the greater time spent in the classroom. Buonanno et al. (2013) and Jeong and Park (2017b) obtained a similar contribution of the schools to the daily exposure (20% in both studies).

Commuting presented the largest exposure and dose intensity (4.0 and 4.6, respectively, while the other ME presented intensities closer to 1) (Figure 44), which means the highest ratio exposure and dose with the respect to the time spent in the ME. This indicates that BC is a

consistent tracer of the impact of road traffic on exposure. The contribution of the commuting to the BC exposure and dose was 21% and 23%, respectively. However, only 5.0% of the time was allocated to this ME. This result is in agreement with Jeong and Park (2017b) and Buonanno et al. (2013) studies, which verified that the contribution to BC exposure in transportation was 15% (for a daily time 7.6%) and 11% (for a daily time of 4.0%), respectively. Regarding the two modes of commuting (car and walking), the active mode (walking) resulted in a lowest contribution to the BC exposure and dose (1.7% and 2.8%) comparing with car (19% and 20%).
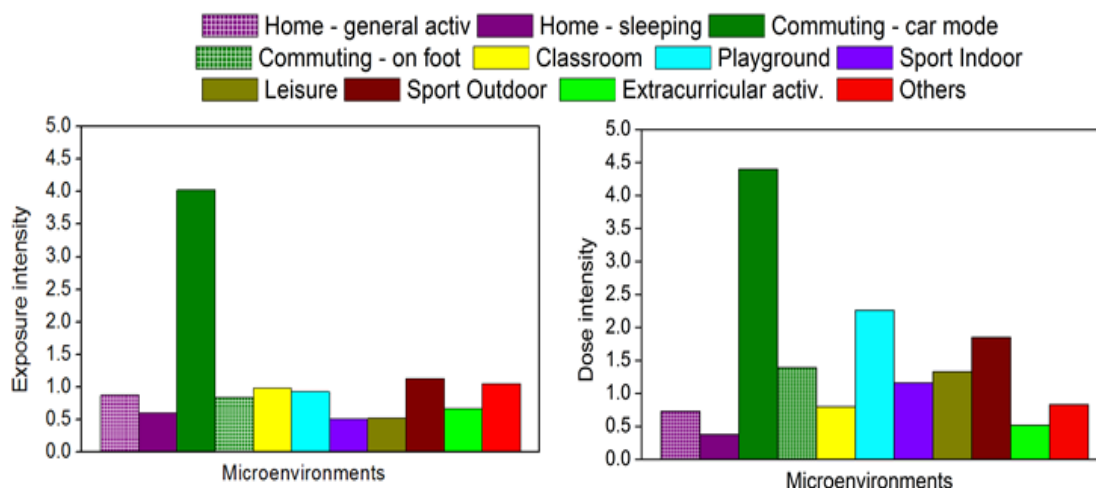

Figure 44 - Exposure and dose average intensities per ME/activity.

The children C4 and C9 presented significantly higher exposure to BC. For child C4, the ME that highly contributed to the BC exposure and inhaled dose was the car. This child was exposed to the highest BC concentration in this ME (8.6 μg/m^3) and spent more time during commuting (10% of the daily time). For children C9, home was the main contributor for the daily exposure and dose. The home of this child presented the highest BC concentrations (2.2 μg/m^3) and the time allocated to this ME was also the highest (about 66% of the daily time).

CONCLUSIONS

The personal exposure of 9 children (aged 7-10 years) who lived and studied in Lisbon metropolitan area was evaluated in terms of sized-fractioned PM and BC concentrations, through the use of a Sioutas personal cascade impactor and a micro-aethalometer. A GPS tracking device and a time-activity diary allowed to identify the activities/ME that make the greatest contribution to the children daily exposure and dose.

The daily exposure depended on the ME frequented and activities performed. The results showed that children spend most of their time indoors (more than 80%), indicating that risk assessment should focus mainly on indoor MEs in order to protect children from adverse health effects that may be caused by PM and more specifically by BC exposure. Home and school were the MEs where the children spent more time and therefore children receive more than half of the BC dose there (62%): 27% in homes and 35% in schools. Nevertheless, the highest BC dose intensity was registered during commuting principally when car (4.4) is used. Considering the results from this work, measures to reduce the exposure to BC should focus on the reduction of traffic around schools. At home, soft measures should be taken such as avoiding to open the windows at rush hour and promoting an efficient exhaust in the kitchen in order to remove the BC emitted from cooking activities. For transportation, routes with less traffic should be selected for the daily commuting in order to help minimize children's exposure.

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