Characterization of ventilation, indoor aerosol and pollution sources of primary schools

Radiation Science and Technology Department

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CHARACTERIZATION OF VENTILATION, INDOOR AEROSOL AND POLLUTION SOURCES OF PRIMARY SCHOOLS

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Proefschrift

ter verkrijging van de graad van doctor
aan de Technische Universiteit Delft,
op gezag van de Rector Magnificus Prof.ir. K.C.A.M Luyben,
voorzitter van het College voor Promoties,
in het openbaar te verdedigen op 10 december 2014 om 10:00 uur

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Dit proefschrift is goedgekeurd door de promotor(en):
Prof. dr. H.Th. Wolterbeek
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The research described in this thesis was performed within the research contract PTDC/SAU-ESA/65597/2006 - Impact of Indoor on Human Health, which was funded by the Fundação para a Ciência e a Tecnologia (FCT; Portugal). The author also acknowledges FCT for his PhD grant (SFRH/BD/72272/2010).

ISBN 978-94-6295-050-4

Keywords: indoor air quality, scholar environemnts, ventilation, passive methodology, biomonitoring, source apportionment

Cover design: Proefschriftmaken.nl || Uitgeverij BOXPress

Printed & Lay Out by: Proefschriftmaken.nl || Uitgeverij BOXPress

Published by: Uitgeverij BOXPress, ‘s-Hertogenbosch

PRINTED IN THE NETHERLANDS

To my dear mum

Table of Contents

1 Introduction

1.1 Motivation

The concern about indoor air quality (IAQ) has increased greatly in recent years along with the characterization of the indoor pollutants and the evidence of their impact on health and performance of people attending those indoor environments.

Since breathing air is a basic human need and each person breathes per day around 12000 to 15000 liters of air, it is easy to understand the potential dose that people are subject to. Moreover, the natural barriers of the human breathing process may not be so effective to stop the pollutants of reaching the bloodstream, especially when the pollutants have a size range in a micro or nano level, which increase their penetrability and effect.

The concentration of pollutants in indoor environments is usually higher than the outdoors, especially if no dilution processes are present in the indoor environments where emissions are continually occurring. Thereby, the predominant presence of people in these environments increases their level of exposure to indoor pollutants.

In susceptible populations, this impact can be even higher. This simple statement conducted to a more careful and dedicated studies about IAQ in classrooms. Outdoor pollutants that penetrate in indoor environments, along with indoor generated pollutants, have been identified and characterized in order to assess the children exposure level. Simultaneously, the impact of the exposures of pollutants on health and performance of the occupants has also been studied extensively. However, these specific indoor micro-environments have characteristics (such as high density of occupancy and the type of activity developed within) that diminish the feasibility of current sampling methodologies. A concrete example is the sampling of particulate matter in classrooms where the noise of equipments may interfere with the classrooms activities.

Ventilation is a crucial factor that may regulate the IAQ of classrooms if it works properly. Therefore, it is very important to know the current ventilation conditions in an occupied room to understand which measures should be undertaken to improve it in order to optimize the IAQ. However, nowadays, ventilation assessment in classrooms can be conducted by different methods using different assumptions.

Moreover, the studies published in the literature are usually only focused on one or just a few parameters. However, indoor air is characterized by a complex mixture of pollutants with synergies between them. Therefore, the full occupants' exposure to pollutants in

indoor air is not really assessed with mono focused studies. Hence, studying the multi-pollutant mixture in indoor air may provide information to understand the pollution sources that are contributing to it.

The main aim of this thesis is to provide tools to understand and to promote healthier learning spaces. For that purpose, this thesis shall address 3 primary goals:

1) Characterization of ventilation conditions in classrooms using practical methodologies;
2) Characterization of IAQ not only by classical methodologies but also by the development of new sampling methodologies;
3) Identification of pollution sources in indoor air of classrooms by the use of source apportionment techniques.

1.2 Indoor Air Quality (IAQ)

Indoor air shortcomings are the most common environmental issues faced nowadays by doctors in medicine (Wilson and Spengler, 1996; Kosonen and Tan, 2004) because indoor air pollution not only can result in health problems, but also increases the human mortality (Jantunen et al., 1997).

The exposure in indoor environments and its health implications varies greatly around the world, depending on the socio-economical development of the countries (Sundell et al., 2004). In developing countries, solid cookfuel use (such as biomass and coal) has a high prevalence which results in exposures to multiple toxic products of incomplete combustion (Balakrishnan et al., 2013). The World Health Organization (WHO) has estimated that the burden disease from household air pollution conducted to 4.3 million deaths in 2012, almost all in low and middle income countries, with main prevalence of deaths by stroke (34%), ischaemic heart disease (26%) and chronic obstructive pulmonary disease (22%) (WHO, 2014). In developed countries, the buildings' conditions and the exposure to pollutants are different and conduct mainly to a high prevalence of allergies, other hypersensitivity reactions, airway infections, and cancers (Sundell et al., 2004).

Mainly in industrialized and developed countries, it is believed that people spend around 90% of their daily time in indoor environments: in between home, school, workplace and in other indoor places where extra and leisure activities are developed (such as shopping, fitness, cultural and even transportation).

The energy crisis of 1973/1974, which resulted from the oil embargo by Arab oil producing countries against the United States, was the turning point to the awareness of the society for the limited sources of energy regarding its demand (Wulfinghoff, 2000). Globally, a new paradigm emerged based in the energy conservation and one of the outcomes was the re-think of the design of new buildings in order to minimize energy losses with tighter envelopes. However, this change promoted inadequate ventilation in buildings.

Later, in the eighties, the impact of IAQ in the health of occupants of buildings in the Western countries was noticed by the increase of health complaints and disease symptoms by their occupants (Jaakkola, 1998). The buildings in these conditions were then considered to be under the effect of the Sick Building Syndrome (SBS), which tried to explain the impact of problems of the IAQ in the health of the occupants (WHO, 1983).

The importance of IAQ has been acknowledged by WHO that, under the principle of the human right to health stated in its Constitution in 1946 (WHO, 2006), established that everyone has the right to breathe healthy indoor air (WHO, 2000) and, therefore, a global effort should be made to satisfy this requirement.

Nazarof (2013) in his editorial of the Indoor Air Journal summarized four simple and basic principles to achieve a good IAQ: 1) minimize indoor emissions; 2) keep it dry, since there is a strong and coherent epidemiological evidences that dampness in buildings is associated with a wide range of respiratory or allergic health effects, as described by the review of Mendell et al. (2011); 3) ventiladed well, ie, to ventilate sufficiently and effectively; and 4) protect against outdoor pollution.

1.2.1 IAQ in schools

Children spend most of their time in indoor environments leading them to a higher exposure to indoor pollutants than outdoor ones. In the specific micro-environments of classrooms, children usually spend around 8h per weekday in scholar facilities from an early age. Additionally, children breathe higher air volumes when compared to their body weight and have a lower capacity to deal with toxic chemicals, which consequently enhances their susceptibility to potential health consequences due to indoor air contaminants (WHO, 2005; Stranger et al., 2008; Selgrade et al., 2007).

Over the last decade, several studies focused on the IAQ in schools because poor IAQ in classrooms, reflected by a poor ventilation which conducts to an indoor accumulation of pollutants, was demonstrated to exert a negative impact on children's learning performance (Mendell and Heath, 2005; Haverinen-Shaughnessy et al., 2011; Wargocki and Wyon,

2007; Bako-Biro et al.; 2012; Twardella et al., 2012), absenteeism (Park et al., 2002; Shendell et al., 2004) and adverse health effects such as increased risk for asthma and other health-related symptoms (Janssen et al., 2003; Salvi, 2007; Sundell et al., 2011; Simoni et al., 2011; Mendell et al, 2013).

1.2.2 IAQ parameters

Classrooms' IAQ comprises a wide range of parameters (Chatzidiakou et al., 2012). Although international guidelines have not been defined for classrooms' IAQ, an international effort has begun to characterize these micro-environments in order to define sampling strategies and guidelines (Chatzidiakou et al., 2012; Annesi-Maesano et al., 2013).

In order to understand the complex physico-chemical system of the indoor air, the mass-balance approach is usually chosen to analyse pollutants' concentrations and also to model and estimate changes in indoor environments (Hänninen et al., 2004, 2013). The mass-balance model, which relies on the principle of conservation of mass, allows to understand the significance of various processes that affect the concentrations and fates of indoor pollutants (Nazaroff, 2004). Basically, all the processes that generate or remove pollutants from an indoor environment are considered and the model provides equations that link input parameters with outcome variables.

Several studies have monitored indoor air concentrations of gaseous compounds (Stranger et al., 2007), particles (Branis et al., 2005; Fromme et al., 2007, 2008), semi-volatile organic compounds (Wu et al., 2010), bioaerosols (Pegas et al., 2010) and allergens (Salo et al., 2009); and other studies have investigated outdoor air contributions (Blondeau et al., 2005; Almeida et al., 2011; Madureira et al., 2012) or the role of different ventilation strategies (Geelen et al., 2008; Guo et al., 2008; Rosbach et al., 2013). Indoor chemistry focused on the formation of secondary organic aerosol, through the reaction of ozone (from outdoors) with terpenes (from indoor sources as cleaning products), has gain special attention on recent years and several studies in schools have now been published (Weschler et al., 2003; Morawaska et al., 2009; Mullen et al., 2011; Fischer et al., 2014) because it has been proven to be responsible for ultrafine particles (UFP) formation in classrooms. Among the terpenes, d-limonene, which is commonly used in cleaning produtcs, conducts to a higher production of UFP during ozonolysis than others (Fischer et al., 2014; Nøjgaard et al., 2006).

1.2.2.1 Particulate Matter (PM)

Health implications due to atmospheric particles pollution have been shown by epidemiological studies where correlations were found between particles concentration and number of deaths from cancer, cardiovascular and respiratory diseases (Pope and Dockery, 2006). Evidence on the increase of hospital admissions due to respiratory and cardiovascular diseases caused by particulate air pollution has also been shown (Middleton et al., 2008). In 2013, the International Agency for Research on Cancer (WHO, 2013) classified particulate matter as carcinogenic to human beings.

The total burden of disease associated with PM has been estimated to be between 6000 and 10 000 disability adjusted life years (DALY) per one million inhabitants (Hänninen and Knol, 2011; Hänninen et al., 2014). This unit, DALY, quantifies both carcinogenic and noncarcinogenic health risks associated to an environmental stressor and it is the measure of health impact due to a disease that takes in account the years of life loss due to premature mortality and the years lost due to disability caused by morbidity (Hänninen and Knol, 2011). Recently, it was estimated that the total burden disease from PM exposure associated only with indoor-generated particles was between 10 and 30% in developed countries (Morawska et al., 2013), which highlights the significant impact that indoor environments have in human health.

Aerosol particles may be originated naturally (e.g. dust, salt, pollen, viruses, fungi, bacteria) or from anthropogenic sources, such as industrial activity, incineration, combustion processes among others (Almeida et al., 2013). The hazardous nature of aerosol particles appears to be related to four factors: the nature and size of the particles, duration of exposure and particle concentration in the breathing zone of the exposed person (Morawska et al., 2013).

The size of particles affects infiltration of outdoor particles in indoor environments (Hänninen et al., 2013) and deposition rates of indoor generated particles (Nazaroff, 2004). In addition, the respiratory tract uptake of particles is also strongly and non-linearly dependent on particle sizes (Hussain et al., 2011; Madl and Hussain, 2011).

The exposure to PM in indoor environments is due to outdoor and indoor sources and differs significantly in composition, temporal patterns and their relationship to personal time-activity patterns (Morawska et al., 2013).

Moreover, PM is also associated with occupancy because some human activities in indoor environments promote significant high concentrations of inhalable particles compared to

background concentrations (Ferro et al., 2004). These particles can come from the body itself (through skin shedding, breathing, couching or sneezing), from human activities that produce PM such as cooking, cleaning, smoking, use of candles or even the use of chalk to write in blackboards, in the specific case of classrooms; or from human activities that promote the aerosolization of particles previously bounded to indoor surfaces (such as walking or sitting) (Qian et al., 2014).

The re-suspension of particles refers to their detachment from surfaces (flooring or furnishing) and reentrainment into the air; and it increases with particle size in the range of 0.7-10 μm (Qian et al., 2014). This phenomenon can increase the risk of exposure to indoor particle through inhalation and non-dietary ingestion.

1.3 Ventilation

Ventilation comes from Latin word ‘‘ventilare’’, which means ‘‘to expose to the wind’’ (Sundell, 2004). The main goal of ventilation is to create optimal conditions of air quality and thermal comfort in indoor environments, taking in account the health, comfort and productivity of their occupants (Liddament, 1996).

Indoor airborne pollutants can be generated by human occupants, their activities, building materials, furnishings, unvented combustion and other processes that emit pollutants into indoor environments of buildings. The concentration of any substance or airborne pollutant in the atmosphere in a building is determined by the generation rate of the pollutants and their removal rate. Ventilatiom is the action of providing outdoor air into a building or a room, promoting its distribution indoors in order to dilute the pollutants generated within and to remove them with the exhaust air. Naturally, the effectiveness of the ventilation process depends greatly on the availability of cleaner outdoor air (Li, 2011).

Different types of ventilation are usually used in classrooms: mechanical, natural or mixed/hybrid systems (Limb, 1997). In colder climates, such as north European countries, buildings need to be airtight as possible to conserve heat and, in these cases, natural ventilation is usually unable to provide adequate ventilation for odour and contaminant removal. Therefore, in these countries, mechanical ventilation is chosen to achieve minimum ventilation rates. However, in warmer regions, natural ventilation systems are usually used and are driven by wind and thermally (stack) generated pressures (Dimitroulopoulou, 2012). Natural ventilation has the benefit to be a low cost ventilation system but, however, it has been proved that naturally ventilated classrooms have often shown to not provide adequate ventilation rates in order to avoid indoor pollutants or bio-

affluents accumulation (Annesi-Maesano et al., 2013). Mechanical ventilation systems provide better ventilation rates in classrooms but, besides the energy requirement, an often maintenance is required in order to assure a good functioning, which adds extra costs (Gao et al., 2014).

The paradigm of low energy buildings had emerged in order to maximize energy savings, which led to a tightening of building envelopes and, when not correctly designed and though, often reduced ventilation conditions (Heinrich, 2011).

Overall, the choice of ventilation strategy depends on indoor air requirements, heating and cooling needs, outdoor climate, building characteristics (as air tightness), cost and design preference (Dimitroulopoulou, 2012).

1.4 Thesis outline

The setting for this thesis is the concern that exposure to indoor air pollutants could cause adverse effects in health, performance and attendance in children attending classrooms. The thesis is focused in three main issues, namely, 1) ventilation, which can influence greatly IAQ; 2) new sampling methodologies to evaluate IAQ and 3) application of source apportionment techniques to understand the main sources of PM air pollution in these microenvironments. The primary impact of this study is to provide tools to evaluate IAQ in classrooms, using practical methodologies, in order to improve it.

Figure 1.1 shows the scheme of the design of this thesis, where the novelty of the work and main outcomes are explained, along with the reasoning beyond it.

Chapter 2 describes the ventilation conditions of classrooms from two countries, Finland and Portugal. The former represents a Northern European country with mechanical ventilation systems typically used in public buildings including schools. Portugal represents Southern European conditions, where natural ventilation systems are dominant. A new method to assess ventilation rates, which is based on a computerized tool that relies on the build-up phase of indoor generated CO_2, was used. This chapter shows for the first time the use of this tool that is under development within a survey program carried out by WHO to assess IAQ in schools.

Chapter 3 describes IAQ assessment by classical methodologies centred on ventilation indicators, a wide range of IAQ parameters and, later, focused on particulate matter. Characterization of ventilation by four different indicators is proposed and the relations

with IAQ parameters were evaluated. A full characterization of the indoor $PM_{2.5}$ levels and chemical composition in classrooms was also conducted and sources were identified.

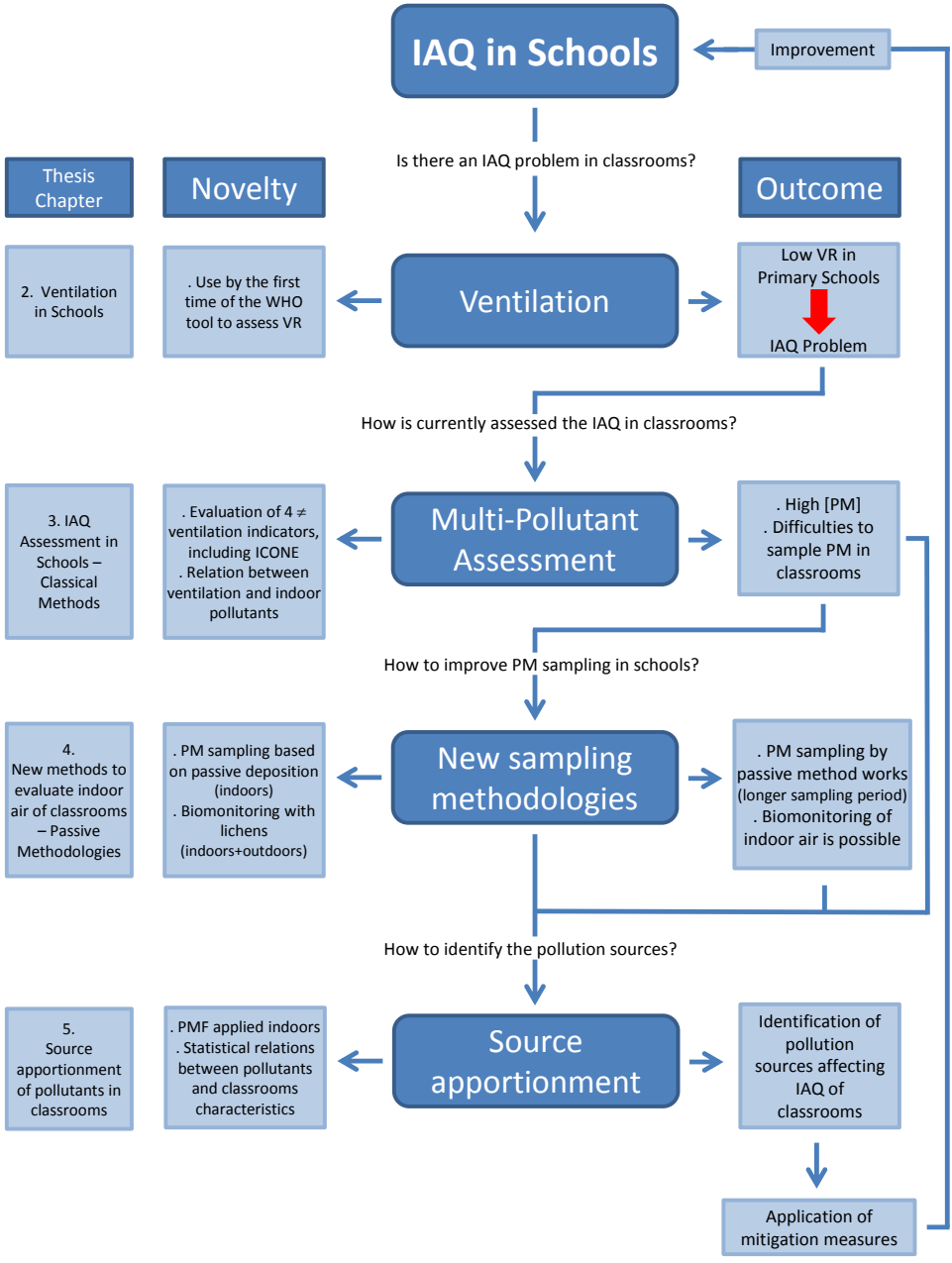

Figure 1.1 Design of the thesis.

Chapter 4 describes the development, applicability and evaluation of new passive sampling methodologies for the indoor air of classrooms: passive sampling of indoor particles on filters and biomonitoring with lichens in indoor and outdoor of classrooms.

Chapter 5 focuses on methods of source apportionment in classrooms to identify pollution sources, by Positive Matrix Factorization technique and by statistical associations between indoor air parameters with the schools' building characteristics.

Chapter 6 provides a summary and discussion of the results, along with some suggestions for future research.

2 Winter Ventilation Rates at Primary Schools: Comparison between Portugal and Finland

Based on article of same title:
Canha N, Almeida SM, Freitas MC, Täubel M & Hänninen O
Journal of Toxicology and Environmental Health, Part A: Current Issues (2013)
76(6), 400-408. DOI: 10.1080/15287394.2013.765372

2.1 Abstract

This study focused on examination of ventilation rates in classrooms with two different types of ventilation systems: natural and mechanical. With this purpose, carbon dioxide (CO_2) measurements were conducted in primary schools of Portugal characterized by natural ventilation and compared to Finland where mechanical ventilation is usual. The winter period was chosen since it has a great influence in the natural ventilation of classrooms, mainly in habits of opening of windows and doors due to outdoor atmospheric conditions. The ventilation rates (VRs) were calculated by the monitoring of the CO_2 concentrations produced by the occupants (used as a tracer gas) and the application of the build-up phase method. A comparison between both countries results was conducted concerning the VRs, and their framing within the national regulations evaluated. Finnish primary schools (n=2) registered a mean VR of 13.3 L/s per person which is above the recommended ventilation standards. However, the Finnish classroom that presented the lowest VR (7.2 L/s per person) had short-term CO_2 levels above 1200 ppm, which is the limit value recommended by national guidelines. Meanwhile the Portuguese classrooms (n=2) showed low VRs, namely mean values of 2.4 L/s per person, which is substantially lower than the minimum recommended value of 7 L/s per person defined by American Society of Heating, Refrigerating and Air-Conditioning Engineers (ASHRAE) and 20% less than the Federation of European Heating, Ventilation and Air-conditioning Associations (REHVA) minimum of 3 L/s per person. Carbon dioxide limit levels of 1000 ppm were also reached in both studied Portuguese classrooms. This situation features a potentially serious indoor air quality (IAQ) problem and strengthens the need for intervention to improve ventilation rates in naturally ventilated classrooms.

2.2 Introduction

Poor ventilation in schools was demonstrated to exert a negative impact on children's learning performance, absenteeism and health effects such as increased risk for asthma and

other health-related symptoms (Annesi-Maesano et al., 2013). Other consequences of poor ventilation are the accumulation of human metabolites, microorganisms, and pollutants emitted from furniture, building materials, and other indoor sources (Dimitroulopoulou, 2012; Almeida et al., 2011). Children are more vulnerable to environmental pollutants compared to adults since they breathe more air relative to their body weight and also have a lower capacity to deal with toxic chemicals (Selgrade et al., 2008; Firestone et al., 2008).

In the recent years, several studies were conducted to determine the relationship between carbon dioxide (CO_2) levels inside the classrooms and student performance. Haverinen-Shaughnessy et al. (2011) performed a study to evaluate the relationship between classroom VRs and academic achievement where 100 elementary schools in southwestern United States were examined. In this study, VRs were estimated from fifth-grade classrooms (one per school) using CO_2 concentrations measured during occupied school days. In addition, standardized test scores and background data related to students in the classrooms were assessed. Of 100 classrooms, 87 had VRs below recommended guidelines based on ASHRAE Standard 62, and a linear association was found between classroom VRs and student academic achievement within the range of 0.9–7.1 L/s per person. For every unit (1 L/s per person) increase in VR within that range, the proportion of students passing standardized test (i.e., scoring satisfactory or above) was expected to rise by 2.9% (95%CI 0.9 – 4.8%) for math and 2.7% (0.5 – 4.9%) for reading.

Sundell et al. (2011) performed a review of the literature regarding VRs in schools and the consequent influence on students. Data demonstrated that low VRs as evidenced by a 1000-ppm(v) rise in dCO_2 (the difference between simultaneously measured indoor and outdoor CO_2 level) in schools were associated with increased absenteeism (0.5–0.9% decrease in annual average daily attendance after controlling for other factors known or suspected to be associated with absence). Moreover, data confirmed the hypothesis that a low air exchange rate in schools may affect the airways and produce nasal mucosa swelling (Walinder et al., 1998).

Twardella et al. (2012) performed a study in 20 classrooms of German primary schools with mechanical ventilation systems for a period of 3 weeks where concentration performance was assessed by a d2-test, which is a one-page, paper-and-pencil test where several parameters are evaluated, such as processing speed, accuracy, and overall concentration. In total, 417 students participated in this study, and it was found that student's accuracy decreased significantly in "worse" test conditions (with a median CO_2 level on average 2115 ppm) comparing with "better" test conditions (with a median CO_2 level on average 1045 ppm).

As a follow up of early studies, Bakó-Biró et al. (2012) published the results of a study carried out in seven British primary schools with natural ventilation. Carbon dioxide concentrations among other parameters were determined and interventions were made to improve the VRs in the classrooms without the knowledge of the occupants, with an improvement of 1 L/s per person until approximately 8 L/s per person was achieved. Computerized performance tasks to assess the pupils' cognitive performance, based on the software VISCoPe, were conducted on the students in both situations. In total 200 pupils participated in this study, and data showed significantly faster and more accurate responses for Choice Reaction (by 2.2%), Color Word Vigilance (by 2.7%), Picture Memory (by 8%) and Word Recognition (by 15%) at the higher VRs compared with low ventilation conditions. Overall, Bakó-Biró et al. (2012) concluded that low VRs in classrooms significantly reduce pupils' attention and vigilance, and negatively affect memory and concentration. Satish et al. (2012) also confirmed that CO_2 levels are directly associated with mental functions and thus adversely affected learning performance of pupils.

Therefore, the study of VRs in academic facilities is of particular importance since it exerts a direct influence on performance and health of the students attending the classrooms. The current study focused on the comparison between two different types of schools ventilation, natural (NV) and mechanical (MV), in winter. Generally, the type of ventilation is an indicator of the country climactic characteristics. South European countries, such as Portugal, have mainly NV-type schools while North European countries, as Finland, have MV-type schools. Increased CO_2 levels have been predominantly recorded in winter in classrooms (Twardella et al., 2012). In fact, due to the cold temperature of outdoor air, the frequency of window opening is diminished, which therefore results in accumulation of CO_2 in indoor air. The CO_2 concentration generated by the occupants was used as a tracer gas for VRs calculation applying the build-up phase method (Hänninen, 2013). A comparison between both countries' results was conducted with respect to VRs and how these values fit within the national regulatory standards.

2.3 Methods

2.3.1 Sampling Sites

A CO_2 survey for one full day was conducted during winter season in primary schools of center mainland of Finland (December) and Portugal (March) Figure 2.1 shows the location of the studied primary schools.

Figure 2.1 Location of the studied primary schools in Portugal and Finland, Europe.

In Finland, two primary schools of the urban area of Kuopio were studied. In each school, the CO_2 measurements were conducted in three classrooms for a full day of classes during the winter period (December 2011). These schools have MV and air conditioning. All classrooms had their doors inside the school building facing an indoor hallway. The classrooms volume ranged from 184 to 231 m^3 and occupancy ranged from 15 to 20 students of approximately 10 years of age.

In Portugal, one primary school was studied in the rural area of Ponte de Sor municipality, in a rural village named Foros de Arrão. At this school, two classrooms were studied for a full day of classes during the winter period (March 2010). The type of ventilation of this school is NV and wood burning is used for house heating during the colder period. Both classrooms had their doors towards the outdoors of the school building. In one classroom a fireplace (FP) was used during the learning period for indoor heating (volume of 179 m^3 and an occupancy of 20 students aged approximately 10 years of age), while in the other classroom a slow combustion stove (CS) was used for the same purpose (volume of 159 m^3 and an occupancy of 19 students aged approximately 10 years old).

2.3.2 Sampling Methodology

The CO_2 measurement devices with nondispersive infra-red used in this study were HD21AB17 (mDelta OHM; range: 0 - 5000 ppm; accuracy: 3%) and ClimaBox3 (supplier: Hanwell; range: 0 - 4000 ppm; accuracy: 3%) in Finland and a Wolfsense IQ-610 (Graywolf Sensing Solutions; range: 0 – 10000 ppm; accuracy: 3%) in Portugal.

Different devices were used in a preliminary evaluation of their performance. It was found that values obtained using different devices only varied between each other by less than 50 ppm under equivalent sampling conditions. Therefore, all three different devices were used for this study since their CO_2 signal was consistent between devices. The devices were placed inside the classrooms before the beginning of the classes, and at the end of the school day were collected. The devices were placed at a height of about 1.2 m to correspond with children's breathing zone.

The sampling was done in continuous mode, and each device, in addition to the CO_2 measurement, also recorded temperature and relative humidity (Table 2.1). The sampling frequency for all the devices was 15 s, except for the ClimaBox3 device where minimum sampling frequency was 1 min.

Table 2.1 Environmental parameters (Relative Humidity and Temperature) in the studied schools.

			Relative Humidity, %		Temperature, ºC	
Country	School	Classroom	Average	Range	Average	Range
Portugal	1	Fireplace (FP)	58 ± 6	49 – 76	20.4 ± 1.0	16.6 - 21.5
		Combustion Stove (CS)	57 ± 4	47 - 65	18.0 ± 0.8	15.1 - 19.0
Finland	1	1	25± 2	22 – 29	22.4 ± 0.4	21.2 - 22.9
		2	26 ± 2	14- 29	22.3 ± 1.1	16.4 - 23.3
		3	34 ± 3	30 – 40	19.5 ± 0.9	18.2 - 21.0
	2	1	24 ± 2	20 - 28	20.7 ± 0.3	20.2 - 21.4
		2	24 ± 2	21 – 28	20.6 ± 0.3	20.1 - 21.1
		3	26 ± 3	20 - 31	21.1 ± 0.4	20.0 - 21.9

At the laboratory, data were downloaded from devices and formatted to comply the input requirements for the Excel tool developed as part of the ongoing World Health Organization Regional Office for Europe school survey at THL to calculate the VRs (WHO, 2000, 2011). This excel tool is based on the CO_2 build-up method to estimate VRs during classes. The method includes a novel second-degree solution to the single-compartment complete mixing mass-balance equation for the steady-state level.

2.3.3 Calculation of Ventilation Rates

The VRs in this study were calculated using the build-up method (Hänninen, 2013) based on a tracer gas approach. This type of approach is based on a definition of a target volume ranging from a complete building to a selected room and an assumption of sufficient

mixing of tracer gas in the airflow through that space. Carbon dioxide provides a significant advantage over other tracer gases since this gas is readily emitted by building occupants and is inert, and heat and activity of occupants contribute to mixing of CO_2 in air. In fact, CO_2 is especially suitable as a tracer gas for high-occupancy spaces like schools, since the overall generation rate is high in comparison to natural background concentrations.

In a CO_2 event, which is a single CO_2 curve obtained over time, it is usually possible to distinguish three different phases: (1) build-up, where the CO_2 emission level is higher than the air exchange rate (AER); (2) steady state, a balance is reached between the CO_2 emission level and the AER; and (3) decay, when the occupants leave the room and the CO_2 level begins to decrease until the gas reaches background level in the air intake (Persily, 1997).

Concerning the build-up phase, after a space becomes occupied, the indoor CO_2 level begins to rise until the emission level and AER are in balance and a steady state is reached. The raising concentration in a well-mixed room can be expressed as:

(Equation 2.1) $$C(t) = \frac{G}{AER \times V}(1 - e^{-AERt}) + C_r$$

Where C(t) is the CO_2 concentration (ppm) at time t (h), G is the CO_2 generation rate (mL h^{-1}) introduced at t = 0, AER is the air exchange rate (h^{-1}), V is the room volume (m^3), and Cr is the CO_2 concentration in the replacement air (ppm(v)). The CO_2 level in the replacement air (Cr) includes the outdoor air background and any potentially existing addition to that due to air recirculation and mixing between zones.

AER can be solved from Equation 2.1 using two concentration readings a suitable time apart.

(Equation 2.2) $$AER = \frac{1}{t}\ln\left(\frac{C_{ss}-C_0}{C_{ss}-C_t}\right) \leftrightarrow AER = \frac{1}{t}\ln\left(1 - \frac{C_t-C_0}{C_{ss}-C_0}\right)$$

Where AER is the air exchange rate (h^{-1}), t is the time (h) between observing C_0 and C_t, C_{ss} is the final steady-state concentration (ppm(v)) as solved in Equation 2.3, and C_0 is the concentration (ppm) at the beginning (t = 0) and C_t is the concentration at time t. The preceding equation requires the knowledge of the steady-state concentration (C_{ss}), which can be either observed by following the build-up as long as to reaching the equilibrium or by solving the equilibrium level from the build-up curve through Equation 2.3 (Hänninen, 2013):

(Equation 2.3) $$C_{ss} = \frac{C_b^2 - C_a C_c}{2C_b - C_a - C_c}$$

Where C_{ss} is the steady-state concentration (ppm(v)) at the final equilibrium, C_a, C_b and C_c are concentrations (ppm) at equally spaced times a, b, and c during the buildup ($a < b < c$ and $b - a = c - b$).

The ventilation rate Q ($m^3\ h^{-1}$) is then given by Equation 2.4, where AER is the air exchange rate calculated previously and V is the volume of the room. The ventilation rate per person VR (L/s per person) is obtained from Equation 2.5 where Q is the ventilation rate previously calculated and n is the number of occupants of the room.

(Equation 2.4) $$Q = AER \times V$$

(Equation 2.5) $$VR = \frac{Q}{3.6n}$$

The build-up method, along with the decay, requires good temporal resolution where there is at least a sampling frequency below 2 min, otherwise it is not possible to (1) obtain a well-defined CO_2 curve of indoor CO_2 levels for both and accurate numerical calculation and (2) recognize the fulfillment of all requirements for analysis assumptions of emission levels, occupancy, and steady ventilation over the target time window. In fact, technical advances in monitoring devices over the last decade have improved the memory capacity and made it feasible to collect longer time series of high-frequency data, allowing for identification of build-up and decay periods for AER estimation.

2.4 Results and Discussion

2.4.1 Comfort Parameters in Classrooms

Temperature and the relative humidity measured inside the classrooms were more variable in Portugal than Finland. In Portugal, the indoor temperature had a median value of 19.1◦C (10% percentile, 17.3◦C; 90% percentile, 21.2◦C) while in Finland the median value of the temperature was 20.2◦C (10% percentile, 20.2◦C; 90% percentile, 22.8◦C). The European Standard EN15251 established the optimal range of temperature for the winter season of 20–22◦C for classrooms.With respect to this guideline, only Finnish school 2 complied with these values while the Portuguese classrooms were slightly below these values and the Finnish school 1 had two classrooms with temperature values above the recommended and one classroom had values below the recommended. Concerning the indoor relative humidity the differences between both countries were greater. In Portugal, the median value of relative humidity was 56% (10% percentile, 52%; 90% percentile, 63%) while in Finland

was 26% (10% percentile, 22%; 90% percentile, 29%), indicating that Finnish classrooms have a substantially drier indoor environment in winter.

2.4.2 CO_2 Concentrations in Classrooms

A number of standards and guidelines for CO_2 have been set in Finland, Portugal, the rest of Europe and the United States (Table 2.2). The EN standard and REHVA recommendations for minimum ventilation are substantially lower than the other listed values. The European Standard EN15251 and REHVA Guidebook 13 propose performance-based standards limiting the levels of CO_2 concentration to 1500 ppm over a full school day from 9:00 to 15:30 while the Portuguese guideline specify a CO_2 limit of 1000 ppm in indoor environments, along with the ASHRAE recommendation in the United States. The Finnish guideline recommends a limit value of CO_2 of 1200 ppm.

Table 2.2 Carbon dioxide and Ventilation Standards/Regulations in Europe and the United States, and the specific ones of the studied countries.

Country/Area	Standard Reference/Guideline	CO_2 limits (ppm) (site)	Ventilation Rate, VR (L/s per person) (site)
USA	ASHRAE, 2007	1000 (Teaching facilities)	7 (Teaching facilities)
Europe	EN15251, 2007	1500[a] (Schools)	3 (Schools)
Europe	REHVA, 2010	1500[a] (Schools)	3 (Schools)
Portugal	RSECE, 2006	1000 (Buildings)	8.3 (Schools)
Finland	NBC – D2, 2010	1200 (Buildings)	6 (Teaching room)

[a] limiting the level of carbon CO_2 concentration to 1500 ppm over a full school day from 9:00 to 15:30

The studied Portuguese classrooms registered CO_2 values higher than the Portuguese limit value of 1000 ppm while only one classroom of one Finnish school (school 1) showed values higher than 1200 ppm, which is the CO_2 level limit recommended by the Finnish guidelines (Table 2.3). All classrooms of Finnish school 2 and the other classrooms of Finnish school 1 registered CO_2 levels always under the national limit of 1200 ppm.

Table 2.3 Carbon dioxide concentrations in the studied schools.

Country	School	Classroom	CO_2 Concentration (ppm)	
			Average	Range
Portugal	1	Fireplace (FP)	850 ± 200	470 - 1300
		Combustion Stove (CS)	750 ± 220	380 - 1200
Finland	1	1	660 ± 150	430 - 920

	2	810 ± 180	450 - 1100
	3	840 ± 270	520 - 1400
2	1	460 ± 90	370 - 650
	2	570 ± 70	490 - 750
	3	570 ± 100	430 - 810

2.4.3 Ventilation Rates in Classrooms

The CO_2 sampling in all the classrooms for both countries is shown in Figure 2.2. The Portuguese classrooms had lessons in the morning and in the afternoon (lunch period at 12:00, which corresponds to the observed decay of CO_2 level). The Finnish schools only had lessons until 14:00. In each classroom it was possible to observe from three to six CO_2 events that corresponded to the lessons that students were attending.

The AERs and VRs calculated from the CO_2 build-up phase for the studied schools are presented in Table 2.4. In total, 11 CO_2 events were used for the calculations of Portuguese data, while in total 19 CO_2 events were used for the Finnish schools.

The standards/regulations related to ventilation rates in classrooms are summarized in Table 2.2.

In teaching facilities, the current ventilation standards and guidelines by ASHRAE recommend a minimum VR of 7 L /s per person (ANSI/ASHRAE Standard 62.1–2007). The European Standard EN15251 and REHVA Guidebook 13 specify a minimum VR of 3 L/s per person in all teaching and learning spaces when occupied. Both studied countries have specific regulations for ventilation control and VR that are recommended for classrooms are 6 and 8.3 L/s per person for classrooms for Finland and Portugal, respectively.

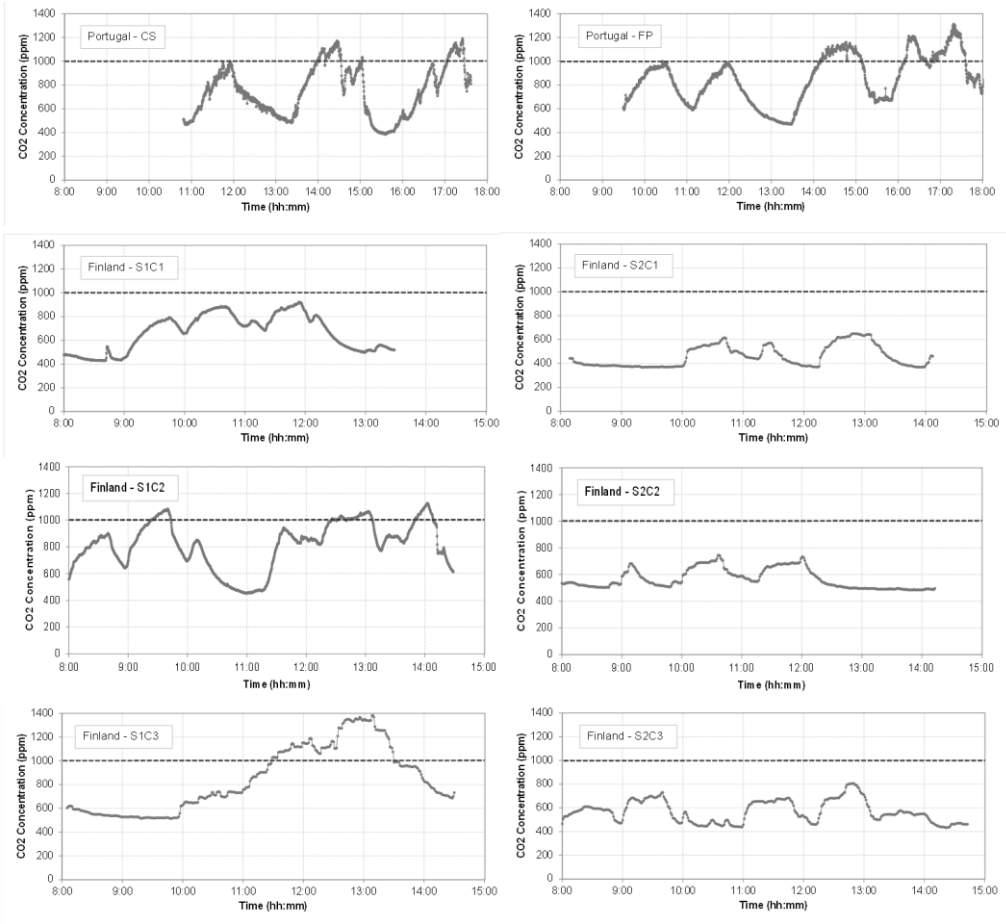

Figure 2.2 Levels of CO_2 measured inside the studied classrooms: Portuguese classrooms with a fireplace (FP) and a slow combustion stove (CS) and Finnish classrooms (S1 and S2 are, respectively, school 1 and school 2; and C1, C2 and C3 are the classrooms 1, 2 and 3, respectively). Dash line is the recommended CO_2 limit value in the Portuguese and Finnish standards.

Major differences in AER were found between both countries (Table 2.4). Monitored Finnish classrooms had an average AER of 4.6 h^{-1}, while in the Portuguese classrooms the mean value was 1.0 h^{-1}. Finnish schools registered mean VRs of 13 L/s per person, which is above the recommended value of 6 L/s per person by the Finnish guideline (NBC–D2, 2010). In contrast, Portuguese classrooms showed low VRs, with mean values of 2.4 L/s per person, which is below the minimum requirements of the national ventilation standard (RSECE, 2006) and even below the lower limit of 3 L/s per person recommended in Europe

by CEN and REHVA. Due to the outdoor conditions, the opening of windows and doors is probably diminished and therefore generates CO_2 accumulation, which is reflected by low VRs.

Table 2.4 Summmary of AERs and VRs calculated from CO_2 build-up phase for the studied schools.

Country	School	Classroom	CO_2 events	AER (h^{-1})	VR (L/s per person)
Portugal	1	Fireplace (FP)	5	1.2 ± 0.1	2.9 ± 0.3
		Combustion Stove (CS)	6	0.90 ± 0.30	2.1 ± 0.7
		School mean		1.0 ± 0.3	2.4 ± 0.7
Finlad	1	1	4	4.1 ± 0.8	14 ± 2
		2	4	3.1 ± 0.4	9.0 ± 2.0
		3	2	3.0 ± 0.3	7.2 ± 0.8
		Overall mean	10	3.5 ± 0.7	11 ± 3
	2	1	2	5.2 ± 1.5	16 ± 4
		2	2	6.5 ± 0.1	20 ± 0
		3	5	5.8 ± 0.6	15 ± 2
		Overall mean	9	5.8 ± 0.8	16 ± 3
		Schools Mean		4.6 ± 1.4	13 ± 4

The Finnish schools that were studied presented an overall mean of 13 ± 4 L/s per person (within a range from 7 to 20 L/s per person), which is clearly above the recommended minimum values by country legislation (6 L/s per person). These values are within the range of the VRs in Finnish primary schools reported by Palonen et al. (2009), where the median value was 4 L/s per student within a range of 1 to 20 L/s per student. In this study, in total 60 primary schools in southern Finland were studied and approximately 15% had passive stack ventilation.

However, although all classrooms of the Finnish school 1 complied with the national ventilation guidelines, one of the classrooms presented VR of 7.2 L/s per person, namely, classroom 3. In this classroom, the recommended CO_2 limit value of 1200 ppm by the Finnish guideline was reached and a maximum value of 1383 ppm was observed. Therefore, the assurance of minimum ventilation recommended by authorities is not a guarantee for compliance with the CO_2 recommended limit values.

2.5 Conclusions

This study indicated that during winter naturally ventilated schools may show ventilation rates clearly below the recommended values. Such cases require intervention to improve a potentially serious indoor air quality problem. Mechanical ventilated schools, even in winter, comply with the ventilation guidelines, as the results from the Finnish studied schools showed.

As it is known, the type of ventilation (mechanical or natural) plays a major role on ventilation rates in primary schools (Dimitroulopoulou, 2012). However, although some Finnish classrooms presented ventilation rates above the recommended values by national standards, CO_2 limit levels were still attained inside the classrooms, indicating that the recommended value of ventilation rate was not sufficient to avert CO_2 accumulation above the 1200-ppm threshold.

In this study, natural ventilation was conducted in classrooms during winter at a time when ventilation rates are low and thus do not allow renewal of indoor air. Consequently, there is an accumulation of indoor pollutants. Hence, corrective measures need to be carried out to improve ventilation rates in naturally ventilated classrooms. Thus, improvement of indoor air quality classrooms will diminish the negative health impact on students.

3 IAQ Assessment in Schools – Classical Methods

3.1 Assessment of ventilation and indoor air pollutants in nursery and elementary schools in France

Based on article of same title:
Canha N, Mandin C, Ramalho O, Wyart G, Ribéron J, Dassonville C, Hänninen O, Almeida SM & Derbez M
Submitted to Indoor Air, July 2014.

3.1.1 Abstract

The aim of the present study was to characterize and assess the relationship between indoor air quality (IAQ) and ventilation in French classrooms. Over one week in 51 classrooms at 17 schools, various parameters were measured, including volatile organic compounds (VOCs), aldehydes, particulate matter ($PM_{2.5}$ mass concentration and number concentration), carbon dioxide (CO_2), air temperature and relative humidity (RH). Ventilation was characterized by a number of indicators that are linked to indoor CO_2 concentration such as the ventilation rate (VR) and the ICONE (Indice de CONfinement d'air dans les Ecoles) air stuffiness index. The influences of season (heating or non-heating), type of school (nursery or elementary) and ventilation on IAQ were studied. Based on the minimum value of 4.2 L/s per person, which is required by the French legislation for mechanically ventilated classrooms, a majority (91%) of the studied classrooms had insufficient ventilation. The VR was significantly higher in mechanically ventilated classrooms compared with naturally ventilated rooms. High VRs were associated with low indoor concentrations of $PM_{2.5}$, 1,4-dichlorobenzene, acetaldehyde, formaldehyde and hexaldehyde. For benzene and for all of the studied aldehydes, the indoor concentrations were significantly different between heating and non-heating seasons.

3.1.2 Introduction

Children constitute a population that is susceptible to exposure to air pollutants, not only because their respiratory and immune systems are not fully developed but also because they breathe higher air volumes in relation to their body weights (WHO, 2005). In that context, the indoor air quality (IAQ) of school environments has become a growing concern within the scientific community; there is evidence that connects poor IAQ to negative impacts on

students' health, performance and attendance (Daisey et al., 2003; Mendell and Heath, 2005).

In France, some studies were conducted in schools, but only in limited numbers (Blondeau et al., 2005; Poupard et al., 2005; Annesi-Maesano et al., 2012) or for a limited number of indoor air pollutants (Michelot et al., 2013).

Because of the lack of knowledge in this field in France, the French Indoor Air Quality Observatory (OQAI) was commissioned to assess children's exposure to various indoor air pollutants in nursery and elementary schools. A study was conducted in 51 classrooms in 17 French nursery and elementary schools. The specific objectives of the study were to (i) characterize IAQ, (ii) characterize ventilation through different complementary means and (iii) study the relationships between indoor air concentrations and ventilation conditions, including the types of ventilation systems. Within the school IAQ literature, few studies have been dedicated to these relationships (Chatzidiakou et al., 2012). The present study considered other potentially influential parameters, such as type of school and sampling season.

3.1.3 Materials and Methods

3.1.3.1 Study Site and School Descriptions

The study area was the town of Clermont-Ferrand and the surrounding area, which has a population of 139,860 inhabitants in 42.68 km^2 and is located in the region of Auvergne in the center of France, 350 km south of Paris. A total of 17 schools were chosen on a voluntary basis to perform this study. The schools included 7 nursery schools and 10 elementary schools. Three classrooms were studied per school. The locations of the studied schools are shown in Figure 3.1.1. All schools were in urban areas except for school 7, which was located in a rural area.

Schools 1 to 10 were evaluated in the heating season (from 01/11/2010 to 04/02/2010), and schools 11 to 17 were evaluated in the non-heating season (from 04/26/2010 to 06/25/2010). Each school was studied during one full week, from Monday to Friday.

The studied classrooms (total of 51) had volumes ranging between 90 and 310 m^3. The majority of the classrooms (63%, n = 32) were located on the ground floor, 35% (n = 18) were located on the first floor and only 2% (n = 1) were located on the second floor. The mean number of children per classroom was 24 ± 4, and their ages ranged between 3 and 10 years old.

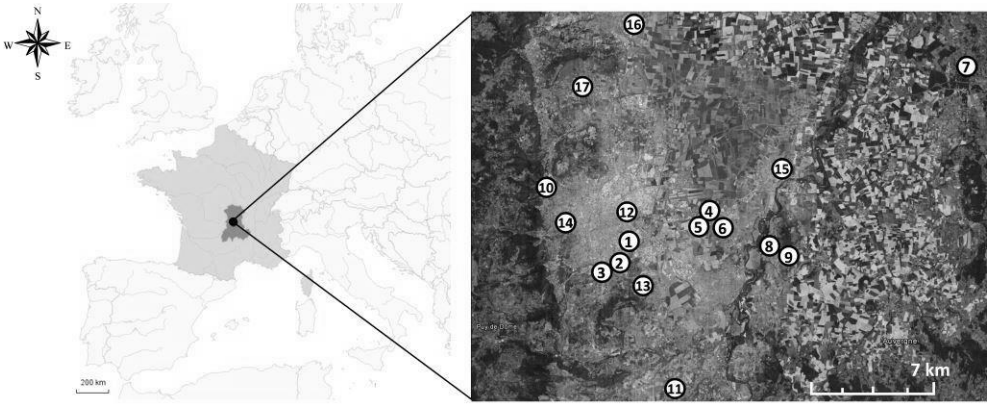

Figure 3.1.1 Location of Auvergne region (dark orange), in center of France (left) and the 17 studied schools in Clermont-Ferrand area (right).

Regarding the type of ventilation, 73% of the classrooms (n = 37) had natural ventilation and 27% (n = 14) were equipped with a mechanical ventilation system (2 classrooms had balanced systems, and 12 classrooms had exhaust-only systems). Natural classroom ventilation refers to ventilation from windows and door openings. Detailed information about each studied classroom is described in Canha et al. (2014c).

3.1.3.2 Sample Collection and Analytical Methods

The sample collection and measurement strategies were conducted in each studied classroom over one school week from Monday morning (8:00 am) until Friday afternoon (5:00 pm).

Indoor levels of carbon dioxide (CO_2) were measured continuously every 10 minutes with the Q-Trak Plus IAQ monitor 8552 (TSI Incorporated, Shoreview, USA). The CO_2 sensor was an infrared sampling device with a measuring range of 0-5000 ppm [accuracy: ± (3% of reading + 50 ppm)]. The CO_2 sensors were calibrated prior to and after each sampling week at two concentrations (0 and 1500 ppm) with standard gas (Lind Gaz, Montereau, France).

Detailed information regarding the sampling of the other IAQ parameters ($PM_{2.5}$, ultrafine particles, VOCs, aldehydes, indoor and outdoor temperature and relative humidity) can be found fully described elsewhere (Canha et al., 2014c).

3.1.3.3 Air Exchange Rates and Ventilation Rates

Air Exchange Rates (AERs - air renewal per hour, h^{-1}) and Ventilation Rates (VRs - air liters per second per person, L/s per person) were calculated for all classrooms using the build-up method, which relies on a computerized tool developed by Hänninen (2013) based on CO_2 concentrations. AER and VR were calculated considering only the occupied periods. The number of students and teachers during each analyzed build-up event was assessed through the questionnaires. In cases of missing information from the questionnaire, a theoretical number of students and teachers in the classroom was used.

3.1.3.4 Air Stuffiness Index - ICONE

Air stuffiness of indoor environments depends on two main factors: the space available inside the room that is occupied and the AER (Ribéron et al., 2012). A good indicator of air stuffiness is the measure of CO_2 concentration, as CO_2 is emitted by occupants' breathing. Hence, air stuffiness characterizes the adequacy of the AER with regard to the number of occupants. Two parameters that affect air stuffiness levels are occupants' CO_2 metabolic production and the room's AER conditions, which depend on air permeability, the existence of a mechanical ventilation system and the opening of windows and doors.
In an intervention study in schools and daycare centers that assessed the impact of opening windows on IAQ (Derbez et al., 2011), Ribéron et al. (2011) developed an air stuffiness index called ICONE (*Indice de CONfinement d'air dans les Ecoles*). The ICONE is used to evaluate air stuffiness during occupied periods. The index considers the frequency and intensity of CO_2 concentrations compared with the defined threshold values of 1000 and 1700 ppm. These values were chosen to frame the threshold value of 1300 ppm required in France by the Règlement Sanitaire Départemental Type (RSDT, 1978). For ICONE calculation, CO_2 concentrations must be measured during children's normal classroom attendance (i.e., when at least half of the usual number of children is present) over a complete school week. Subsequently, CO_2 values are classified according to their level: n_0 – values < 1000 ppm, n_1 – values between 1000 and 1700 ppm and n_2 – values > 1700 ppm. The ICONE air stuffiness index is then calculated by applying Equation 3.1.1 (Ribéron et al., 2012), where f_1 is the proportion of CO_2 values between 1000 and 1700 ppm ($f_1 = \frac{n_1}{n_0+n_1+n_2}$) and f_2 is the proportion of CO_2 values above 1700 ppm ($f_2 = \frac{n_2}{n_0+n_1+n_2}$).

(Equation 3.1.1) $$ICONE = \left(\frac{2.5}{log_{10}(2)}\right) log_{10}(1 + f_1 + 3f_2)$$

The final results for characterizing a given classroom should be rounded to the nearest integer. The air stuffiness level of the room is then expressed by the ICONE score, which ranges from 0-5, where 0 corresponds to non-stuffy air (CO_2 concentration always below 1000 ppm, which represents the most favorable conditions), and 5 corresponds to extremely

stuffy air (CO_2 concentration always above 1700 ppm during children's occupancy, which represents the worst conditions). ICONE scores between 0 and 5 correspond to an air stuffiness gradient: 0 – none, 1 – low, 2 – average, 3 – high, 4 – very high and 5 – extreme air stuffiness (Ramalho et al., 2013). As such, the ICONE score represents a method of assessing occupants' exposure to air stuffiness. The higher the score, the higher the risk of exposure to elevated concentrations of other pollutants when specific pollutant sources are present or activated.

In 2012, the ICONE air stuffiness index was integrated into the mandatory monitoring of IAQ in public buildings in France (Décret n° 2012-14 du 05/01/2012, 2012).

3.1.3.5 Statistical Treatment

An analysis of variance of the results was performed using nonparametric statistics at a significance level of 0.05. The Mann-Whitney U test was used for binary independent groups, and the Kruskal-Wallis test was used for multiple independent groups. Correlations between variables were expressed by Spearman correlation coefficients, as the continuous data distribution was neither normal nor log-normal. All statistical analyses were conducted using the XLSTAT 2014 software (Addinsoft, France).

3.1.4 Results and Discussion

3.1.4.1 Ventilation Indicators

The monitored CO_2 concentration was analyzed by different means to provide different ventilation indicators, including the 1) distribution of indoor CO_2 concentration, 2) AERs, 3) VRs and 4) ICONE index air stuffiness score. The total duration of opened windows during the school week was considered an additional ventilation indicator. However, because of poorly reported information by the teachers, this duration could not be calculated. Each of these indicators provides specific information on classroom ventilation conditions. Although all of the indicators are related to CO_2 concentration, they offer a better glimpse of ventilation conditions collectively rather than individually.

3.1.4.1.1 CO_2 concentrations

Table 3.1.1 shows the overall results of CO_2 concentrations for the studied classrooms during the periods of occupancy.

The mean CO_2 concentration in the 50 studied classrooms was 1300 ppm during the occupied period, with a median of 1300 ppm and a maximum of 2200 ppm. The CO_2 concentrations in this period were slightly higher than during the period of "Other activities", which corresponds to the time period when the children may have been absent from the classroom but the teachers were present.

Table 3.1.1 Distribution of the CO_2 concentrations (ppm) over the sampling week (n=50 classrooms).

Period	Mean	Min	P5	P25	Median	P75	P95	Max
Weekly mean concentration								
Occupied	1300	530	730	970	1300	1700	1900	2200
Other activities	1200	520	620	820	1100	1500	2000	2200
Minimum concentration over the sampling week								
Occupied	440	360	380	410	430	460	570	60
Maximum concentration over the sampling week								
Occupied	2400	580	1100	1900	2300	3200	3900	4300

A number of standards and guidelines for CO_2 concentrations have been established for school environments. The European Standard EN15251 (European Committee for Standardization, 2006) and REHVA Guidebook 13 (d'Ambrosio Alfano et al., 2010) proposed performance-based standards that limit CO_2 concentration to 1500 ppm over a full school day. The French RSDT (RSDT, 1978) mandates that concentrations not exceed 1300 ppm at any time in rooms in which smoking is prohibited. Overall, the studied classrooms presented CO_2 concentrations above 1300 ppm and 1500 ppm, respectively, during 46% and 35% of the occupied period.

3.1.4.1.2 Air Exchange Rates

Figure 3.1.2 presents the AERs for the studied classrooms during 459 analyzed CO_2 build-up events. A mean of 9 build-up events was analyzed per classroom, and each event had a mean duration of 43 minutes.

The mean AER varied between 0.3 and 3.1 h^{-1} among all studied classrooms. For the classrooms that were studied during the heating season, the AER ranged between 0.3 and 3.1 h^{-1}, with a mean value of 1.5 ± 0.7 h^{-1}; during the non-heating season, the AER ranged between 0.5 and 2.0 h^{-1}, with a mean value of 1.2 ± 0.4 h^{-1}. Nursery classrooms presented a range between 0.5 and 3.1 h^{-1}, with a mean value of 1.4 ± 0.6 h^{-1}, and elementary school

classrooms presented a range between 0.3 and 3.0 h^{-1}, with a mean value of 1.3 ± 0.6 h^{-1}. In mechanically ventilated classrooms, the AER ranged between 1.1 and 3.1 h^{-1}, with a mean value of 1.8 ± 0.5 h^{-1}; for naturally ventilated classrooms, the AER ranged between 0.3 and 3.0 h^{-1}, with a mean value of 1.2 ± 0.6 h^{-1}.

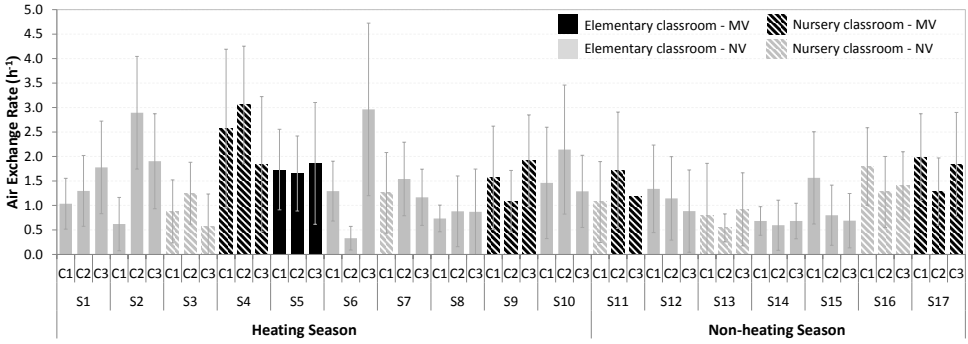

Figure 3.1.2. Air exchange rates (h^{-1}) of the studied classrooms (C) of the 17 schools (S) during the occupied period. (MV – Mechanically Ventilated; NV – Naturally Ventilated)

3.1.4.1.3 Ventilation Rates

Figure 3.1.3 presents the VRs for the studied classrooms, which were determined from the AER calculations described above.

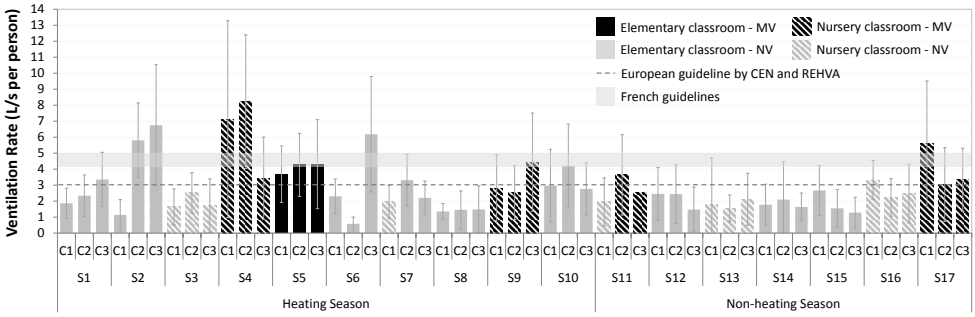

Figure 3.1.3 Ventilation rates (L/s per person) of the studied classrooms (C) of the 17 schools (S) during the occupied period. (MV – Mechanically Ventilated; NV – Naturally Ventilated)

VRs varied between 0.6 and 8.2 L/s per person among all studied classrooms. Nursery classrooms presented VRs ranging between 1.6 and 8.2 L/s per person; the VRs ranged between 0.6 and 6.7 L/s per person in elementary classrooms. These VRs are within ranges of values previously reported in the literature (Sundell et al., 2011; Canha et al., 2013a).

Global standards and guidelines related to minimum classroom VRs are inconsistent. For instance, in the United States, the American Society of Heating, Refrigeration and Air Conditioning Engineers (ASHRAE) recommends a minimum VR of 7 L/s per person (ASHRAE Standard 62.1–2007) for teaching facilities. In Europe, the European Standard EN15251 (2006) and REHVA Guidebook 13 (2010) specify a minimum VR of 3 L/s per person in all occupied teaching and learning spaces. However, European countries have specific VR guidelines that vary substantially, from 4.2-12 L/s per person (Brelih and Seppänen, 2011). For instance, in France, the minimum recommended VR ranges between 4.2 and 5.0 L/s per person for classrooms equipped with mechanical ventilation (RSDT, 1978; Mandin and Kirchner, 2005), depending on the type of activity being performed and the numbers and ages of the children.

From the 51 studied classrooms, 37% (n = 19) presented mean VRs above 3 L/s per person (EN15251/REHVA guideline), and 9% (n = 9) presented mean VRs above 4.2 L/s per person, which is the minimum requirement by the French guideline. Among the 14 classrooms that were equipped with a mechanical ventilation system, 79% (n = 11) showed mean VRs above 3 L/s per person, and 43% (n = 6) presented mean VRs above 4.2 L/s per person. Among the naturally ventilated classrooms (n = 37), only 22% (n = 8) presented mean VRs higher than 3 L/s per person, and only 11% (n = 4) presented mean rates higher than 4.2 L/s per person.

Regarding the type of classroom, 43% (9 out of 21) of the nursery classrooms had mean VRs higher than 3 L/s per person, and 19% (4 out of 21) presented mean VRs higher than 4.2 L/s per person. For elementary classrooms, 33% (10 out of 30) presented mean VRs higher than 3 L/s per person, and 20% (6 out of 30) presented mean rates higher than 4.2 L/s per person.

3.1.4.1.4 ICONE Index of Air Stuffiness

Figure 3.1.4 shows the ICONE scores obtained for the studied classrooms. Classrooms with CO_2 data available for less than 5 hours of occupancy were not considered for the ICONE calculation; therefore, only 42 classrooms were assessed for ICONE scores.

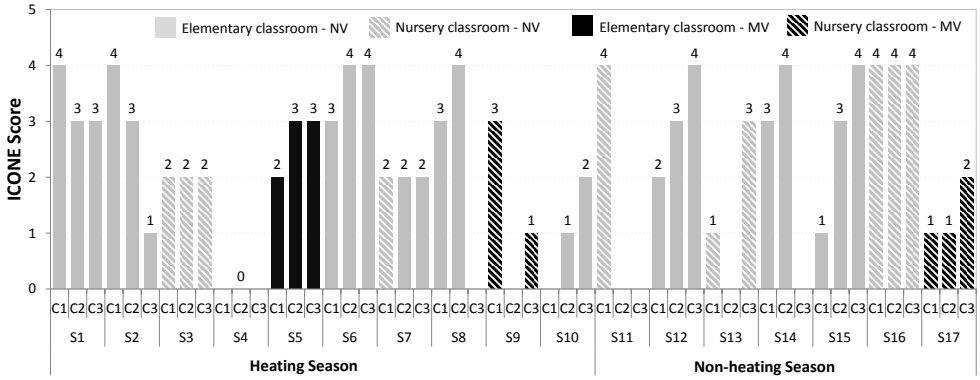

Figure 3.1.4. Air Stuffiness Index ICONE in the studied classrooms (C) of the 17 schools (S) during the occupied period. (MV – Mechanically Ventilated; NV – Naturally Ventilated)

No classroom showed to have extreme air stuffiness (ICONE score = 5). Among the classrooms with calculated ICONE scores, 12 (29%) had very high air stuffiness (ICONE score = 4), 12 (29%) had high air stuffiness (ICONE score = 3), 10 (24%) had average air stuffiness (ICONE score = 2) and only 8 (19%) had no or little air stuffiness (ICONE score = 0 or 1).

Figure 3.1.5 shows the ICONE profiles in this study and the profiles that were calculated in 310 schools and daycare centers distributed in all regions of France (Ramalho et al., 2013).

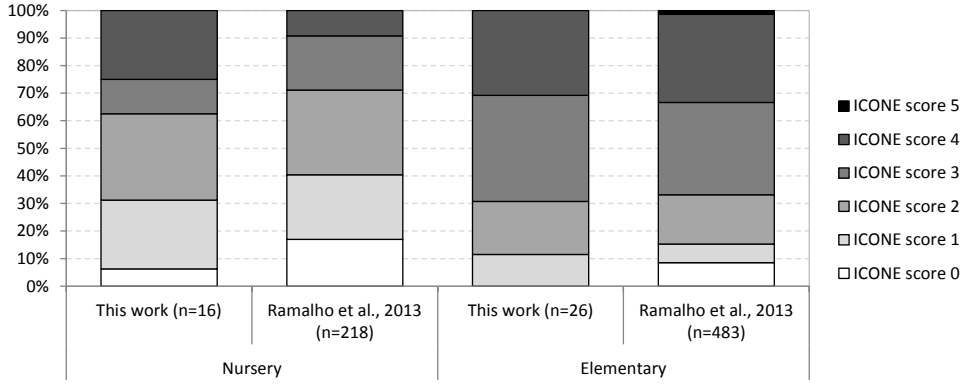

Figure 3.1.5 ICONE profiles per type of schools.

The ICONE profiles obtained in the present study are similar to the profiles that were described by Ramalho et al. (2013) for both types of schools, nursery and elementary. In the previous and current study, elementary schools had higher percentages of high air stuffiness (ICONE score ≥ 3) than did nursery schools. High air stuffiness was found in 69% of the elementary schools in the present study and in 67% of the schools in the study by Ramalho et al. (2013), whereas 38% and 29% of the nursery schools presented high air stuffiness in this study and in that of Ramalho et al. (2013), respectively.

3.1.4.1.5 Influence of Various Parameters on Ventilation Indicators

Table 3.1.2 summarizes the mean ventilation indicator values in the studied classrooms according to the sampling season, type of classroom and type of ventilation. All ventilation indicators only presented significant differences between classrooms with different types of ventilation. This finding shows that the type of ventilation in a classroom is strongly correlated with ventilation indicators, with mechanical ventilation showing higher VRs and AERs along with lower mean CO2 concentrations and ICONE scores compared to natural ventilation.

Table 3.1.2 Ventilation indicators (mean ± SD) according to the sampling season, type of classroom and type of ventilation. Bold values indicate significant *p-values* (mann-whitney u tests were used for all ventilation indicators except icone, for which a Z test for two proportions was applied).

		Ventilation Indicator			
		VR (L/s per person)	AER (h^{-1})	Mean CO_2 (ppm)	ICONE > 3 (%)
Season	Heating	3.3 ± 1.8	1.5 ± 0.7	1200 ± 400	20%
	Non-heating	2.4 ± 1.0	1.2 ± 0.4	1400 ± 400	41%
	p-value	0.119	0.065	0.168	0.136
Classroom	Nursery	3.2 ± 1.8	1.4 ± 0.6	1200 ± 400	25%
	Elementary	2.7 ± 1.6	1.3 ± 0.6	1300 ± 400	31%
	p-value	0.213	0.397	0.140	0.688
Type of Ventilation	Mechanical	4.2 ± 1.7	1.8 ± 0.5	970 ± 250	0%
	Natural	2.4 ± 1.4	1.2 ± 0.6	1400 ± 400	36%
	p-value	**< 0.001**	**0.001**	**0.016**	**0.032**

3.1.4.2 Gaseous pollutants

3.1.4.2.1 Volatile Organic Compounds

Description of VOC concentrations in the classrooms and outdoors can be found elsewhere (Canha et al., 2014c). Mean concentrations were always higher indoors than outdoors for all of the VOCs. For tetrachloroethylene and 1,4-dichlorobenzene, this comparison was difficult to make, as the indoor and outdoor concentrations were often below the limits of detection.

Among the aromatic hydrocarbons, toluene, ethylbenzene, m,p-xylene and styrene were detected and quantified in all classrooms. Benzene was detected in all samples but quantified in only 68% of them. Regarding chlorinated hydrocarbons, tetrachloroethylene was detected in approximately 26% of samples but only quantified in approximately half of them (14%).

No significant differences in VOC concentrations were found between the types of classrooms (all p-values > 0.050 with the Mann-Whitney test), as shown in Table 3.1.3. Only benzene presented significantly higher concentrations in the heating season compared with the non-heating season (p-values < 0.001). Regarding the type of ventilation, toluene, m,p-xylene and o-xylene had significantly lower concentrations in mechanically ventilated classrooms compared with naturally ventilated classrooms (p-values < 0.050). Because trichloroethylene, tetrachloroethylene and 1,4-dichlorobenzene had values less than 30% above the limit of quantification, they were excluded from the statistical analysis.

3.1.4.2.2 Aldehydes

Description of the concentrations of the 4 studied aldehydes can be found elsewhere (Canha et al., 2014c). Formaldehyde, acetaldehyde and butyraldehyde were detected and measured in all 51 classrooms, but hexaldehyde was only detected in 90% of the classrooms. All of the aldehydes showed higher concentrations indoors than outdoors.

Significantly higher concentrations were measured during the non-heating season for all of the aldehydes (p-values < 0.050), as shown in Table 3.1.4. This finding can be attributed to higher indoor temperatures, which promote the volatilization of pollutants (Sarigiannis et al., 2011).

Table 3.1.3 VOC concentration (µg m^{-3}) according to the sampling season, type of classroom and type of ventilation. Bold values represent p-values which are statistically different (Mann-Whitney U Test).

	Season			Classroom			Type of Ventilation		
Pollutant (µg m^{-3})	**Heating**	**Non-heating**	**p-value**	**Nursery**	**Elementary**	**p-value**	**Mechanical**	**Natural**	**p-value**
Benzene	2.8 ± 2.6	1.0 ± 0.3	**<0.001**	1.3 ± 0.4	2.2 ± 2.2	0.537	1.5 ± 0.3	2.2 ± 2.4	0.392
Toluene	6.1 ± 6.4	3.8 ± 1.7	0.781	3.4 ± 1.5	5.0 ± 5.3	0.287	2.4 ± 0.7	5.8 ± 5.5	**0.008**
Ethylbenzene	2.4 ± 1.5	1.9 ± 0.9	0.272	4.8 ± 0.7	2.1 ± 1.3	0.906	1.5 ± 0.2	2.4 ± 1.4	0.130
m,p-xylene	4.6 ± 3.5	4.1 ± 3.7	0.968	3.7 ± 3.0	3.9 ± 2.9	0.118	1.9 ± 0.2	5.0 ± 3.7	**0.001**
o-xylene	1.5 ± 1.7	1.8 ± 2.5	0.412	1.2 ± 1.9	1.2 ± 1.4	0.180	0.3 ± 0.2	1.9 ± 2.2	**0.001**
Styrene	1.6 ± 0.9	1.2 ± 0.2	0.250	1.2 ± 0.2	1.5 ± 0.7	0.420	1.2 ± 0.2	1.5 ± 0.8	0.439

Table 3.1.4 Aldehyde concentration (µg m^{-3}) according to the sampling season, type of classroom and type of ventilation. Bold values represent p-values which are statistically different (Mann-Whitney U Test).

	Season			Classroom			Type of Ventilation		
Pollutant (µg m^{-3})	**Heating**	**Non-heating**	**p-value**	**Nursery**	**Elementary**	**p-value**	**Mechanical**	**Natural**	**p-value**
Formaldehyde	19 ± 9	31 ± 17	**0.003**	28 ± 17	23 ± 13	0.346	18 ± 7	28 ± 16	**0.042**
Acetaldehyde	5.5 ± 1.9	7.1 ± 2.1	**0.010**	6.5 ± 2.4	6.1 ± 2.0	0.634	4.8 ± 1.6	6.9 ± 2.1	**0.002**
Butyraldehyde	10 ± 4	18 ± 11	**< 0.001**	17 ± 12	12 ± 5	**0.049**	12 ± 3	15 ± 11	0.642
Hexaldehyde	7.0 ± 4.7	17 ± 7	**< 0.001**	13 ± 7	11 ± 8	0.287	7.6 ± 4.5	13 ± 8	**0.020**

Regarding the type of classroom, only butyraldehyde showed significant differences in mean concentrations, with higher values in nursery rather than classrooms of elementary schools. Compared to naturally ventilated classrooms, mechanically ventilated classrooms had lower significant mean concentrations of formaldehyde, acetaldehyde and hexaldehyde (p-values < 0.050).

3.1.4.3 Particulate Matter

3.1.4.3.1 $PM_{2.5}$ Mass Concentrations

Among the 51 studied schools, $PM_{2.5}$ concentrations could not be assessed in 6 classrooms because of problems with the setup of devices (4 classrooms) and because the sampling flow rates were outside of the acceptable range (2 classrooms). Therefore, Figure 3.1.6 shows the $PM_{2.5}$ concentrations in 45 classrooms.

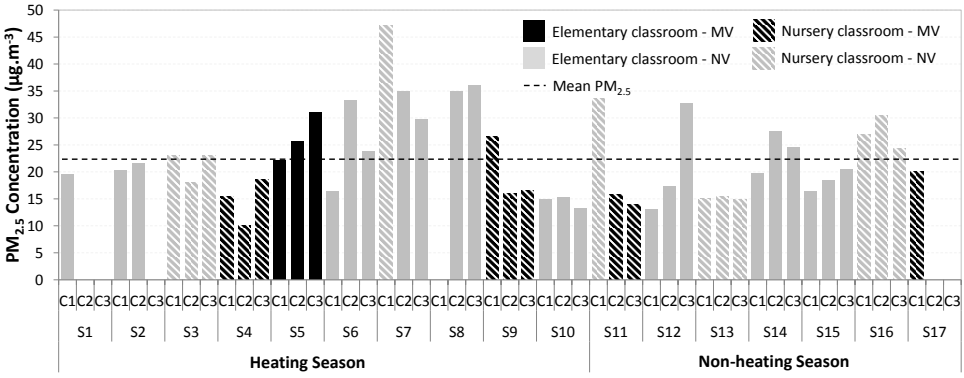

Figure 3.1.6 $PM_{2.5}$ concentrations (µg m^{-3}) in the studied classrooms (C) of the 17 schools (S). (MV – Mechanically Ventilated; NV – Naturally Ventilated)

The mean indoor $PM_{2.5}$ concentration was 22.4 ± 7.9 µg m^{-3}, with values ranging from 10.1- 47.1 µg m^{-3}. Mean $PM_{2.5}$ concentrations of 23.4 ± 8.8 µg m^{-3} and 21.1 ± 6.6 µg m^{-3} were measured in the heating and non-heating seasons, respectively. No significant differences were observed according to the sampling season, type of classroom or type of ventilation (p-values > 0.050).

All classrooms had indoor concentrations above 10 µg m^{-3}, which is the limit established by the WHO for $PM_{2.5}$ in the ambient air over long exposure periods (annual mean) (WHO, 2006). The WHO also established a limit of 25 µg m^{-3} per 24 hours, which was exceeded in 31% of the classrooms in this study.

The indoor $PM_{2.5}$ concentrations assessed in this study are similar to values previously observed in 24 schools in the Netherlands (mean of 23 ± 6 µg m^{-3}, Janssen et al., 2001), 108 schools in France (mean of 20 µg m^{-3}, Annesi-Maesano et al., 2012) and 64 schools in Germany (mean of 22 µg m^{-3}, Fromme et al., 2007).

A small number of studies showed lower mean values than the values in the present study, including studies in Sweden (mean of 8 µg m^{-3}, Molnár et al., 2007), the United States (mean of 17 ± 14 µg m^{-3}, John et al., 2007) and Portugal (mean of 10 µg m^{-3}, Almeida et al., 2011). Other studies in the literature have shown higher values than those in this work (Annesi-Maesano et al., 2013). For example, a mean concentration of 44 µg m^{-3} was measured in schools in Beijing, China (Liu et al., 2004), and in some studies, concentrations were ten times higher than the present values, including a study in India in the winter (Habil and Taneja, 2011).

3.1.4.3.2 Particle Number Concentrations

Figure 3.1.7 shows the median particle number (PN) concentrations measured in 25 classrooms based on occupancy. Concentrations were higher during occupied periods for both types of particles. Nevertheless, the difference between the occupied and non-occupied periods was greater for particles with diameters of 1-20 µm than for those with diameters of 0.3-1 µm.

Figure 3.1.7 Median particle number concentrations (number of particles.cm^{-3}) during the different sampling periods for particles with an aerodynamic diameter of 0.3-1 µm (left) and 1-20 µm (right).

These results are similar to the ones observed by Blondeau et al. (2005) in 8 French classrooms. Larger particles presented higher concentrations during occupied periods compared with non-occupied periods, and this difference between periods was higher than for fine particles, the concentrations of which did not show important variation between

types of sampling periods. This pattern is associated with the indoor generation of large particles by the occupants themselves, which can occur during school activities that create blackboard dust or re-suspension of settled particles (Blondeau et al., 2005).

The comparison of fine and large particle concentrations according to the sampling season, type of classroom and type of ventilation is shown in Table 3.1.5. For both types of particles, the mean concentrations were not significantly different (p-values > 0.050) in any of the studied cases.

Table 3.1.5 Concentration of particles (number of particles per cm^{-3}) during the occupied period according to the sampling season, type of classroom and type of ventilation (Mann-Whitney test).

	Mean Particle Number concentration ± SD (particles cm^{-3})		**p-value**
Size of particles	**Heating season (n=14)**	**Non-heating season (n=11)**	
0.3 – 1 µm	61 ± 38	44 ± 21	0.218
1 - 20 µm	19 ± 26	20 ± 38	0.565
Size of particles	**Elementary School (n=14)**	**Nursery (n=11)**	
0.3 – 1 µm	46 ± 27	63 ± 37	0.218
1 - 20 µm	15 ± 25	24 ± 38	0.603
Size of particles	**Natural Ventilation (n=20)**	**Mechanical Ventilation (n=5)**	
0.3 – 1 µm	51 ± 32	61 ± 36	0.476
1 - 20 µm	16 ± 27	33 ± 45	0.325

3.1.4.4 Relationships between Ventilation Indicators and Indoor Air Concentrations

Table 3.1.6 presents the Spearman correlations between the ventilation indicators and the studied indoor air parameters. All of the ventilation indicators had significant correlations with each other, with high correlations found between AERs and VRs ($R = 0.940$, $p < 0.001$) and between mean CO_2 concentrations and ICONE scores ($R = 0.990$, $p < 0.001$). Regarding the ventilation indicators, it is possible to distinguish two main groups taking in account the significance of the correlations between them ($R > 0.9$).

Table 3.1.6 Spearman correlations between ventilation indicators and indoor air pollutants (p-values in brackets) and significant correlations in bold.

	Ventilation Indicator			
Parameters	CO_2 concentration	ICONE	VR	AER
CO_2 concentration	1	**0.990 (<0.001)**	**-0.461 (0.001)**	**-0.341 (0.018)**
ICONE	**0.990 (<0.001)**	1	**-0.515 (<0.001)**	**-0.417 (0.004)**
VR	**-0.461 (0.001)**	**-0.515 (<0.001)**	1	**0.940 (<0.001)**
AER	**-0.341 (0.018)**	**-0.417 (0.004)**	**0.940 (<0.001)**	1
Indoor Temperature	0.014 (0.928)	0.066 (0.678)	-0.201(0.190)	-0.130 (0.398)
Indoor Specific Humidity	0.296 (0.055)	**0.333 (0.032)**	-0.268 (0.079)	-0.235 (0.124)
Formaldehyde	**0.465 (0.001)**	**0.465 (0.001)**	**-0.284 (0.044)**	-0.242 (0.087)
Acetaldehyde	**0.368 (0.011)**	**0.450 (0.002)**	**-0.402 (0.004)**	**-0.375(0.007)**
Butyraldehyde	0.173 (0.238)	0.218 (0.141)	-0.186 (0.190)	-0.161 (0.259)
Hexaldehyde	0.172 (0.242)	0.157 (0.291)	**-0.306 (0.029)**	-0.275 (0.051)
Benzene	0.105 (0.525)	0.034 (0.841)	0.070 (0.661)	0.134 (0.403)
Toluene	**0.325 (0.044)**	0.306 (0.062)	0.038 (0.815)	0.084 (0.602)
Ethylbenzene	0.130 (0.429)	0.087 (0.602)	0.267 (0.091)	0.288 (0.068)
m,p-xylene	**0.326 (0.043)**	0.316 (0.054)	0.025 (0.875)	0.078 (0.626)
o-xylene	**0.410 (0.010)**	**0.409 (0.011)**	-0.035 (0.826)	0.006 (0.969)
Styrene	0.117 (0.476)	0.072 (0.664)	0.298 (0.059)	0.272 (0.085)
Trichloroethylene	0.236 (0.143)	0.170 (0.300)	-0.065 (0.682)	0.005 (0.975)
Tetrachloroethylene	0.031 (0.847)	0.046 (0.779)	0.099 (0.533)	0.102 (0.519)
1,4-dichlorobenzene	0.239(0.137)	0.269 (0.097)	**-0.467 (0.002)**	**-0.451 (0.003)**
$PM_{2.5}$	**0.533 (<0.001)**	**0.578 (<0.001)**	**-0.300 (0.046)**	-0.193 (0.205)
$PN_{0.3-1}$	0.256 (0.215)	0.176 (0.409)	-0.105 (0.615)	-0.008 (0.968)
PN_{1-20}	**0.472 (0.018)**	**0.428 (0.038)**	0.022 (0.918)	0.128 (0.538)

By one side, AERs and VRs are both associated with the ventilation conditions of the classroom and its effectiveness. VRs assume different ventilation conditions according to the number of occupants and different volumes of the classroom, while AERs assume the same ventilation conditions whatever these characteristics. Moreover, VR is related to the measure of the exposure of the occupants to the pollutants' concentrations, while AER stands out for the leakiness of the classroom's envelope. Either way, both indicators are related with the dilution of the pollutants' concentrations promoted by the ventilation of the

classroom and, therefore, both present negative correlations with the pollutants'concentrations. AERs and VRs presented negative and significant correlations with few indoor parameters. AERs showed a significant and negative correlation with acetaldehyde and 1,4-dichlorobenzene, and VRs showed a significant and negative correlation with three more parameters: formaldehyde, hexaldehyde and $PM_{2.5}$.

By the other side, CO_2 concentration and ICONE scores are indicators that are related with the occupancy of the classroom and the indoor accumulation of pollutants. CO_2 concentrations provide information on the equilibrium between the production of CO_2 and the ventilation conditions, while the ICONE takes into account the frequency of CO_2 concentration peaks and their intensity, which is a measure of the intensity of the exposure to stuffy air and, therefore, to the pollutants. CO_2 concentrations showed positive and significant correlations with formaldehyde, acetaldehyde, toluene, m,p,o-xylenes, $PM_{2.5}$ and $PN_{1\text{-}20}$ (particle number concentrations). The ICONE scores also showed positive and significant correlations with the same indoor parameters (except for toluene and m,p-xylenes) and with the indoor specific humidity.

Overall, each of these ventilation indicators provides specific information on classroom ventilation conditions or regarding the exposure of the children. Although all of the indicators are related to indoor CO_2 levels, they offer a better glimpse of ventilation conditions collectively rather than individually.

Only acetaldehyde showed significant correlations with all four ventilation indicators, whereas $PM_{2.5}$ and formaldehyde presented significant correlations with only three ventilation indicators, including the CO_2 concentration, ICONE score and VR.

Most of the existing studies on ventilation in schools have focused on relationships with health outcomes or performance (Annesi-Maesano et al., 2013; Daisey et al., 2003). Few studies have reported correlations between VRs and IAQ in schools. Godwin and Batterman (2007) showed negative correlations between AERs and indoor concentrations of toluene, m,p-xylene, alpha-pinene and limonene in a set of 64 schools in Michigan in the United States (aldehydes and PM were not measured).

3.1.5 Conclusions

The present study measured IAQ and ventilation in 51 classrooms. Ventilation indicators such as the mean CO_2 concentration, AER (h^{-1}), VR (L/s per person) and ICONE air stuffiness index score were evaluated to assess classroom ventilation and to understand the underlying processes that determine IAQ. On the basis of existing French guidelines, a majority (91%) of the studied classrooms had insufficient ventilation: only 9% of the

classrooms complied with the minimum value of 4.2 L/s per person that is required by the French legislation. The use of different indicators provides complementary evaluations of ventilation and they can be used individually taking in account specific guidelines or then collectively to fully characterize the ventilation. This study also improved our understanding of the influence of ventilation on IAQ, along with other factors such, type of season, type of school andtype of ventilation system. For benzene and for all of the studied aldehydes, the indoor concentrations were significantly different between the heating and non-heating seasons.

In mechanically ventilated classrooms, the VRs were approximately two times higher than the rates in naturally ventilated classrooms. High VRs were associated with low indoor concentrations of $PM_{2.5}$, 1,4-dichlorobenzene, acetaldehyde, formaldehyde and hexaldehyde.

These findings need to be confirmed with further studies that consider a larger set of classrooms. With this in mind, in 2013, the OQAI began a nationwide survey of 300 randomly selected French schools, including 600 classrooms. The sampling and analytical protocols that were implemented in the 17 schools of the present study were shown to be feasible and relevant, and they are currently being deployed in the national survey.

3.2 Children exposure to atmospheric particles in indoor of Lisbon primary schools Based on article of same title:

Based on article of same title:
Almeida SM, Canha N, Silva A, Freitas MC, Pegas P, Alves C, Evtyugina M & Pio CA

Atmospheric Environment (2011) 45(40): 7594-7599.
DOI:10.1016/j.atmosenv.2010.11.052

3.2.1 Abstract

Evidence continues to emerge showing that poor Indoor Air Quality (IAQ) can cause illness requiring absence from schools, and can cause acute health symptoms that decrease students' performance. Since children spend on average 7-11 h per weekday at school, the IAQ in classrooms is expected to play a key role in the assessment of the effects of their personal exposure to air pollution. Within this context the present study was conducted in order to fulfill three primary objectives 1) to measure the levels and the element composition of $PM_{2.5}$ and $PM_{2.5-10}$, in three primary schools placed in Lisbon, in order to assess the children exposure to these pollutants; 2) to study the relationship between indoor and outdoor atmospheric particles concentrations and 3) to investigate the sources of high aerosols concentrations in classrooms. In the studied classrooms, the concentrations of coarse particles significantly exceeded the ambient levels. Element concentrations suggested that the physical activity of students highly contributed to the re-suspension of sedimented particles. The high levels of CO_2 indicated that in these schools the ventilation was inadequate. This fact contributed to the establishment of poor IAQ.

3.2.2 Introduction

Due to the increasing of industrial emissions and traffic, outdoor air quality has become of growing concern during the past decades. Nevertheless, evidence has been made that children spend most of their time in indoor environments and therefore are more exposed to pollution indoors than outdoors. In their critical review, Mendell and Heath (2005) concluded that poor indoor environment quality in schools has a great influence on the performance and attendance of students. The exposure to contaminants in such indoor environments may lead children to develop potential health consequences as they are more

susceptible to air pollutants than adults because they breathe higher volumes of air relative to their body weights and their tissue and organs are growing (Mendell and Heath, 2005).

Poor indoor environments in schools may be attributed to three primary causes: i) inexistence or inadequate operation and maintenance of ventilation systems, ii) infrequent and unthoroughly cleaned indoor surfaces, and iii) a large number of students in relation to room area and volume, with constant re-suspension of particles from room surfaces.

Epidemiological studies have consistently shown an association between atmospheric particles pollution and the number of deaths from cancer and cardiovascular and respiratory diseases (Pope et al., 2002). There is also evidence linking particulate air pollution and increases in hospital admissions for respiratory and cardiovascular diseases (Zanobetti and Schwartz, 2005; Wellenius et al., 2006; Middleton et al., 2008). Evidence has pointed towards fine particles, which usually contain hazardous substances and are able to penetrate deep into the human lung provoking inflammation. Reports about measurements of particles in schools have been recently published (Blondeau et al., 2005; Fromme et al., 2007; Goyal and Khare, 2009; Tippayawong et al., 2009). These works showed that there is a growing evidence of comparatively high concentrations of atmospheric particles in classrooms. However, these high concentrations do not necessarily result in higher health risks to students, because the sources and the composition of atmospheric particles in indoor air may differ from those of outdoor air (e.g. Fromme et al., 2008). Therefore, assessing children's exposure to atmospheric particles and the associated health risks requires the knowledge of outdoor and indoor particle composition. In spite of the various studies performed worldwide to assess the students' exposure to particles, only few works were devoted to their element characterization (Molnár et al., 2007; Stranger et al., 2008; Fromme et al., 2008; Avigo et al., 2008). Therefore, the composition of indoor atmospheric particles and its sources still need to be clarified.

This study was developed within the project "Impact of Indoor on Human Health". In this project a number of indoor air parameters have been measured in 14 Lisbon Primary Schools including: 1) chemical pollutants (volatile organic compounds, carbon dioxide, particles, nitrogen dioxide); 2) biological pollutants (fungi and bacteria) and 3) physical parameters (temperature and humidity) (Pegas et al., 2010, 2011). In this project, element characterization of particles sampled inside schools was done by the first time in Portugal.

The aim of this study was to provide data on compared outdoor and indoor atmospheric particles concentrations levels in school buildings, as well as information on the sources influencing the relationship between outdoor and indoor air quality. Improving the

understanding of the sources of the high atmospheric particles in schools, this study will contribute to identify what sort of additional actions should be taken to enforce an effective improvement of IAQ in schools.

3.2.3 Materials and methods

3.2.3.1 Sampling Site and Schools Description

This study was carried out in Lisbon, which is the largest city of Portugal and the westernmost capital in mainland Europe. Lisbon is located in the west of Portugal, on the Atlantic Ocean coast at the point where the river Tagus flows into the Atlantic. Lisbon has a population of about 500,000 inhabitants in 84.8 km^2 while the metropolitan area of 2870 km^2 has around 2.8 million of inhabitants. Figure 3.2.1 shows the localization of the schools.

School 1 is placed in a residential area in a low traffic zone. School 2 is located in the center of the city near a major road. School 3 is in the center of the city but far from a main road. Information concerning the school building characteristics and the number of students attending the lessons were assessed and used in the interpretation of the data. Table 3.2.1 presents an overview of these data. All the schools have natural ventilation, which means that there is no forced ventilation or air conditioning system in use; ventilation is done by opening doors and single glazing windows.

Figure 3.2.1 Spatial distribution of the 3 schools in Lisbon, Portugal.

Table 3.2.1 Overview of the school characteristics.

	School 1	**School 2**	**School 3**
Area (m^2) × height (m)	65 × 3.7	50 × 3.5	46 × 3.5
Number of students	23	21	24
Ventilation	Natural	Natural	Natural
Windows	Single glazing	Single glazing	Single glazing
Board	Blackboard/chalk	Blackboard/chalk	Blackboard/chalk
Floor covering	Brick	Brick	Brick
Floor	Ground	Ground	Ground
Direct outdoor door	Y	N	N
Classroom adjacent to playground	Y	Y	Y
Classroom adjacent to street	N	N	N
Year of construction	1970	1840	1961

3.2.3.2 Sampling and Chemical Analysis

Six Gent samplers were used to collect simultaneously atmospheric particles in three classrooms and corresponding playgrounds in Lisbon. Sampling was performed in two campaigns (May 2009 and November 2009) with two weeks each. Sampling periods started Monday morning and finished Friday afternoon. In order to prevent overloading of the filters, timers were used to turn the pump on (during the first 20 min of each hour) and turn the pump off (during the last 40 min of each hour). Therefore, measurements represent all the day and not only the periods with students' occupation. The sampling position in classrooms was opposite to the blackboard, about 1 m above the floor level, the level at which the students would normally inhale, and away from the door, thus avoiding disturbances resulting from air currents.

The Gent samplers were equipped with a stacked filter unit, which carried, in two sequential stages, 47 mm Nuclepore polycarbonate filters, with 8 and 0.4 μm pore size. Upstream of the coarse filter a pre-impactor stage was located. The air was sampled at a rate of 15-16 L min^{-1}, which allowed the collection of coarse particles with aerodynamic diameters (AD) between 10 and 2.5 μm, in the first stage, and fine particles with AD < 2.5 μm in the second stage (Maenhaut, 1992). The filter loads were measured by gravimetry in a controlled clean room (class 10,000) with a semi-micro balance. Filter mass before and after sampling was obtained as the average of three measurements, when observed variations were less than 5%.

The exposed filters were analyzed by Instrumental Neutron Activation Analysis (INAA) (Cornelis et al., 1976) with the k_0 methodology (De Corte, 1987).

Previous to the sampling campaign, tests of reproducibility within the filters and between filters were taken, using parallel sampling with two similar sampling units and measuring the particle species by INAA. Results were reproducible to within 5-15%, providing strong support for the validity of the analytical techniques. The details of sampling and analytical control tests are given in Almeida et al. (2003a,b). The accuracy of analytical methods was evaluated with NIST filter standards, revealing results with an agreement of ± 10% (Almeida et al., 2006a).

Blank Nuclepore filters were treated in the same way as regular samples. All measured species were very homogeneously distributed; therefore concentrations were corrected by subtracting the filter blank contents.

In order to evaluate the occupancy and the ventilation efficiency, CO_2 concentrations were measured in the campaign performed in May with an automatic portable Indoor Air IQ-610 Quality Probe (GrayWolf monitor).

3.2.3.3 Statistical Analysis

Statistical calculations were performed using STATISCA software. Wilcoxon Matched pairs and Mann-Whitney U were used. These tests are non-parametric - hence they do not consider any assumptions related to the distribution and basically are the same in that they compare between two medians to suggest whether both samples come from the same population or not. When both of the samples were not entirely independent of each other and had some factor in common, the Wilcoxon Matched pairs test was applied (differences between pairs of indoor and outdoor levels). When the samples were independent ManneWhitney U test was applied (differences between schools and sampling periods). Statistical significance refers to $p < 0.050$.

3.2.4 Results and Discussion

3.2.4.1 $PM_{2.5}$ and $PM_{2.5-10}$ concentrations

Figure 3.2.2 summarizes the indoor and outdoor total $PM_{2.5}$ and $PM_{2.5-10}$ mass concentrations obtained in the two sampling campaigns.

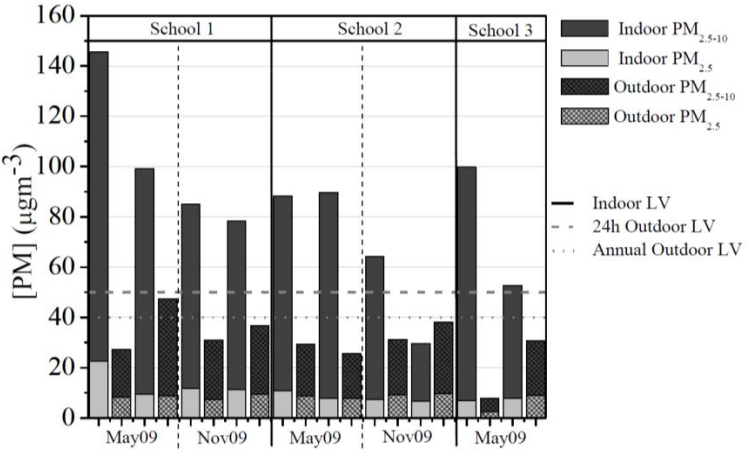

Figure 3.2.2 $PM_{2.5}$ and $PM_{2.5-10}$ mass concentration measured in the indoors and outdoors (values in μg m^{-3}; PM_{10} Limit Value - LV).

The average indoor $PM_{2.5}$ and $PM_{2.5-10}$ total mass concentration was 10 μg m^{-3} and 73 μg m^{-3}, respectively. PM_{10} indoor concentrations varied between 30 μg m^{-3} and 146 μg m^{-3}.

PM_{10} concentrations did not exceed the limit value of 150 μg m^{-3} established by the Portuguese legislation for indoor air (RSECE, 2006). However, as this study included time periods, in which no students were in class, atmospheric particles concentrations might be underestimating the children exposure to particles. In an investigation in the US, after the modification of the sampling procedure from 24 to 8 h measurements, the mean PM_{10} values were twice as high as before (Yip et al., 2004). Stranger et al. (2008) showed, in a pilot study made in Belgium classrooms, that 12 h $PM_{2.5}$ concentrations exceeded those of 24 h by 40%. In Netherlands, in three schools where PM_{10} measurements were carried out, concentrations during students' occupancy were about twice as high as 24 h average classroom concentrations (Janssen et al., 1999). Besides the differences between sampling periods, previous studies have shown that personal exposure often is higher than indoor levels (Molnár et al., 2007).

3.2.4.2 Indoor and outdoor concentrations

PM_{10} and $PM_{2.5}$ outdoor concentrations ranged from 8 to 47 μg m^{-3} and from 3 to 10 μg m^{-3}, respectively (Figure 3.2.2). There were no statistically significant differences between $PM_{2.5}$ measured indoors and outdoors ($p = 0.60$). However, statistical analysis showed that $PM_{2.5-10}$ concentrations were significantly higher indoor ($p = 0.00$), indicating that coarse particles measured in classrooms have major sources other than outdoor particles. Our

results are in line with findings of previous studies on atmospheric particles levels in indoor air of schools. Blondeau et al. (2005) studied the particle number (within 15 size intervals ranging from 0.3 to 15 μm) in eight schools and observed that indoor concentrations of the finest particles closely track the outdoor ones, while the apparent correlation is far less obvious for larger particles. Occupancy, through re-suspension of previously deposited particles and possible particle generation, strongly influences the indoor concentration level of airborne particles. However, this influence decreases with particle size, reflecting the way deposition velocities vary as a function of size. Fromme et al. (2007) observed increased atmospheric particles concentrations in low level classes and in rooms with high number of pupils, which suggest that the physical activity of pupils (assumed to be more intense in younger children), contributes to a constant process of re-suspension of sedimented particles. Analysis with Scanning Electron Microscopy performed by Fromme et al. (2008) showed that besides particles with mineral origin (resulting from re-suspension) additional coarse particles arise from semi-transparent skin flakes.

For smaller particles, other processes such as homogeneous reactions between ozone and terpenes (coming from cleaning products, perfumes, personal care products), may also contribute to indoor particles (Sarwar et al., 2003; Weschler and Shields, 2003). Significant high concentrations of particles were registered in the classroom from school 1. In this school, the doors of the classrooms open directly to the playground, whereas in the others schools, the doors of the classrooms open to the interior of the building. This fact can contribute to increase the transport of dust from the playground to the interior of the classroom from school 1.

3.2.4.3 Element concentrations

The average of the indoor and outdoor element concentrations measured both inside and outside of the schools is presented in Table 3.2.2. In the fine fraction, indoor and outdoor concentrations were not significantly different, except for Na, which originates essentially from the sea. In the coarse fraction, the indoor concentrations of Fe, La, Sc, Sm, K, Ca, Cr, Se and Zn were found to be enriched in comparison with the outdoor concentrations.

The crustal enrichment factor method has been used as an attempt to evaluate the strength of the crustal and non-crustal origin of the elements. Enrichment factors (EF), using Sc as a crustal reference element, were calculated based on Equation 3.2.1 and using Mason and Moore (1982) soil composition (Figure 3.2.3):

(Equation 3.2.1) $$EF_X = \frac{\left(\frac{[X]}{[Sc]}\right)_{PM}}{\left(\frac{[X]}{[Sc]}\right)_{crustal}}$$

Where EF_X is the enrichment factor of the element X, $\left(\frac{[X]}{[Sc]}\right)_{PM}$ is the ratio between X and Sc in the PM, and $\left(\frac{[X]}{[Sc]}\right)_{Crustal}$ is the ratio between X and Sc in the soil.

Table 3.2.2 Indoor and outdoor $PM_{2.5}$ and $PM_{2.5-10}$ element concentrations.

		$PM_{2.5}$		$PM_{2.5-10}$	
Element	Unit	Indoor (n=8)	Outdoor (n=8)	Indoor (n=8)	Outdoor (n=8)
As	ng m^{-3}	0.26 ± 0.104	0.25 ± 0.09	0.80 ± 0.20	0.24 ± 0.14
Ba	ng m^{-3}	4.2 ± 5.5	5.4 ± 4.4	32 ± 18	20 ± 23
Br	ng m^{-3}	(a)	(a)	6.3 ± 1.8	6.4 ± 2.8
Ca	µg m^{-3}	4.7 ± 5.3	2.6 ± 2.4	10 ± 3.7	2.3 ± 1.5
Co	ng m^{-3}	0.15 ± 0.22	0.21 ± 0.29	0.56 ± 0.35	0.21 ± 0.13
Cr	ng m^{-3}	(a)	(a)	11 ± 3	6.0 ± 3.3
Fe	µg m^{-3}	0.14 ± 0.08	0.11 ± 0.02	0.86 ± 0.42	0.31 ± 0.11
Hf	ng m^{-3}	0.031 ± 0.034	0.006 ± 0.001	0.11 ± 0.05	0.045 ± 0.014
K	µg m^{-3}	0.12 ± 0.05	0.085 ± 0.060	1.1 ± 0.4	0.19 ± 0.08
La	ng m^{-3}	0.058 ± 0.061	0.006 ± 0.002	0.76 ± 0.23	0.21 ± 0.13
Na	µg m^{-3}	0.21 ± 0.11	0.56 ± 0.20	1.5 ± 0.6	1.8 ± 0.7
Sb	ng m^{-3}	0.78 ± 0.58	1.1 ± 0.9	3.9 ± 2.9	1.3 ± 0.4
Sc	ng m^{-3}	0.023 ± 0.019	0.043 ± 0.074	0.16 ± 0.11	0.055 ± 0.039
Se	ng m^{-3}	0.73 ± 0.94	0.40 ± 0.24	0.49 ± 0.19	0.20 ± 0.08
Sm	ng m^{-3}	0.019 ± 0.012	0.050 ± 0.071	0.14 ± 0.07	0.040 ± 0.027
Zn	ng m^{-3}	8.2 ± 3.6	5.9 ± 2.7	86 ± 32	17 ± 5

(a) Below the detection limit

Sc was used as a reference element because previous studies performed in Lisbon showed that this element has a crustal origin with a negligible anthropogenic source to the atmosphere (Almeida et al., 2005). Given the local variation in soil composition, $EF_X > 10$ suggests that a significant fraction of the element X is contributed by non-crustal sources.

EFs indicated that Co, Fe, La, Sc, Sm and K were associated with soil emissions. These results agreed with source apportionment studies performed in the Lisbon region (Almeida et al., 2005, 2006b). Indoor concentrations for these elements in $PM_{2.5-10}$ were significantly higher than in outdoors. This fact indicates that the most probable cause of increased classroom coarse particle concentrations was the penetration of mineral dust through the windows and the re-suspension of settled dust or suspension of soil material brought in by the children's shoes.

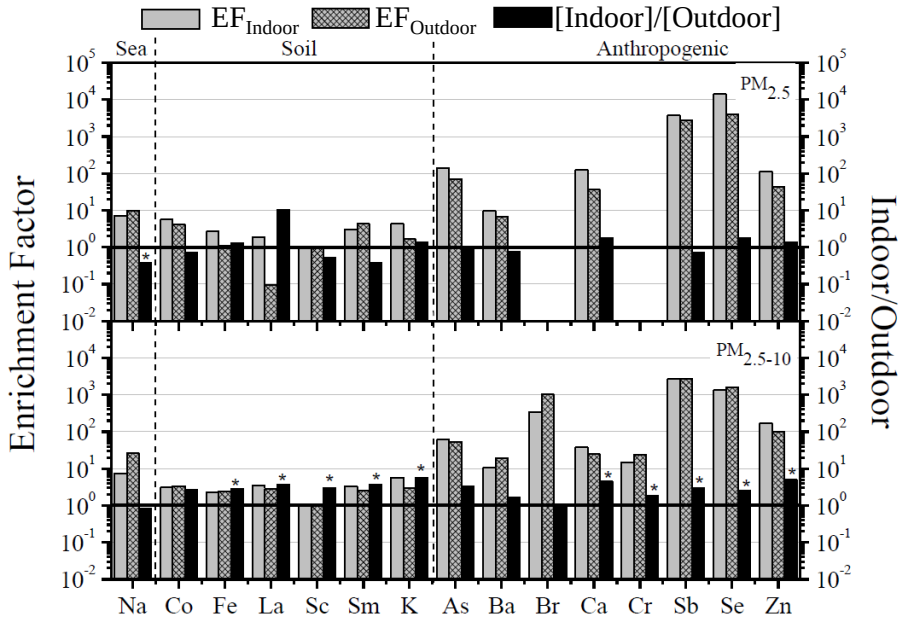

Figure 3.2.3 Enrichment factor for indoor and outdoor environments using Sc as a reference element and Mason and Moore (1982) soil composition. Average Indoor/Outdoor ratios for the element mass concentration. (* - indoor and outdoor concentrations which are significantly different)

For the strongly enriched elements (EF > 10) like As, Ba, Br, Ca, Cr, Sb, Se and Zn, an anthropogenic origin can be suggested, such as traffic and industrial emissions. In the fine fraction, the indoor and outdoor concentrations for these elements (except for Cr, which was below the detection limit) were not significantly different, suggesting that air infiltration is the main source for them. In the coarse fraction significant high concentrations were found for Ca, Cr, Sb, Se and Zn indicating the existence of an indoor source for these elements.

At both indoor and outdoor particles, Ca presented EF > 10 indicating the existence of non-mineral sources associated with this element. In the coarse fraction, Ca was detected at very high concentrations (10,000 ng m^{-3}). This lead to the idea that Ca could be attributed to a real indoor source, probably originating from the chalk (mainly $CaSO_4$), used in the blackboards, and/or the gypsum walls and plasters used as building materials.

In $PM_{2.5-10}$, Cr, Sb and Se presented significant high concentrations in the classrooms. However, the indoor EF_{Sc} for these elements were lower, indicating the existence of a mixture of anthropogenic elements with dust, which was re-suspended.

Inside the classrooms significant high concentrations of Zn were measured for the coarse fraction (for $PM_{2.5}$ a p-value of 0.063 by Wilcoxon Matched Pair Test was found). This fact has already been observed by Avigo Jr. et al. (2008) in Brazilian elementary schools and indicates the existence of a Zn indoor source. In the market, several products using Zn, to be applied indoors to protect steel, walls, wood surfaces, doors and windows, are sold.

The outdoor concentrations of Na were found to be enriched in comparison with the indoor concentrations. This fact was expected as this element has marine origin.

Our results can support the idea posed by other authors (Fromme et al., 2008) that indoor-generated particles may have lower health impacts compared to outdoor particles. In one hand, indoor-generated particles are more associated with the coarse fraction, and in the other hand these particles have principally a crustal origin. This would be in line with results obtained by Koenig et al. (2005) that shown that indoor-generated component of $PM_{2.5}$ is less associated with inflammation markers in asthmatic children than the ambient-generated component. Laden et al. (2000) showed that crustal particles in the fine fraction are not associated with increased mortality.

3.2.5 Conclusions

This study provides information on magnitude and element characterization of particles along with the relationships between size-dependent indoor and outdoor concentrations as described by Hänninen et al. (2013). Besides characterizing the particles in classrooms and identifying possible sources, these findings may be used as a valuable contribution to improve the IAQ and to suggest effective mitigation strategies.

The element composition of the classrooms' particles suggested that earth crustal materials, detritions of the building materials and chalk have an important role in the particles levels and characteristics. Physical activity of the pupils led to re-suspension of mainly coarse particles and largely contributed to increased $PM_{2.5-10}$ concentration in classrooms. Assuming that crustal materials and combustion-related particles vary in toxicity, our findings on concentrations of particle components support the hypothesis that indoor-generated APM may be less toxic compared to APM in ambient air.

Results showed that local measurements of outdoor air concentrations do not provide an accurate estimation of the children's personal exposure to particles and specific elements because they spend most of their time inside the buildings. Therefore, the composition of atmospheric particles indoors is a concern and needs further investigation.

3.3 Overall conclusions

This chapter describes the assessment of IAQ parameters using classical sampling methods, which are mandatory and are often active sampling methods, such as the specific case of particulate matter.

The first study allowed performing a characterization of a wide range of IAQ parameters in a set of 51 classrooms, with several distinguishable factors between them (type of classrooms, ventilation systems and sampling seasons). From the CO_2 monitoring performed in each classrooms, it was possible to determine four different ventilation indicators to characterize the classroom ventilation conditions, namely, CO_2 concentrations, ICONE index, air exchange rates and ventilation rates. Each ventilation indicator provides different information about the ventilation conditions of the classroom, which indicates the exposure level of the occupants to the indoor accumulation of pollutants. Their use may be complementary or specific towards the guidelines that are considered.

The type of ventilation was the factor that showed significant differences between all ventilation indicators, with mechanically ventilated classrooms showing ventilation rates almost two times higher than naturally ventilated classrooms.

The second study performed a characterization of particulate matter both indoor and outdoors of classrooms to identify levels and sources. Levels of indoor particles were higher than outdoors, which highlight the higher exposure of children when attending classes, especially when the ventilation conditions are not enough to allow an efficient removal of the pollutants from indoors. Higher levels of coarse particles were found indoors and a chemical characterization allowed to identify their sources, which are mainly indoors (particles re-suspension, chalk, detritions of the building materials).

The present chapter allowed to understand the implications of poor ventilation on the increase of children exposure to IAQ parameters, such as $PM_{2.5}$. Moreover, classical sampling methods of particulate matter in classrooms supply information about exposure levels and, through a chemical characterization, it is possible to understand which main sources are contributing for the particulate matter indoors.

However, as proved in the sampling field of particulate matter, active sampling methods have some disavantages when applied to classrooms monitoring. The noise of pumps and its interference on the classrooms activities conducted to some teachers to refuse to continue with the study in their classrooms. Moreover, this method implies the use of specialized and expensive equipment, the need of a power source, skilled personnel and, due to these constraints, it is not possible to perform a spatial survey in several classrooms at the same time. Therefore, new sampling strategies to evaluate levels of particulate matter in classrooms are needed.

4 New methods to evaluate indoor air of classrooms – Passive Methodologies

4.1 Particulate matter analysis in indoor environments of urban and rural primary schools using passive sampling methodology

Based on article of same title:
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Atmospheric Environment (2014) 83: 21-34.

DOI: 10.1016/j.atmosenv.2013.10.061

4.1.1 Abstract

Passive sampling methodology was applied to collect particulate matter (PM) in classrooms of urban and rural primary schools. The samples were taken during a year by passive deposition allowing the study of seasonal variability of the particles masses and chemical content. Chemical characterization of the collected particles was performed in order to measure its soluble ions content and elemental composition. To identify the main polluting sources, correlations between parameters and enrichment factors were studied. Higher particle masses concentrations were registered in autumn, with a mean of 1.54 ± 0.74 μg day^{-1} cm^{-2}. The major element in the collected particles was calcium, representing 63 to 73% of the analysed mass of the particles inside the urban classrooms. In the rural cluster, calcium remained the major component but with a slight lower contribution to the overall particles composition (42 to 46%). The calcium source was hypothesized to be the chalk used in the blackboards of the classrooms due to a strong correlation found between Ca^{2+} and SO_4^{2-}. Soil re-suspension, traffic and other anthropogenic emission sources were also identified. Analysis showed enrichment of the particles with Br, Ca, Zn and Sb in the urban cluster and enrichment of the same elements, except for Ca, in the rural cluster. The comparison between the results from both clusters allowed the identification of classrooms

with higher particles concentrations that can indicate potential indoor air quality problems (reflected by an indoor accumulation of pollutants).

4.1.2 Introduction

The indoor environmental quality at schools can be characterized by: 1) insufficient ventilation, especially in winter; 2) infrequent and inadequate cleaning of indoor surfaces and 3) a large number of students per classroom area and volume, with constant re-suspension of particles from room surfaces along with suspension of soil material due to the activity of the children (Janssen et al., 1999). As a result, particulate matter (PM) concentrations in classrooms are about six times higher than outdoor air (Oeder et al., 2012). On an equal weight base, indoor air PM_{10} has been shown to be toxicologically more active than outdoor PM_{10}, with the main difference being the higher concentration of organic and silicate particles in indoor air (Oeder et al., 2012).

The indoor guideline values for particulate matter vary a lot within the few countries that have already defined such regulation (Stranger et al., 2007). For $PM_{2.5}$, Norway established the limit value of 20 μg m^{-3} (averaged over a 24 h sampling period), while Belgium established the limit value of 15 μg m^{-3} (averaged over one year) and Canada introduced acceptance values below 40 μg m^{-3} (averaged over one hour). Concerning indoor PM_{10}, Belgium established a limit value of 40 μg m^{-3} (averaged over one year) while China and Portugal (RSECE, 2006) introduced the limit value of 150 μg m^{-3}.

Due to its importance, several studies have been conducted to assess the particulate matter (PM_{10}, $PM_{2.5}$ and ultrafine particles) in indoor environments of schools concerning their concentrations and chemical composition (Blondeau et al., 2005; Fromme et al., 2008; Zhang and Zhu, 2012). Despite the several studies performed in the last years, few aimed to study the particulate matter composition and its elemental and water soluble ions contents in order to understand their sources and trends (John et al., 2007). Moreover, in these studies sampling was not usually performed simultaneously in the schools of interest and sampling was limited to a period of time (from days to a few weeks). Therefore, this sampling method has several limitations and do not constitute a full representative exposure assessment of the children attending the classrooms.

Particulate matter is usually collected with active samplers, a sampling methodology widely used. However, there are some disadvantages of active samplers such as the need of expensive equipment and additional accessories, like a power supply, air-flow meters and a pump, which are not very convenient or feasible for use in remote areas or to do

simultaneous sampling on multiple sites (Guéguen et al., 2012). Additionally, optical methods do not control for humidity or density of the specific aerosol monitored (Fromme et al., 2007; Morawska and Salthamer, 2003). Moreover, indoor active sampling in classrooms is limited because it can interfere with the classrooms activities due to, for instance, the noise of the equipment.

In the last years, several studies have applied passive sampling methodologies to assess several environmental parameters, including particulate matter (Seethapathy et al., 2008). For example, Wagner and Leith (2001a, 2001b) developed a passive sampler to collect $PM_{2.5-10}$ (Wagner and Macher, 2003) which was improved with protective shelters (Ott et al., 2008).

A passive sampler, called Sigma-2 (VDI 2119, 2011), was also developed to collect the ambient-air particles with sizes in the range of 2.5-80 µm, which are mainly deposited via sedimentation into a small acceptor dish (~5.5 cm in diameter). Einstein et al. (2012) developed the Einstein-Lioy Deposition Sampler (ELDS) that uses 37 mm filters to collect surface deposition samples through passive deposition. Several configurations were optimized (with a protective hood or not; suspension with a specific support) to allow indoor and outdoor sampling.

This study focuses on the application of a new passive methodology to collect particulate matter in different classrooms of primary schools simultaneously. The experimental work was carried in urban and rural environments to understand the differences in different type of clusters. The seasonal variability was assessed by the sampling methodology since it covered 4 seasons over a 1 year period. The collected particulate matter was analysed gravimetrically and the water soluble ions content and chemical composition were determined. The main components of the collected particles and their sources were assessed to understand the children exposure at classroom environments.

4.1.3 Materials and methods

4.1.3.1 Sampling Site and Schools Description

This study was performed in primary schools of two distinct types of areas, urban and rural, of mainland Portugal. The chosen urban area was Lisbon, which is the largest city of Portugal and the westernmost capital in mainland Europe. Lisbon city has a population density of 6663 inhabitants/km^2 while its metropolitan area has a population density of 976 inhabitants/km^2. The chosen rural area was the municipality of Ponte de Sor where primary

schools of 3 villages were studied, namely Foros de Arrão, Longomel and Vale de Açor with a population density of 12.4, 32.3 and 13.2 inhabitants/km^2, respectively. The location of the primary schools for both clusters is shown in Figure 4.1.1.

The schools had natural ventilation and no other ventilation or air conditioning system was used. Students' age attending the classrooms ranged from 6 to 12 years old.

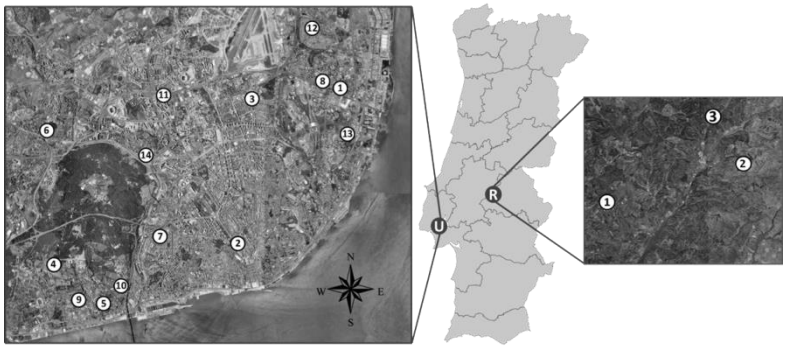

Figure 4.1.1 Location of studied primary schools at urban and rural areas. U means urban cluster and 1, …, 14 refer to urban schools. R means rural cluster and 1, 2, 3 refer to rural schools. In urban cluster, distance between schools 1 and 2 is 5.3 Km and, in rural cluster, is 28.3 Km.

4.1.3.2 Sampling

This study was conducted in 4 sampling campaigns, namely during the autumn, winter, spring and summer of 2009 and 2010. The summer campaign was done during the school holidays, therefore this campaign represents the absence of students in the classrooms during the sampling ("blank" sample). The sampling periods are shown in Table 4.1.1. The rural cluster has only information for 3 of the 4 sampling campaigns, namely, winter, spring and summer. For the urban primary schools, two classrooms were studied per school while in the rural primary schools only one classroom per school was studied. The number of students attending the classrooms during the different sampling seasons remained constant. All the studied classrooms had a similar number of students, with a mean of 21.0 ± 1.5 students per classroom.

Filters were passively exposed, as shown in Figure 4.1.2. A total of six 47-mm diameter Millipore (Isopore^{TM}) polycarbonate filters (with a pore size of 0.4 µm) and two 47-µm diameter quartz were exposed in each classroom, distributed over a tray with an area of 25

cm × 20 cm, at 120-cm high to approximate the breathing height of children inside the classrooms. Each filter was placed inside an uncovered plastic Petri dish. For each sampling campaign a set of 4 filters were used as blanks.

Table 4.1.1 Resume of the sampling campaigns' periods.

Season/ Campaign	Sampling Months	Sampling Period (days)	Notes
Autumn	October-December 2009	62; 68	With Students
Winter	January - March 2010	76; 78	With Students
Spring	March – June 2010	57 - 69	With Students
Summer	July – September 2010	41 - 43	Without students

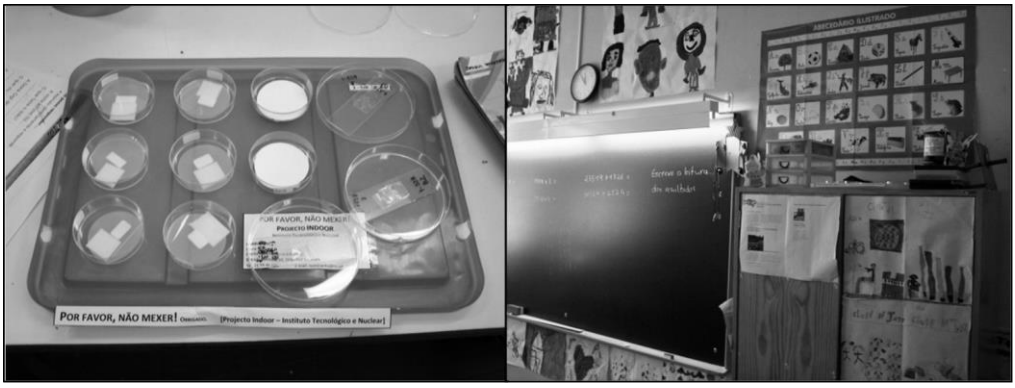

Figure 4.1.2 TPM sampling apparatus inside the classrooms for the sampling campaigns.

4.1.3.3 Analysis of Collected Total Particulate Matter (TPM)

4.1.3.3.1 Masses

The weighing of filters was performed using a UMT5 Comparator balance (Mettler Toledo GmbH 2000, Greifensee, Switzerland) with 0.1-µg resolution after 48-h equilibration at 50 ± 5 % relative humidity and 20 ± 1 ºC (controlled clean room - class 10,000). Filter mass before and after sampling was obtained by averaging three measurements, when observed variations were less than 5%.

4.1.3.3.2 Water-Soluble Inorganic Ions

For each classroom, a set of 2–4 filters was used together as a unique sample. The filters with particulate matter were placed into polyethylene containers. TPM on the samples was extracted with 25 mL of water by ultrasonication (30 minutes) followed by mechanical shaking for 15 hours with 15 revolutions per minute. Afterwards, the mixture was filtered on a cellulose acetate syringe filter of 0.45-µm pore size (SARTORIUS, Goettingen, Germany). Blank reagent was done following the same experimental procedure in each set extraction batch. In the aqueous extract, anions (Cl^-, NO_3^-, PO_4^{3-} and SO_4^{2-}) and cations (Na^+, K^+, Mg^{2+} and Ca^{2+}) were determined by ion chromatography (IC) and flame atomic absorption spectrometry (FAAS), respectively. All the procedures used in this work have been previously reported (Trancoso et al., 2012). The method used for filter extraction was the standard method suggested by EPA (2009) for the analysis of cations and anions, where the filter extraction efficiency is nearby 100% for the polycarbonate filter type. Quality control was assessed by the simultaneous analysis of certified reference materials (CRM). The certified reference material SPS-NUTR-WW2 ("Waste water", Batch 107, from Spectrapure Standards, Oslo, Norway) and the certified reference material CRM 1643a ("Trace elements in water", NIST, Gaithersburg, MD) were used for the analysis of anions and cations, respectively.

4.1.3.3.3 Chemical Element Content by Instrumental Neutron Activation Analysis (k_0-INAA)

The exposed Millipore-polycarbonate filters and their corresponding blank filters were irradiated at the Portuguese Research Reactor (RPI-CTN/IST/UTL; nominal power: 1 MW) for analyses by k_0-INAA (Freitas et al., 2003). Irradiation time was 5 h at a neutron flux density of 8×10^{12} $cm^{-2}s^{-1}$, at an irradiation position with 103.4 ± 1.3 thermal-to-epithermal neutron flux ratio and a $1/E^{1+\alpha}$ epithermal neutron flux distribution shape factor of -0.0351 ± 0.0004.

Each sample was rolled up and put into an aluminium foil for irradiation, removed from the foil after irradiation and put in a polyethylene container for measurement. Samples were measured 7 h after 3–5 days and after 3–4 weeks, with an ORTEC® automatic sample changer, equipped with an ORTEC® coaxial hyperpure germanium detector (1.90 keV resolution at 1.33 MeV; 30% relative efficiency). One Al-0.1%Au alloy disc with a thickness of 125 µm and a diameter of 0.5 cm was used as comparator for the k_0-methodology and irradiated concurrently with the samples.

Quality control was asserted by analyzing NIST-SRM® 1633a (Coal Fly Ash) following the same procedure as for the samples. Each replicate of the reference material weighed between 20-30 mg and was irradiated together with the samples, with measuring times of 1 h and 2h30 after 3–5 days and after 3–4 weeks, respectively. A total of 10 replicates of the reference material were analyzed.

A total of 23 elements were analyzed: As, Ba, Br, Ca, Ce, Co, Cr, Cs, Eu, Fe, Ga, Hf, K, La, Na, Rb, Sb, Sc, Sm, Ta, Th, W and Zn .

4.1.3.3.4 Statistical Treatment

The analysis of variance of the results was performed by nonparametrics statistics for a significance level of 0.050, the Mann-Whitney was used for binary independent groups and Kruskal-Wallis for multiple independent groups. All the analyses were conducted using the software STATISTIC version 10.

4.1.4 Results and Discussion

4.1.4.1 Passive Sampling Method

4.1.4.1.1 Efficiency of the sampling

Some filters were lost at the end of the sampling campaigns probably due to the interference with the sampling apparatus by the children or the school staff and/or strong air flows in the classroom. The total amount of filters collected in each sampling campaign is shown in Table 4.1.2.

Table 4.1.2 Number of filters collected after the exposure period for each sampling campaign and for each type of filter. (n.a. - not available)

	Season	**Autumn**		**Winter**		**Spring**		**Summer**	
	Classroom	**A**	**B**	**A**	**B**	**A**	**B**	**A**	**B**
Cluster	**School**	Type of filter: Polycarbonate / Quartz							
Urban	1	4 / 1	4 / 1	5 / 1	5 / 1	5 / 1	5 / 1	5 / 1	5 / 1
	2	4 / 1	4 / 1	5 / 1	4 / 1	5 / 1	5 / 1	1 / 1	5 / 1
	3	3 / 1	4 / 1	5 / 1	5 / 1	5 / 0	5 / 1	5 / 1	0 / 0
	4	4 / 1	4 / 1	5 / 1	5 / 1	5 / 0	5 / 0	0 / 0	0 / 0
	5	3 / 1	4 / 1	4 / 1	5 / 1	5 / 1	4 / 1	0 / 0	0 / 0
	6	4 / 1	4 / 1	5 / 1	5 / 1	5 / 0	5 / 0	0 / 0	0 / 0
	7	4 / 1	4 / 1	5 / 1	5 / 1	5 / 1	5 / 1	0 / 1	5 / 1
	8	4 / 1	4 / 1	5 / 1	5 / 1	5 / 1	5 / 1	5 / 1	5 / 1
	9	4 / 1	3 / 1	5 / 1	5 / 1	4 / 1	4 / 1	0 / 0	0 / 0
	10	1 / 1	4 / 1	5 / 1	5 / 1	5 / 1	5 / 1	3 / 1	4 / 1
	11	4 / 1	1 / 0	4 / 1	5 / 1	1 / 1	5 / 1	5 / 1	4 / 1
	12	4 / 1	4 / 1	5 / 1	5 / 1	5 / 1	5 / 1	5 / 1	4 / 1
	13	3 / 1	4 / 1	5 / 1	5 / 1	5 / 0	5 / 0	5 / 1	5 / 1
	14	3 / 1	3 / 1	5 / 1	5 / 1	5 / 1	5 / 1	5 / 1	4 / 1
Rural	1	n.a.	n.a.	5 / 1	n.a.	5 / 0	n.a.	5 / 1	n.a.
	2	n.a.	n.a.	5 / 1	n.a.	5 / 1	n.a.	5 / 1	n.a.
	3	n.a.	n.a.	5 / 1	n.a.	5 / 0	n.a.	1 / 1	n.a.

4.1.4.1.2 Comparison between Filter Matrices

A very good correlation between the masses collected for both type of filters for all seasons was found (r, the coefficient of linear correlation, is always above 0.90). The significant linear relations between both types of filters and the correlation parameters for all seasons are shown in Figure 4.1.3 and Table 4.1.3.

Table 4.1.3 Correlation parameters between the collected masses in polycarbonate and quartz filters. Statistical significantly values have a p-value below 0.050.

Season	Slope	Intercept	R^2	R	p-value
Autumn	1.07	0.26	0.848	0.921	0.000
Winter	1.40	-0.32	0.902	0.950	0.000
Spring	1.22	0.12	0.826	0.909	0.000
Summer	1.20	0.15	0.847	0.920	0.000

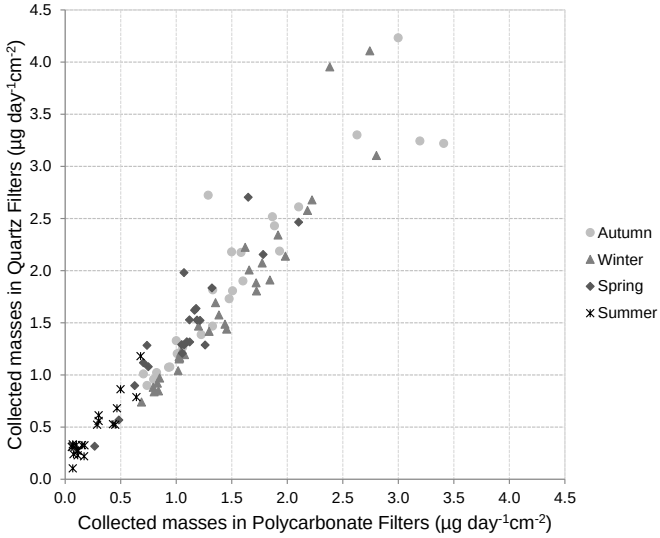

Figure 4.1.3 Correlations between the collected mass per both type of filters, polycarbonate and quartz, for all sampling seasons.

Although both filter matrices presented a very good correlation between themselves, it is possible to observe a slightly trend of higher loads of particles in the quartz matrix than in the polycarbonate one. This observation can be explained by the surface type of the filters, since it can or cannot conduct to a higher accumulation of the particles. In fact, polycarbonate filters have a smooth and thin surface with straight through capillary holes and retain static charge. Quartz filters have a white opaque surface of pure quartz filters and have high particle collection efficiencies. Moreover, quartz filters passively adsorbs organic vapors (HNO_3, NO_2 and SO_2) as well (Chow and Watson, 1998). Therefore, particles in the quartz filters surfaces can easily be trapped in the fibers of the surface of the filter when

comparing with the polycarbonate filters, which may be responsible for the observed difference in the trends of loadings.

Since the quartz matrix has a higher background than the polycarbonate matrix and the samples were obtained in minimum quantities, the polycarbonate matrix was chosen for further analytical analyses (chemical elements and water soluble ions contents). Therefore, from now on, all discussion about masses values are only regarding to polycarbonate filters.

4.1.4.1.3 Deposition rate of particles

In order to evaluate the deposition rate of the particles in both sampling settings, a weekly study was conducted in the spring campaign for one classroom per studied cluster. Several filters were exposed in a tray which was placed inside the classroom and, once per week, a filter was collected. The results are shown in Figure 4.1.4.

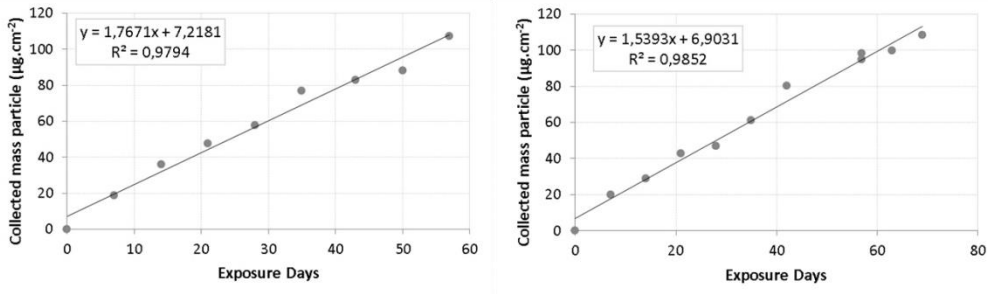

Figure 4.1.4 Collected particle masses along the period of exposure in urban environment (left) and rural environment (right) for the weekly deposition rate study.

The daily collected particles showed very good correlations: R^2 values of 0.9794 and 0.9852 for the urban and rural classroom, respectively. The urban study presented a significant correlation ($p = 0.000$) and a correlation coefficient of 0.9896. The rural study presented a significant correlation ($p = 0.000$) and a correlation coefficient of 0.9926.

The mean daily deposition rate was of 2.17 ± 0.33 µg $day^{-1}cm^{-2}$ for the urban environment and slightly lower for the rural environment, namely of 1.88 ± 0.38 µg $day^{-1}cm^{-2}$.

4.1.4.2 Total Particulate Matter

The collected particles mass obtained per school and its classrooms for each season campaign for the polycarbonate filters is shown in Figure 4.1.5.

When comparing both clusters and seasons, autumn was the season that presented a higher content of collected particles inside the urban classrooms with an average value of 1.54 ± 0.74 µg $day^{-1}cm^{-2}$. In this season, 5 classrooms presented collected mass values higher than 2 µg day^{-1} cm^{-2}, namely 3-B, 8-A, 8-B, 13-A and 13-B.

In winter, the urban schools presented a collected particles average of 1.49 ± 0.58 µg $day^{-1}cm^{-2}$ (with values above 2 µg $day^{-1}cm^{-2}$ in classrooms 3-B, 7-B, 8-A and 8-B), while rural schools presented a lower average of 1.35 ± 0.73 µg $day^{-1}cm^{-2}$ (with classroom 1 showing values above 2 µg$day^{-1}cm^{-2}$).

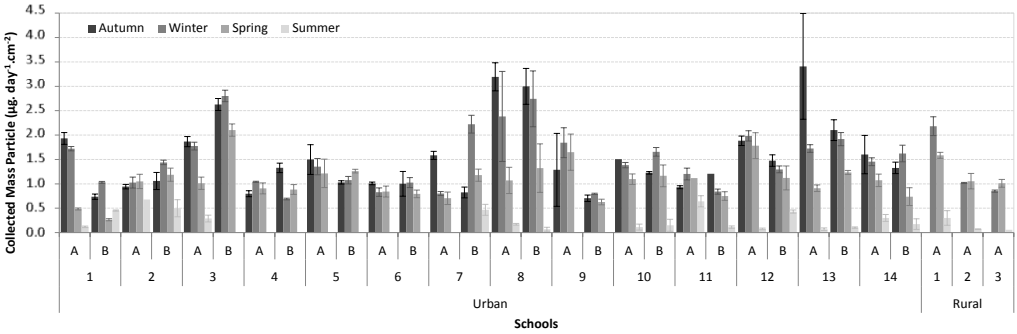

Figure 4.1.5 Seasonal variation of the collected particle mass per school and its classrooms for the polycarbonate filters.

Spring season showed lower average values of the collected particle masses than autumn and winter. In the urban area, classrooms presented a mean value of 1.05 ± 0.38 µg $day^{-1}cm^{-2}$ and only classroom 3-B showed a higher value than 2 µg $day^{-1}cm^{-2}$. For rural classrooms the observed mean value of 1.22 ± 0.32 µg $day^{-1}cm^{-2}$ was higher.

The lowest collected masses were in the summer period (with no students attending classes). The urban cluster presented mean values of 0.27 ± 0.20 µg $day^{-1}cm^{-2}$ while the rural cluster presented an even lower mean value, 0.14 ± 0.14 µg $day^{-1}cm^{-2}$.

This seasonal trend of higher amounts of indoor particles in the coldest months is in line with other particulate matter studies ($PM_{2.5}$ and PM_{10}) conducted in schools (Fromme et al., 2007; Polednik, 2013), where higher levels of indoor particles were measured in winter. This observation is probably due to different ventilation practices during the studied seasons, showing that in the colder period the natural ventilation decrease leading to higher indoor accumulation of pollutants (Canha et al., 2013a).

In a similar study, Estokova and Stevulova (2012) measured particulate matter using passive deposition sampling in 3 different rooms of a house and reported an average

concentration of 1.6 µg $day^{-1}cm^{-2}$. However the authors used petri dishes instead of filters, their result coincides with the results of the present study for the autumn concentration (1.54 ± 0.74 µg $day^{-1}cm^{-2}$), for example.

4.1.4.2.1 Seasonal Variability

The seasonal variability was studied by assessing the statistical significance within seasons and the results are described in Table 4.1.4.

Table 4.1.4 Statistical treatment of collected masses in each classroom within seasons, by Mann-Whitney and Kruskal-Wallis tests. Statistical significantly values are shown in bold (p-value below 0.050). A – autumn, W – winter, Sp – spring and Su – summer. (n.a. - not available)

		Test	**Mann-Whitney**						**Kruskal-Wallis**
Cluster	**School**	**Classroom**	**A/W**	**A/Sp**	**A/Su**	**W/Sp**	**W/Su**	**Sp/Su**	**All**
Urban	1	A	**0.037**	**0.020**	**0.020**	**0.012**	**0.012**	**0.012**	**0.000**
		B	**0.020**	**0.020**	**0.020**	**0.012**	**0.012**	**0.012**	**0.000**
	2	A	0.270	0.210	n.a.	0.835	n.a.	n.a.	0.497
		B	**0.030**	0.270	**0.020**	**0.020**	**0.020**	**0.012**	**0.027**
	3	A	0.371	**0.037**	**0.037**	**0.012**	**0.020**	**0.012**	**0.002**
		B	0.111	**0.020**	n.a.	**0.012**	n.a.	n.a.	**0.007**
	4	A	**0.020**	0.066	n.a.	0.144	n.a.	n.a.	**0.010**
		B	**0.020**	**0.020**	n.a.	**0.012**	n.a.	n.a.	**0.010**
	5	A	0.377	0.371	n.a.	0.391	n.a.	n.a.	0.209
		B	0.270	**0.030**	n.a.	**0.020**	n.a.	n.a.	**0.017**
	6	A	**0.020**	**0.020**	n.a.	1.000	n.a.	n.a.	**0.050**
		B	0.540	0.270	n.a.	**0.012**	n.a.	n.a.	0.540
	7	A	**0.020**	**0.020**	n.a.	0.296	n.a.	n.a.	**0.050**
		B	**0.020**	**0.020**	**0.020**	**0.012**	**0.012**	**0.012**	**0.001**
	8	A	0.270	**0.020**	**0.020**	**0.037**	**0.012**	**0.012**	**0.006**
		B	0.540	**0.020**	**0.020**	**0.012**	**0.012**	**0.012**	**0.000**
	9	A	0.178	0.665	n.a.	0.540	n.a.	n.a.	0.568
		B	0.074	0.216	n.a.	**0.020**	n.a.	n.a.	**0.009**
	10	A	n.a.	n.a.	n.a.	**0.012**	**0.019**	**0.037**	**0.013**
		B	0.052	1.000	**0.030**	**0.012**	**0.020**	**0.020**	**0.027**
	11	A	**0.030**	n.a.	**0.020**	n.a.	**0.020**	n.a.	**0.019**
		B	n.a.	n.a.	n.a.	0.095	**0.020**	**0.020**	0.073
	12	A	0.270	0.270	**0.020**	0.144	**0.012**	**0.012**	**0.005**
		B	0.066	**0.037**	**0.030**	0.210	**0.020**	**0.020**	**0.009**
	13	A	**0.037**	**0.037**	**0.037**	**0.012**	**0.012**	**0.012**	**0.002**
		B	0.178	**0.020**	**0.020**	**0.012**	**0.012**	**0.012**	**0.000**
	14	A	0.551	0.074	**0.037**	**0.012**	**0.020**	**0.012**	**0.002**
		B	0.074	**0.037**	0.052	**0.012**	**0.020**	**0.020**	**0.001**
Rural	1	A	n.a.	n.a.	n.a.	**0.012**	**0.012**	**0.012**	**0.006**
	2	A	n.a.	n.a.	n.a.	0.676	**0.012**	**0.012**	**0.031**
	3	A	n.a.	n.a.	n.a.	**0.012**	n.a.	n.a.	**0.004**

When applied the Mann-Whitney test to the binaries groups including summer, it was found that summer was significantly different when compared to the other seasons (p-values always lower than 0.050, except only once for the binary group autumn/summer for classroom 14-B).

The main difference in summer when compared to other seasons is the absence of students in the classroom. The binary group that showed less significant difference was autumn/winter (only 38% of the cases), which can be explained by the similar ventilation and behavior of particles' deposition in both seasons as a result of colder environment temperatures. The binaries groups with spring, namely autumn/spring and winter/spring, have a higher prevalence of significant differences results with 60 and 67% of the cases, respectively. The Kruskal-Wallis test showed significant differences for seasonal collected masses ($p<0.050$) for 84 % of the cases. Exceptions were only found for 5 classrooms out of a total of 31, namely classrooms 2-A, 5-A, 6-A, 9-A and 11-B.

4.1.4.2.2 Comparison between Classrooms

The masses of particles collected in both classrooms of each school were analyzed for polycarbonate filters. The significant differences between collected masses in both classrooms are shown in Table 4.1.5.

Table 4.1.5 Statistical differences between the mass collected in the two classrooms (A and B) of the studied schools. Significant differences are shown in bold (p-value below 0.050). (n.a. - not available)

School	Autumn	Winter	Spring	Summer
1	**< 0.001**	**< 0.001**	**< 0.001**	**< 0.001**
2	0.248	**< 0.001**	0.161	0.406
3	**< 0.001**	**< 0.001**	**< 0.001**	n.a.
4	**< 0.001**	**< 0.001**	0.728	n.a.
5	**0.025**	**0.013**	0.765	n.a.
6	0.950	**0.011**	0.476	n.a.
7	**< 0.001**	**< 0.001**	**< 0.001**	n.a.
8	0.434	0.480	0.351	**0.001**
9	0.246	**< 0.001**	**0.002**	n.a.
10	**0.002**	**< 0.001**	0.553	0.647
11	**0.004**	**< 0.001**	**0.019**	**< 0.001**
12	**0.002**	**< 0.001**	**0.004**	**< 0.001**
13	0.060	**0.025**	**< 0.001**	**0.040**
14	0.313	0.082	**0.010**	0.072

Winter was the season that registered higher significant differences between both classrooms (86% against 57% of autumn and spring). This fact indicates that in colder periods, characterized by closed windows and doors due to outside low temperatures, the collected masses reflects the singular environment of each classroom. When the outdoor contribution is higher, such as in autumn and spring due to the opening of the windows, the masses collected in different classrooms of the same school present less significant differences between them.

4.1.4.2.3 Urban vs. Rural

The mean values of the collected masses in both clusters are presented in Table 4.1.6. It is shown that both clusters are not statistically different between themselves all the seasons (p-values higher than 0.050). Winter presented the higher mean values of the collected masses for both type of clusters. Except for the spring season, the rural cluster always presented lower values of the collected masses when compared with the urban cluster.

Table 4.1.6 Mean values of the collected masses in both studied clusters, urban and rural. N is the number of classrooms where it was possible to recover the exposed filters and p-value is the value obtained by a Mann-Whitney test (statistical significantly values have a p-value below 0.050).

	Sampling campaigns											
	Winter				**Spring**				**summer**			
	Mean	**SD**	**N**	**p-value**	**Mean**	**SD**	**N**	**p-value**	**Mean**	**SD**	**N**	**p-value**
Cluster	**Polycarbonate filters**											
Urban	1.5	0.6	28	0.616	1.1	0.4	28	0.664	0.3	0.2	19	0.214
Rural	1.4	0.6	3		1.2	0.3	3		0.1	0.1	3	

From this study, it is possible to conclude that there is not significant difference between both clusters, which reveals that the indoor environment of the classrooms is more related with the specific characteristics of the classrooms and their occupancy than with the outdoor conditions.

4.1.4.3 Composition of the Particles

4.1.4.3.1 Chemical Elements of TPM

The ratio between the obtained results of this study and the certified values for the NIST-SRM® 1633a, with uncertainties of 95% confidence level, is shown in Figure 4.1.6. Overall, the data ratio is acceptable, although it was verified that Ba, Eu and Hf presented average values below the reference value (with a deviation of 12, 12 and 16%, respectively). However, all the elements presented an overall deviation within ± 3% regarding the reference values.

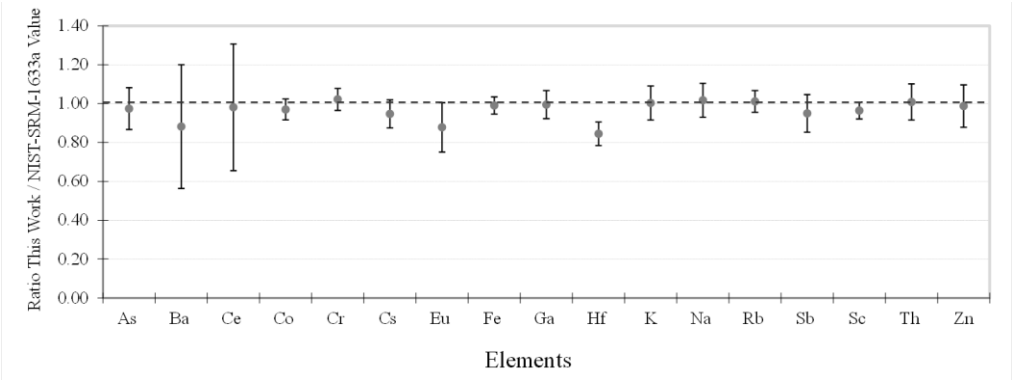

Figure 4.1.6 Ratios between the concentration results in this work for the NIST-SRM-1633a (coal fly ash) and their consensus values (Roelandts and Gladney, 1998), with uncertainties at the 95% confidence level. Dash line represents the ratio equal to 1.

The u-score test was applied for all elements and determined as the ratio between the difference, in module, of both the result and the certified value and the square root of the sum of the quadratic uncertainties of result and certified value (Dung et al., 2010). The u-score values were always below 1.64, which means that the obtained results do not differ significantly from the recommended ones, except for Hf that presented a value of 2.57 for the u-score. Since the u-score value for Hf was between 1.96 and 2.58 it means that it is not clear whether the laboratory result differs significantly from the assigned value.

The chemical elements obtained by INAA in the filters, with uncertainties at 67% confidence level, are shown in Table 4.1.7. The major elements were (by decreasing order) Ca, Fe, K, Na, Zn and Ba in a magnitude of ng $day^{-1}cm^{-2}$, while the other chemical elements ranged between pg $day^{-1}cm^{-2}$ and fg $day^{-1}cm^{-2}$.

The results obtained for the major elements in particles are consistent with other published studies that refer to major elements assessed in PM_{10} or $PM_{2.5}$ in indoor environments of

schools. Janssen et al. (1999) evaluated the PM_{10} in two Dutch schools and found that the major components of the indoor aerosol were Si, Ca, Cl, Fe, S and K, with values of 7.1, 4.6, 2.3, 1.4, 1.0 and 0.99 μg m^{-3}, respectively. Jonh et al., 2007 studied indoor $PM_{2.5}$ in three U.S.A. elementary schools and concluded that the major chemical elements in this type of particulate matter were S, Si, Ca and Fe, with values of 0.64, 0.32, 0.18 and 0.08 μg m^{-3}, respectively. Stranger et al. (2008) performed a similar study in 27 elementary schools of Belgium and concluded that the elements with the highest contributions to the indoor PM were Ca, S, Si and Al, with Ca showing the highest concentration with 2.2±0.7 and 1.8±0.6 μg m^{-3} for urban and suburban clusters, respectively. Heavy metals such as Cu, Pb, Zn, Ni, Cr, and V were also found but at minor concentrations.

Darus et al. (2012) studied the indoor floor dust in three nurseries schools of Malaysia and found that the heavy metal concentration followed the order Fe > Al > Zn > Pb > Ba > Cu > Cr > Ni, with Fe reaching maximum values of 7919 mg kg^{-1}. Source apportionment techniques indicated that indoor contaminant sources were of mixed origin with automobile emission being considered as the major source of heavy metals in indoor dust. This study also concluded that heavy metal concentration was influenced by the dustiness and ventilation of the building.

In the present study, calcium was the chemical element with higher concentration for all seasons when compared with others. This result is in agreement with similar studies conducted in schools and already described in the literature (Canha et al., 2012b; Stranger et al., 2008; Avigo et al., 2008). Estokova and Stevulova (2012), who studied the settled particulate matter in a Slovakian home, obtained calcium concentrations of 49.5 ng $day^{-1}cm^{-2}$, while in the present study results showed a higher average of 130 ng $day^{-1}cm^{-2}$. This difference is probably due to the specific characteristics of the sampling sites as in the present study the classrooms contain an indoor source of Ca from the chalk used in the blackboard. Regarding Fe, Zn, As and Cr, the Slovakian home study showed concentrations of 108, 47.6, 3.57 and 1.43 ng $day^{-1}cm^{-2}$, respectively, however, lower concentrations were obtained in the present study by, at least, one order of magnitude. In the present study, mean concentrations of Fe and Zn in the classrooms were 12.7 and 1.39 ng $day^{-1}cm^{-2}$, respectively; while for As and Cr values of 6.21 and 256 pg $day^{-1}cm^{-2}$ were respectively achieved.

Table 4.1.7 Concentrations of the chemical elements present in the particles in all the sampling campaigns. N is the number of classrooms studied.

		Autumn				Winter				Spring				Summer			
Element	**Unit**	**N**	**Mean**	**SD**	**Range**	**N**	**Mean**	**SD**	**Range**	**N**	**Mean**	**SD**	**Range**	**N**	**Mean**	**SD**	**Range**
As	pg $day^{-1}cm^{-2}$	3	5.7	3.8	[3 - 10]	6	7.6	4.8	[2 - 20]	27	8.3	13.6	[1 - 74]	15	2.5	2.0	[0.3 - 7]
Ba	ng $day^{-1}cm^{-2}$	10	0.75	0.49	[0.2 - 2]	11	62	370	[50 – 1000]	17	0.66	0.41	[0.2 - 2]	-	-	-	-
Br	pg $day^{-1}cm^{-2}$	9	82	52	[10 - 200]	3	28	24	[6 - 50]	30	36	21	[10 - 90]	-	-	-	-
Ca	ng $day^{-1}cm^{-2}$	14	180	100	[80 - 400]	18	160	110	[40 - 400]	27	130	80	[40 - 500]	12	45	30	[10 - 100]
Ce	pg $day^{-1}cm^{-2}$	13	59	33	[20 - 100]	23	43	33	[5 - 100]	27	37	25	[6 - 100]	17	10	7	[2 - 20]
Co	pg $day^{-1}cm^{-2}$	21	11	8	[2 - 30]	27	16	14	[4 - 60]	27	5.3	3.4	[2 - 10]	10	2.3	1.6	[0.4 - 5]
Cr	pg $day^{-1}cm^{-2}$	23	320	270	[20 - 1000]	29	350	140	[200 - 700]	29	200	80	[50 - 400]	21	150	110	[20 - 300]
Cs	pg $day^{-1}cm^{-2}$	13	4.3	3.2	[1 -10]	13	4.7	3.2	[0.4 - 10]	18	2.4	1.8	[0.5 - 6]	13	0.57	0.58	[0.01 - 2]
Eu	fg $day^{-1}cm^{-2}$	18	770	540	[200 - 2000]	20	940	1100	[90 - 5000]	28	510	330	[60 - 1000]	15	200	110	[80 - 400]
Fe	ng $day^{-1}cm^{-2}$	25	18	15	[2 - 60]	26	14	9	[0.7 - 30]	29	13	7	[2 - 30]	19	4.5	3.7	[0.01 - 10]
Ga	pg $day^{-1}cm^{-2}$	8	17	6	[6 - 20]	12	10	6	[2 - 20]	16	8.7	3.4	[2 - 10]	6	4.2	1.1	[2 - 5]
Hf	pg $day^{-1}cm^{-2}$	16	3.5	2.6	[0.7 - 10]	22	2.6	1.4	[0.8 - 6]	25	2.3	1.2	[0.4 - 4]	14	0.96	0.60	[0.3 - 2]
K	ng $day^{-1}cm^{-2}$	20	17	14	[4 - 60]	23	13	13	[3 - 60]	31	14	7	[2 - 30]	21	3.1	3.3	[0.3 - 10]
La	pg $day^{-1}cm^{-2}$	19	20	17	[3 - 70]	22	17	13	[3 - 50]	31	17	12	[3 - 60]	21	4.0	3.3	[0.2 - 10]
Na	ng $day^{-1}cm^{-2}$	20	14	7	[6 - 30]	22	10	4	[5 - 20]	31	14	5	[5 - 30]	21	3.8	2.2	[0.3 - 9]
Rb	pg $day^{-1}cm^{-2}$	9	180	130	[60 - 400]	15	110	60	[60 - 300]	13	70	34	[30 - 100]	6	40	11	[30 - 60]
Sb	pg $day^{-1}cm^{-2}$	25	13	5	[6 - 20]	27	12	18	[2 - 100]	30	10	5	[2 - 20]	20	4.4	3.6	[0.2 - 10]
Sc	pg $day^{-1}cm^{-2}$	26	4.3	3.3	[0.3 - 10]	26	3.9	2.7	[0.4 - 10]	28	3.2	1.9	[0.4 - 9]	19	1.2	0.9	[0.06 - 3]
Sm	pg $day^{-1}cm^{-2}$	18	3.8	3.4	[0.04 - 10]	20	2.8	2.5	[0.07 - 9]	26	3.1	2.0	[0.5 - 7]	20	0.88	0.71	[0.05 - 2]
Ta	pg $day^{-1}cm^{-2}$	17	1.6	2.2	[0.03 - 9]	21	1.1	1.5	[0.002 - 7]	17	2.4	4.4	[0.04 - 10]	8	0.74	0.56	[0.3 - 2]
Th	pg $day^{-1}cm^{-2}$	19	4.0	3.0	[1 - 10]	22	4.7	4.0	[1 - 10]	26	3.5	2.6	[0.6 - 9]	18	1.2	0.7	[0.4 - 2]
W	pg $day^{-1}cm^{-2}$	18	4.4	2.5	[1 - 10]	19	3.1	1.1	[1 - 5]	20	3.2	2.9	[0.9 - 10]	13	5.5	11.3	[0.5 - 40]
Zn	ng $day^{-1}cm^{-2}$	28	2.2	1.3	[0.6 - 6]	31	1.8	1.3	[0.6 - 6]	29	1.3	0.7	[0.1 - 3]	21	0.23	0.22	[0.01 - 0.8]

4.1.4.3.2 Water Soluble Ions of TPM

The quality control of the soluble ions determination, using certified reference materials, was previously described by Trancoso et al (2012). Overall, the trueness was estimated in terms of recovery, obtained from the analysis of independent sets of reference materials. The measurements in extraction solutions were considered unbiased whenever the recoveries were within the interval of 1.00 ± 0.10, which was fulfilled for all ions. Matrix influence on the ions analysis was also evaluated by spiking the digestion solutions with known amounts of ions. For FAAS, target recoveries of 1.00 ± 0.10 were always achieved, therefore the matrix effects on calibration were considered negligible and direct calibrations curves were used for analysis.

The concentrations of soluble ions in the collected particles for all the seasons are described in Table 4.1.8.

The highest average value of NO_3^- was registered in summer which can be explained by the higher concentrations of NO_3^- in the coarse particle fraction, presumably because of photochemically produced gaseous nitric acid reaction with marine and mineral coarse particles and the existence of higher temperatures in the summer that hinder the competitive formation of ammonium nitrate fine particles (Almeida et al., 2005).

The highest sulfate concentrations were found during the summer season (mean value of 24 ng $day^{-1}cm^{-2}$). This result may be explained by the higher photochemical activity and ozone concentration, which increase the oxidation of SO_2 and its conversion rate to sulfate (Khoder, 2002).

Calcium cation was the water soluble ion which showed higher concentrations when comparing to the others for all seasons. The water soluble ions concentrations were, by decreasing order, $Ca^{2+} > Cl^- > SO_4^{2-} > K^+ > Na^+$ (in autumn); $Ca^{2+} > SO_4^{2-} > Na^+ > Cl^- > K^+$ (in winter); $Ca^{2+} > Cl^- > SO_4^{2-} > Na^+ > K^+$ (in spring) and $Ca^{2+} > SO_4^{2-} > Cl- > NO_3^- > Na^+$ (in summer).

John et al. (2007) studied the water soluble ions of $PM_{2.5}$ from the indoor of three elementary U.S.A. schools and found that the anions concentrations were, by decreasing order, $SO_4^{2-} > NO_3^- > Cl^-$, while the cations concentrations were, by a decreasing order, $NH_4^+ > Ca^{2+} > Na^+ > K^+ > Mg^{2+}$. Pegas et al. (2012) assessed the water soluble ions content of PM_{10} collected in a Portuguese school and found carbonate as the dominant ion, followed by the calcium ion, hypothesized to be mainly originated from the chalk crayons.

Table 4.1.8 Concentrations of the soluble ions assessed in the collected particles in the four sampling campaigns. N is the number of classrooms studied.

		Autumn				**Winter**				**spring**				**Summer**			
Water-Soluble Ion	**Unit**	**N**	**Mean**	**SD**	**Range**	**N**	**Mean**	**SD**	**Range**	**N**	**Mean**	**SD**	**Range**	**N**	**Mean**	**SD**	**Range**
Ca^{2+}	ng $day^{-1}cm^{-2}$	26	5	12	[40 - 100]	31	34	11	[20 - 80]	30	37	9	[30 - 60]	8	48	29	[20 - 100]
K^{+}	ng $day^{-1}cm^{-2}$	26	10	12	[3 - 50]	31	4.8	4.4	[2 - 30]	29	4.4	1.6	[2 - 9]	6	2.3	0.9	[1 -4]
Mg^{2+}	ng $day^{-1}cm^{-2}$	26	1.4	0.6	[0.7 - 3]	31	1.1	0.6	[0.4 - 3]	30	0.96	0.37	[0.3 - 2]	8	0.91	0.45	[0.5 - 2]
Na^{+}	ng $day^{-1}cm^{-2}$	26	9.9	4.1	[5 - 20]	31	9.4	4.9	[4 - 20]	29	8.4	2.4	[5 -14]	8	4.9	2.0	[3 - 8]
Cl^{-}	ng $day^{-1}cm^{-2}$	26	21	38	[5 - 200]	31	8.1	3.4	[3 - 20]	30	12	4	[5 - 20]	8	8.9	2.2	[6 - 10]
NO_2^{-}	pg $day^{-1}cm^{-2}$	21	220	280	[10 - 1000]	18	320	360	[40 - 2000]	22	280	170	[100 - 800]	7	1200	600	[300 - 2000]
NO_3^{-}	ng $day^{-1}cm^{-2}$	25	3.3	2.5	[0.9 - 10]	31	2.9	2.0	[0.4 - 9]	30	4.0	1.7	[1 - 8]	8	7.3	2.1	[5 -10]
PO_4^{3-}	ng $day^{-1}cm^{-2}$	26	4.3	9.6	[0.4 - 50]	31	2.1	1.1	[1 - 9]	29	2.7	1.3	[1 -5]	6	1.5	0.7	[1 -2]
SO_4^{2-}	ng $day^{-1}cm^{-2}$	26	18	41	[3 - 200]	31	13	22	[2 - 100]	28	11	14	[4 - 80]	7	25	47	[6 - 100]
F^{-}	ng $day^{-1}cm^{-2}$	25	2.1	0.8	[0.3 - 4]	31	1.5	0.6	[1 -3]	29	2.2	0.7	[1 - 4]	6	0.98	0.22	[0.8 - 1]

4.1.4.3.3 Assessed Percentage of the TPM

The analyzed content of the particles collected inside the classrooms was compared with the total masses, along with percentages of the analyzed components by season and by cluster (Figure 4.1.7).

The average percentage of analyzed mass over the total mass by season was of 11.0 ± 7.0, 10.3 ± 6.6, 17.6 ± 6.7 and 17.5 ± 16.2% for autumn, winter, spring and summer, respectively. One of the main reasons for this lower percentage of analyzed contents is the fact that the carbonaceous aerosols present in the collected particles were not analytically assessed, along with oxides and silicates from the mineral particles.

In fact, carbonaceous aerosols are a significant fraction of atmospheric aerosols and compromise a wide range of compounds. The carbon in aerosols can be classified in carbonates, elemental carbon (EC) or black carbon (BC) and organic carbon (OC). In previous studies, it has been estimated that this fraction is between 20 and 50% of the $PM_{2.5}$ mass in urban and rural locations (Calvo et al., 2013).

Calcium represented 63 - 73% of the total analyzed mass in the urban cluster with exception to summer. However, in the rural cluster, calcium represented only 42 - 46% of the total mass analyzed, which shows a minor contribution of this element when compared with the urban cluster. A better ventilation of the classrooms in the rural cluster was probably responsible for the smaller calcium accumulation indoors, since its origin is mainly the blackboard chalk.

Regarding potassium, the urban cluster showed very low values of this element in all seasons (ranging from 4 to 8% of the analyzed mass). However, the rural cluster presented a substantial higher value of potassium for the winter and spring seasons, 22 and 18% of the analyzed mass, respectively. Since soluble K is known to be one of the main components of the wood ash, the high content of elemental potassium can be due to its high soluble percentage, which comes from burning wood in rural areas (Canha et al., 2012a).

In fact, school 1 from the rural cluster uses as heating system the burning of wood in the classrooms (in one classroom, there is a fireplace and in the other, there is a slow combustion stove). The amount of K in this specific school is 5.5 times higher than the overall mean of the rest of the schools in the present study. Therefore, the highest content of K in the rural cluster is probably due to the contribution of the burning wood source.

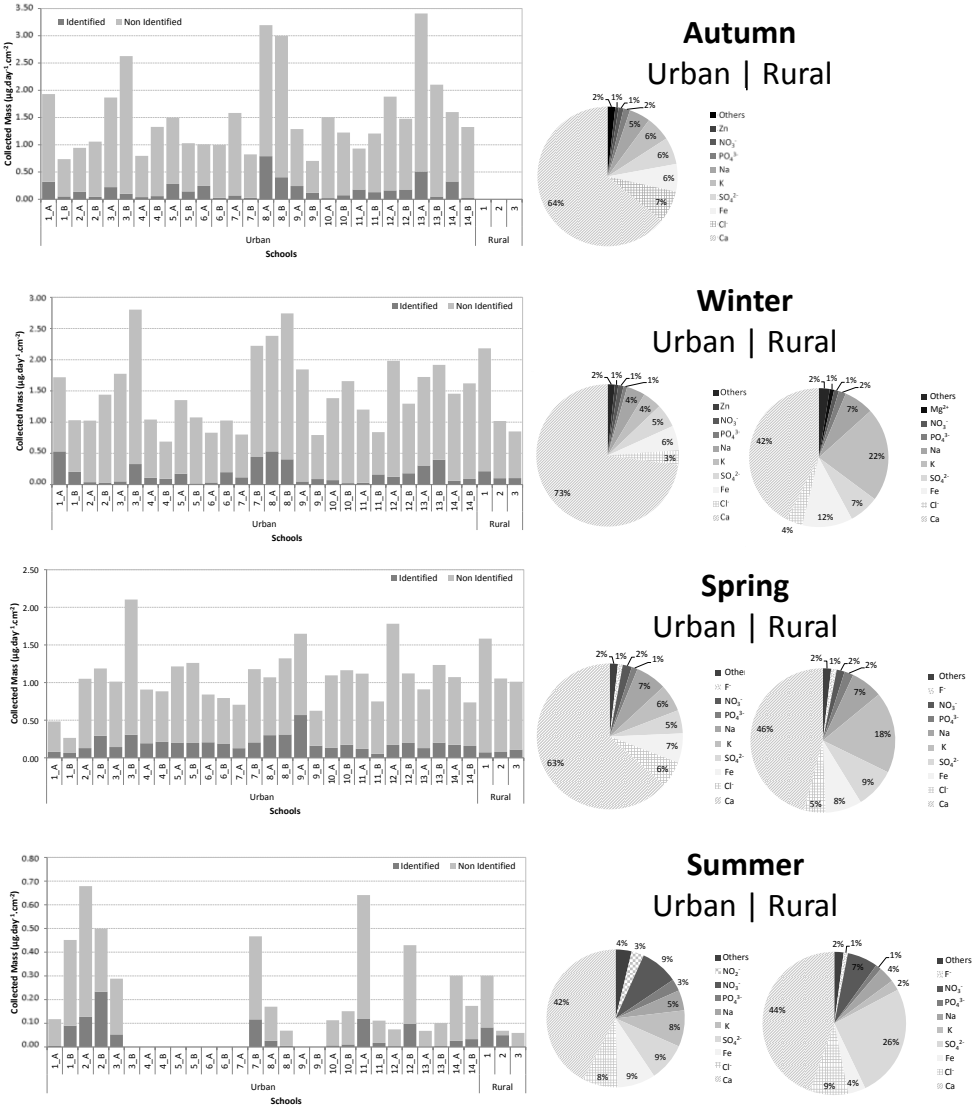

Figure 4.1.7 Identified and non-identified mass components for each season (left) and pie charts for the percentage of identified compounds of the collected particles for each season and for each type of environment, urban or rural (right).

Overall, calcium had the highest levels in both type of clusters. In the urban cluster, Fe was also one of the main elements in all seasons, along with Cl (in autumn), SO_4^{2-} (in winter), Na (in spring) and NO_3^- and SO_4^{2-} (in summer). The major difference between rural and urban clusters was the high levels of K registered in the rural cluster, as described above, in winter and spring. In the rural cluster, along with Ca and K, high levels of Fe were also

registered (in winter), as well as SO_4^{2-} (in spring) and SO_4^{2-} and Cl^- (in summer). These results agree with other studies described in the literature.

John et al. (2007) found high levels of Na, Cl and K in $PM_{2.5}$ from U.S.A. schools of a rural area, when compared with schools of an urban area. Overall, it was found that the major chemical elements in the indoor $PM_{2.5}$ were S, Si, Ca and Fe. In The Netherlands (Janssen et al., 1999), PM_{10} was sampled in two schools and the main components of the indoor aerosol were, by decreasing order, Si, Ca, Cl, Fe, S and K, which had considerable lower values in the outdoor.

In France, Tran et al. (2012) conducted a study over 3 elementary schools to assess the PM and its elemental composition, with main focus on heavy metals. PM_{10} concentrations rose during children's activities. Crustal elements represented an important portion (7 - 10%) of the indoor PM_{10} mass, mostly driven by the Ca content (4.4 - 7.2%) due to the use of chalk (which was the element with higher indoor concentrations). Chalk dusts, re-suspension by children activities and transport of outdoor soil dust were specified as the main sources of Ca, Al, Fe, Sr, and Ti. In Stockholm, Molnár et al. (2007) studied the chemical characterization of $PM_{2.5}$ in five elementary schools concluded that elements with the largest contribution to the aerosol were S, Fe, K and Ca, in decreasing order. It was found that Ti was significantly higher indoors in all locations, probably due to the use of TiO_2 indoors, as a paint pigment.

4.1.4.3.4 Source Apportionment

4.1.4.3.4.1 Correlations

Correlations between chemical elements and water soluble ions were evaluated for each season and only parameters with, at least, 40% of the results per season were considered. Several significant correlations were found in each season. However only the most relevant significant correlations concerning to source apportionment are described next.

A significant correlation between the ions Ca^{2+} and SO_4^{2-} was found in all seasons. Both autumn and summer showed a very good correlation ($r > 0.80$) while winter and spring revealed a good correlation ($60 < r < 80$). This correlation can be explained by the local use of blackboard chalk in all studied classrooms, which is mainly Ca_2SO_4 (Almeida et al., 2011).

The elements that are typically associated with soil source (Canha et al., 2010c; Calvo et al., 2013) namely, Ce, Eu, Fe, Hf, K, La, Sc, Th and Sm, showed a good or very good correlation between themselves for all seasons.

A sea salt spray source was also identified due to correlations observed between Na^+, Cl^- and Mg^{2+} (Almeida et al., 2013) in all the seasons. In autumn, a weak correlation ($r < 0.50$) was found between elemental Na and Mg^{2+}. A good and a very good correlations between Cl^-, Mg^{2+} and Na^+ were found in winter and in spring, respectively. In this last season, a good correlation between Na and Br was also observed (Br is also usually associated with a marine source). In summer, only a very good correlation between Na^+ and Cl^- was found.

A secondary aerosols source, which is usually characterized by the ions SO_4^{2-}, NO_3^- and NH_4^+ (Almeida et al., 2009), was not assessed since no correlations were found between SO_4^{2-} and NO_3^- for any season. The cation ammonium could not be analytical determined because it was already volatilized, since the ammonium nitrate is unstable because of the higher vapor pressure of NH_3 and HNO_3, which conducts to its partial volatilization above 20ºC and complete at more than 25ºC (Calvo et al., 2013). Considering that the sampling period of the campaigns ranged between 2 to 3 months and that indoor temperature of the classrooms varied between 18ºC to 22ºC, after the collection of the exposed samples and despite the careful handling and storage of samples, it was not possible to determine this cation. In fact, no correlation was found between SO_4^{2-} and NO_3^-, which are usually present in source apportionment studies of particulate matter (Canha et al., 2012a) to characterize a secondary aerosol source.

Zinc is usually associated with anthropogenic sources and in this study it was possible to found some correlations with some other anthropogenic elements, such as Sb (spring and summer). However, during autumn, winter and spring, Zn showed correlations with elements with characteristics from other sources, such as Fe (weak correlation in autumn) and Na (moderate correlation in autumn, where moderate corresponds to $0.50 < r < 0.60$), which can be associated to a soil source. In winter, Zn only presented a good correlation with NO_3^-. Although, in spring, Zn presented correlations with Br + Na^+ + Ca + K (weak), K^+ + F^- (moderate) and Ba + Na + Sb (good). In summer, Zn presented moderate and good correlations with elements typically associated with soil sources (As, Ce, Hf and Sm – moderate correlations; Ca, Eu, Fe, La, Sc – good correlations), along with a correlation with Sb. Zinc and Sb are both associated with heavy industries and Zn by itself is associated with mechanical abrasion of tyres (Almeida-Silva et al., 2011). Antimony also showed a very good correlation with sodium in the spring season.

4.1.4.3.4.2 Enrichment factors

The crustal enrichment factors (EF) analysis is used to evaluate the strength of the crustal and non-crustal origin of the elements. The enrichment factors were calculated, using Sc as a crustal reference element (except for the rural cluster in the spring season as Sc values were not available, therefore Sm was used instead since both elements were correlated - coefficient of determination $R^2 = 0.97$) and the soil composition reference values from Mason and Moore (1982). The EFs were calculated based on Equation 3.2.1 (Chapter 3.2.4.3).

The enrichment factors for both clusters and all studied seasons are shown in Figure 4.1.8. Elements with EF values that approach unity can be considered predominantly from crustal source. If the evaluated element has EF values higher than 10 its provenance is asserted mainly to local, regional and/or long transportation phenomena from other natural and/or anthropogenic sources (Canha et al., 2010b).

For the urban cluster, Sb and Zn presented values of EFs above 10 for all seasons. Additionally, in autumn it was also observed the enrichment for Br and Ca (EFs > 10), in winter for Ca and in spring for Br. This fact suggests that there is a non-crustal origin for these elements. Usually, Sb and Zn are associated with sources such as combustion, incineration and traffic (mainly tires and brake wear) (Almeida et al., 2005). However, an anthropogenic contribution of Zn inside classrooms was already observed by Avigo Jr. et al. (2008) and Almeida et al. (2011), in Brasilian and Portuguese elementary schools, respectively, which indicates the existence of a Zn indoor source. In fact, nowadays, several products using Zn are available in the market for indoor application, namely to protect steel, walls, wood surfaces, doors and windows (Almeida et al., 2011). Zinc compounds are often used in paintings and driers in indoor environments. Driers are used to develop a rapidly drying skin on paint by oxidation and can be divided in two classes: those that affect the oxidation of oils and those that affect the polymerization process itself.

The polymerizing driers are often metals with only one possible oxidation state, such as Zn, Ca, K, Li and Na (Ravikumar et al., 2012). One of the inorganic pigments used in yellow paints is zinc chromate. Due to their anti-corrosive properties, zinc compounds (such as zinc phosphate, zinc chromate and zinc molybdate) are also used to protect iron and steel, through galvanic-type coatings containing zinc powder (Ravikumar et al., 2012).

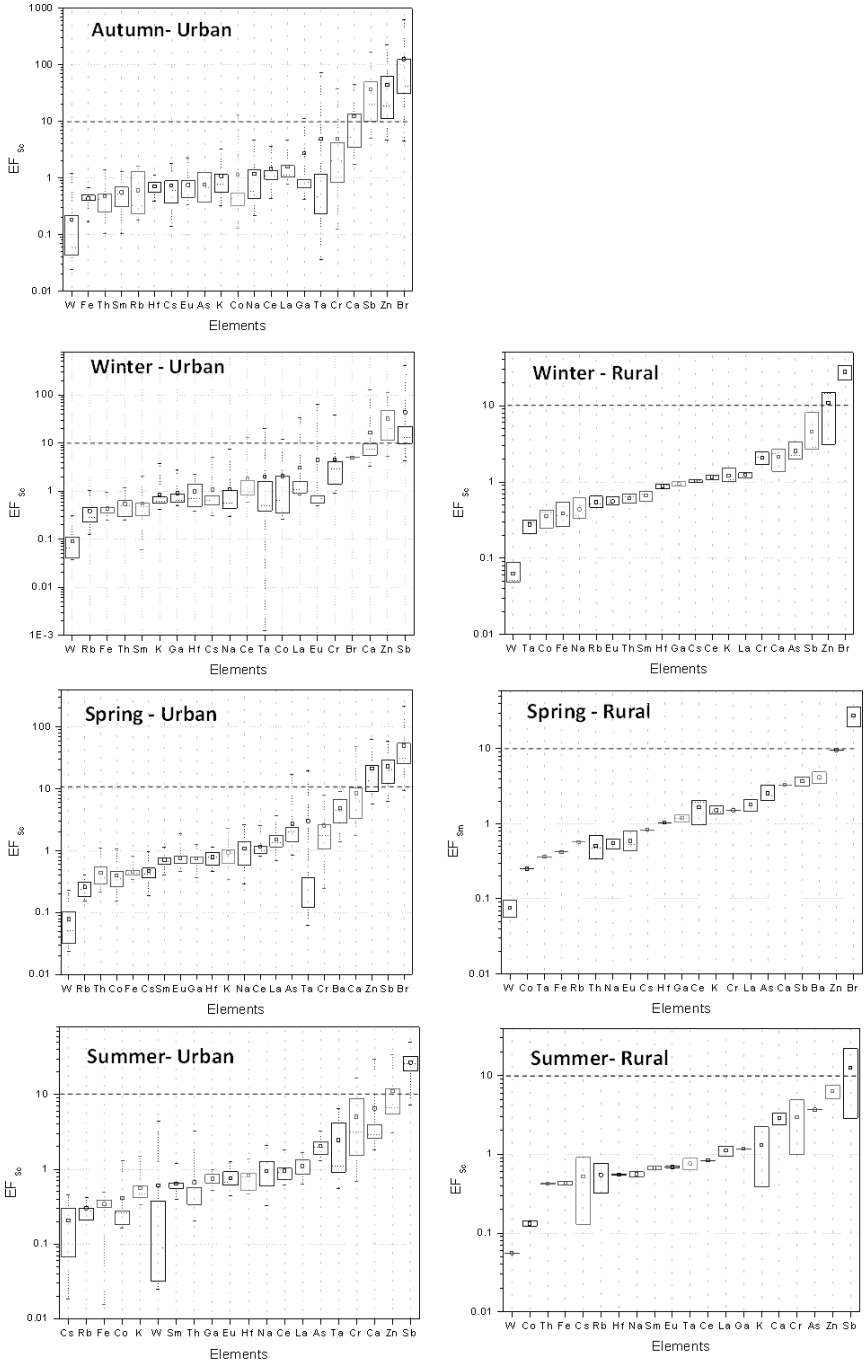

Figure 4.1.8 Crustal Enrichment Factors for the particles collected in all seasons and in urban (left) and rural (right) environments.

Therefore, it is possible to conclude that the anthropogenic source of Zn present inside the classrooms can be related to the outdoor and traffic related source, but also due to contribution of a specific indoor source of Zn, namely from the wall painting and protective coating of iron and steel present indoors.

The enrichment in calcium was only verified in autumn and winter. These seasons are characterized by closed doors and windows due to the atmospheric outdoor conditions (cold period). This specific condition can promote the accumulation of blackboard chalk dust in indoors environments, as the correlations analysis showed it is characterized by a strong correlation between Ca and SO_4^{2-}, which is reflected by the Ca enrichment factors.

In the urban cluster, it was also observed an enrichment of bromine in autumn and in spring. This enrichment has a marine source since bromine is usually associated with sea salt elements (Calvo et al., 2013).

In the rural cluster, it was observed an enrichment of bromine in winter and spring, probably due to a marine source. An enrichment of Zn was also observed for winter and spring probably due to a higher indoor accumulation of this element with an indoor source and Sb for summer which probably reflects a traffic source.

4.1.5 Conclusions

This study has successfully applied passive methodology to collect particulate matter in indoor environments of primary schools. The collected samples were then characterized using classical analytical techniques. This method have several great advantages: (i) no disruption during the classes due to the absence of noise, contrasting with the noisy pumps used in traditional automatically methods; (2) no need of expensive equipment and technical knowledge to monitor the equipment; and (3) simultaneously spatial and temporal survey of different classrooms clusters with little financial settling costs. Although, this method is limited to qualitative data, since the air volume sampled is not known, it can be used as an efficient tool to obtain preliminary or qualitative information in indoor environments. Other disadvantage of the method of passive sampling is that the size of particles has influence in the deposition rate since larger particles have a more rapid settling rate than smaller particles, which conducts to a higher collection of coarse particles than fine or ultra-fine particles. Additionally, the present study showed that passive sampling method can be used to compare different classrooms in different clusters and that source apportionment techniques can be applied to investigate the origin of the particles present in the indoor of the classrooms. These results represent an important source of information,

which can be used for further mitigation and improvement measurements of indoor air quality in classrooms that show greater indoor concentration of particles and/or of a specific component of the particles.

The major role of natural ventilation in the accumulation of indoor particles can be evidenced by the seasonal trends of indoor particles where low ventilation habits (opening of doors and windows) resulted in higher indoor concentration of particles.

In schools using blackboard chalk in their daily activities, calcium was identified as the major component of the indoor particles. Zinc as also showed a relevant importance in indoor particles, probably due to indoor sources such as paint. Soil re-suspension (from student's activities) and traffic sources were also found in the indoor particles, showing the influence of the outdoor over the indoor.

This study also confirmed that urban and rural schools present similar indoor particles behavior revealing that the characteristics of the classroom indoor, its occupancy and ventilation habits are the major contributors to the variability of indoor particles.

4.2 Indoor and Outdoor Biomonitoring using Lichens at Urban and Rural Primary Schools

Based on article of same title:
Canha N, Almeida, SM, Freitas MC & Wolterbeek HT

Journal of Toxicology and Environmental Health, Part A (2014) 77 (14-16): 900-915.

DOI: 10.1080/15287394.2014.911130

4.2.1 Abstract

Monitoring particulate matter and its chemical constituents in classrooms is a subject of special concern within the scientific community in order to control and minimize children exposure. Regulatory sampling methods have presented several limitations in their application to larger number of classrooms due to operational and financial constraints. Consequently, passive sampling methodologies using filters were developed for indoor sampling. However, such methodologies could not provide parallel information for outdoors which is important to identify pollution sources and to assess the outdoor contribution to the indoor. Therefore, biomonitoring with transplanted lichens - a technique usually applied for outdoor studies - was used in indoor and outdoor of classrooms. Three main objectives were proposed: (i) to characterize simultaneously the indoor and outdoor of classrooms regarding the inorganic air pollutants; (ii) to investigate spatial patterns of lichen conductivity, and (iii) to assess pollution sources that contribute to a poor indoor air quality in schools. Lichens *Flavoparmelia caperata* were transplanted to the indoor and outdoor of classrooms during 59 days. After exposure, electric conductivity of lichens leachate was measured to evaluate lichen vitality and cell damage. At outdoors, lichens conductivity was higher nearby the main highways and, at indoors, a great variability of values was found which may indicate different emissions sources and different ventilation patterns. Chemical content of lichens was assessed by INAA and As, Br, Ca, Ce, Co, Cr, Cs, Eu, Fe, Hf, K, La, Na, Rb, Sb, Sc, Sm, Sr, Ta, Th, Yb and Zn were determined. Element accumulation, crustal enrichment factors and spatial variability of elements were analyzed and contaminants from anthropogenic sources, such as traffic (As, Sb and Zn) and indoor chalk (Ca) found. Classrooms with potential indoor air quality problems were identified by presenting higher accumulation of inorganic pollutants in the exposed biomonitors.

4.2.2 Introduction

Indoor air monitoring is an important issue in order to (1) assess indoor air quality (IAQ) that people breathe, (2) determine exposure levels, (3) identify emission sources, and (4) apply mitigation measures to improve it.

Among the several indoor air pollutants, particulate matter (PM) is one of special concern due to its relation with morbidity and mortality for both cardiovascular and pulmonary causes (Martinelli et al., 2013) that vary in effect depending on aerodynamic diameter and chemical composition (Oeder et al., 2012).

Standard sampling methods to monitor PM are predominantly based on active sampling methodologies (Council Directive EU, 2008). However, generalized and regulatory use of air filters with air pumping devices (Almeida et al., 2011) raises several practical issues, which limit their applicability and adequacy in schools due to noise and sampling apparatus interference with students' performance. To overcome these constraints, a passive sampling methodology was developed to collect total PM inside classrooms based upon passive deposition of particles in filters (Canha et al., 2014a). Child exposure to inorganic pollutants was previously assessed (Canha et al., 2010a) and an association between collected PM mass and rhinitis symptoms was noted (Canha et al., 2011). This passive sampling methodology displays several advantages, including (1) low interference on classroom activities, (2) no need for expensive equipment and technical knowledge to deal with, and (3) allowing a simultaneously spatial and temporal survey of classrooms with limited financial resources. Despite the disadvantage of not being a volumetric or quantitative method, this passive methodology was used as an efficient tool to obtain qualitative information regarding the studied indoor environments. A drawback of this passive method is the inability to sample outdoors due to airflows and wind that disturb the sampling apparatus, and this fact limits the study of outdoor contribution to the classrooms IAQ.

To overcome this issue, biomonitoring with lichens appears as a possible solution since the application of this technique to outdoor air pollution assessment was previously shown to be reliable (Augusto et al., 2004; Garty, 2010).

Lichens are symbiotic organisms consisting of fungi and algae or cyanobacteria (Augusto et al., 2007) and have the ability to accumulate elements in excess of physiological requirements in close correlation with atmospheric element levels (Sloof, 1995; Bargagli et al., 2002; Canha et al., 2013b). In contrast to vascular plants that have a waxy cuticle, lichens do not possess this outer protection barrier and, hence, their thalli are susceptible to

penetration by airbone substances, some of which are essential for cell functions while others may be toxic (Weissman et al., 2006). Another key parameter to evaluate pollution effect on lichens is lichen physiological vitality, as determined from lichen membrane permeability (Garty et al., 1997; 2000; Garty, 2001). Lichen membranes organize the interior of cells into different compartments and use pore size, pumps, and carriers that control uptake, release, and relocation of molecules and ions (Almeida et al., 2012). Pollution produces disturbance of this organization, thereby changing membrane permeability to ions with an accompanying loss of electrolytes, mainly of K and Mg (Nash, 1996). Several experimental procedures to evaluate the impact of environmental pollution on lichen vitality are available (Mulgrew and Williams, 2000), but measuring the electric conductivity of a leachate with an appropriate electrode is the easiest way to monitor membrane integrity (Godinho et al., 2004; Marques and Freitas, 2005).

Leachate conductivity is considered the most sensitive indicator of general lichen vitality (Sloof, 1995; Frati et al., 2005), and is influenced by stress that lichens are subjected to at the transplantation site due to atmospheric conditions and due to local environmental pollution impact. Atmospheric conditions may produce changes in photosynthetic processes of lichens since environment determines (1) intensity, quality, and period of light radiation reaching lichen thalli during the day, as well as the exposure period; (2) temperature, which affects lichen optimal metabolism; and (3) water availability in the form of precipitation, humidity, fog, or dew, influencing the degree of thallus hydration (Kershaw, 1985; Pirintsos et al., 2011; Canha et al., 2013b). Further, along with the impact of local environmental pollution as previously described, electrolyte leakage is a measure of lichen cell membrane damage, that is, lichen vitality.

However, until now there have been few indoor biomonitoring studies and these were limited to only higher plants (Rzepka et al., 2010). Specific physical conditions of indoor environments, such as temperature and humidity, may produce physiological stress (Marques and Freitas, 2005), which may interfere in the accumulation process of air pollutants by lichens (Canha et al., 2013b). A pilot study with biomonitoring with lichens in indoors classrooms was conducted to determine its feasibility and to assess major atmospheric air contaminants from anthropogenic sources, such as Sb from traffic (Canha et al., 2012c). Therefore, biomonitoring with lichens may be applied to study outdoor and indoor environments simultaneously, which might provide relevant information regarding contribution of outdoor sources to indoors.

This investigation is a follow-up study where biomonitoring with lichens was applied to a larger number of classrooms from different clusters (rural and urban) to evaluate IAQ in

terms of air inorganic pollutants and vitality of lichens. IAQ characterization of classrooms was conducted and main sources of pollution were assessed. Classrooms with potential IAQ problems were identified to be designated for further studies and application of mitigation measures to decrease children exposure to air pollutants.

4.2.3 Materials and Methods

4.2.3.1 Description of the Sampling Site

The sampling sites were already described in section 4.1.3.1 of the previous subchapter 4.1 Particulate matter analysis in indoor environments of urban and rural primary schools using passive sampling methodology.

4.2.3.2 Sampling and Transplantation

Samples of the lichen *Flavoparmelia caperata* (L.) Hale and tree bark (*Olea europaea* Lineu, commonly known as olive tree) were collected from olive trees at about 1.5 m above the soil in Montargil (39◦03'24'' N, 8◦10'36'' W) in April 2010. Montargil is a Portuguese rural area considered clean from an air pollution point of view (Almeida et al., 2012).

In the laboratory, 10 lichens were separated randomly as reference base levels. After 1 week, lichen samples still attached to their substrate olive bark (in pieces of around 6 cm × 6 cm each, with an average of 3.3 g of lichen) were suspended into courtyards trees (using a nylon string) at about 1.8 m above the soil and on trays inside classrooms of the studied schools (at about 1.8 m above the floor). In urban areas, two classrooms were studied per school, while in rural area only one classroom was examined per school. In total, three sets of lichens with substrate were exposed in each sampling site. Exposure period ranged from 20 April 2010 to 18 June 2010, with a total of 59 days.

During the exposure period, in the urban area, the average temperature was 17.7 ± 4.2 ºC (9.5 – 32.3 ºC), average relative humidity was 70 ± 16 % (22-99%) and only one rainy day was registered. In rural area, the average temperature was 17.7 ± 5.8 ºC (5.6 – 33.0 ºC), average relative humidity was 61 ± 19 % (22-99%), and three rainy days were recorded.

4.2.3.3 Assessment of Cell Membrane - Electric Conductivity

After exposure, all lichen samples were sorted and cleared of extraneous material such as dust, leaf debris, fungus contamination, and degraded material in the lab. To assess lichen

vitality, samples were soaked in demineralized water and water conductivity was subsequently measured. The adopted procedure was based upon approaches developed by Garty et al. (2000) and applied by Almeida et al. (2012): (1) Lichen material was cleaned and rinsed during 5 s with demineralized water, repeating this step more 2 times; (2) after drying during 24h, about 100 mg was weighed and immersed in 10 ml demineralized water for 1 h; and (3) after removal of lichens, electric conductivity of solution was measured with a Conductometer Metrohm 712. Blanks were made by repeating the same procedure without immersing lichens and were subtracted from conductivity of the sample solution (0.2 ± 0.059 mS m^{-1} on average, n = 27). The electric conductivity of the demineralized water was always measured before solution conductivity measurements. Each sampling site had a total of four replicates analyzed.

4.2.3.4 Chemical Analysis - INAA

After cleaning and dry processes, samples were freeze-dried and ground in Teflon (balls and capsule) mills. After thorough homogenization, pellets of 250-300 mg were prepared and pelletized for element characterization by Instrumental Neutron Activation Analysis – INAA (Freitas et al., 2003). Therefore, chemical composition of exposed and unexposed biomonitors was assessed and in total 22 chemical elements were analyzed, namely, As, Br, Ca, Ce, Co, Cr, Cs, Eu, Fe, Hf, K, La, Na, Rb, Sb, Sc, Sm, Sr, Ta, Th, Yb, Zn. Three replicates were analyzed per sample and all of them were irradiated for 5 h at a thermal neutron flux density of $2.6–2.9\times1012$ $cm^{-2}.s^{-1}$ at the Portuguese Research Reactor (RPI-CTN/IST/UTL; nominal power 1MW). Gamma spectra of the irradiated samples were acquired with high-resolution, hyperpure Ge detectors, for a period of 2 and 3.5 h, after 4 days and 4 weeks, respectively. The k_0-INAA method (Freitas et al., 2004; Almeida et al., 2014) was used and 0.1% Au-Al alloy discs were employed as comparators and irradiated concurrently with the samples.

Quality control was affirmed by analyzing Lichen Reference Material (RM) IAEA-336, which was prepared as were the samples and was co-irradiated with them. In total, 23 RM replicates were done.

4.2.3.5 Quality control of INAA results

The ratio between the results obtained in this work and certified values for RM IAEA-336, with uncertainties at 95% confidence level, is shown in Figure 4.2.1. Moreover, the u-score test (Dung et al., 2010) was applied for all determined elements. The u-Score test is a rating system to evaluate analyses of performance and includes uncertainties of the measurements

and uncertainty of the assigned value. The u-score values for all analyzed elements were always below 1.64, indicating that the obtained results do not differ significantly from the certified ones.

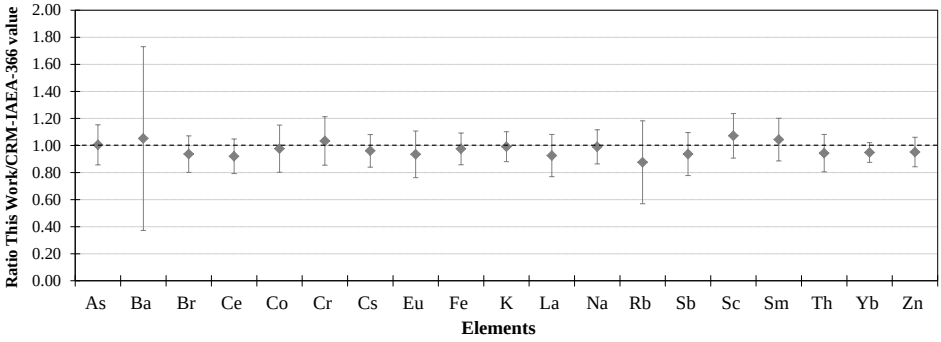

Figure 4.4.1 Ratios between concentrations obtained in this work for RM IAEA-366 and their certified values, with uncertainties at 95% confidence level.

4.2.3.6 Statistical Treatment

Statistical calculations were performed using STATISTICA software. Normality of data was tested using the Shapiro-Wilk test, and results showed that data did not present a normal distribution (p-value below 0.050). Therefore, Wilcoxon matched pairs and the Mann-Whitney U-Test were used. These tests are nonparametric; hence they do not consider any assumptions related to the distribution and basically are the same in that they compare between two medians to suggest whether both samples come from the same population or not. When both of the samples were not entirely independent of each other and had some factor in common, the Wilcoxon matched pairs test was applied (differences between pairs of indoor and outdoor levels). When the samples were independent, Mann-Whitney U-test was applied (differences between exposed and unexposed lichens). Statistical significance refers to $p < 0.050$. The geostatistical modelling map was built using GeoMS software (GeoMS, 2011) with the aim of assessing the spatial distribution of the electric conductivity in the city of Lisbon.

4.2.4 Results and Discussion

4.2.4.1 Integrity of Lichens Cell Membrane

Reference base levels of electric conductivity were determined for 10 lichens that were not transplanted but collected in the same area and on the same day as transplanted ones. The mean electric conductivity levels for reference lichens was 7.4 ± 2.0 mS $m^{-1}g^{-1}$ (n = 10).

Mean values of electric conductivity of exposed lichens were 13.2 ± 3.9 mS m^{-1} g^{-1} and 8.0 ± 1.2 mS $m^{-1}g^{-1}$ for urban and rural outdoor environments, respectively. Results demonstrated that exposed lichens in urban outdoors presented significant higher conductivity levels than reference values (p-value = 0.000), while exposed lichens in rural outdoors did not present significant differences with reference values (p-value = 0.581). Significant higher mean values of electric conductivity of exposed lichens were found for indoor environments, namely, 39 ± 15 mS m^{-1} g^{-1} for urban schools and 26.9 ± 5.8 mS $m^{-1}g^{-1}$ for rural schools (both with p-values below 0.050), attributed to physical specifications of indoor environments such as less light, less ventilation, and accumulation of gaseous pollutants as carbon monoxide (CO) and carbon dioxide (CO_2).

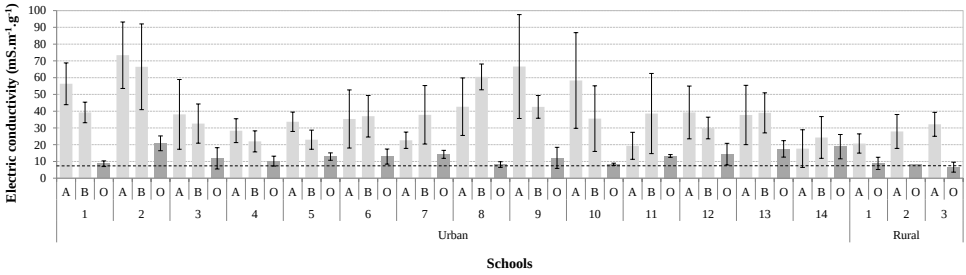

Figure 4.2.2. Conductivity levels measured in transplanted lichens (values in mS m^{-1} g^{-1}) at the sampling sites (A – classroom A; B – classroom B and O – outdoor). Dash line corresponds to conductivity value measured in unexposed lichens.

Figure 4.2.2 shows electric conductivities of exposed lichens in the studied environments. Differences between classrooms of the same school were observed, which indicates that ventilation habits used in a specific classroom play an important role in the classroom characteristics and consequently on the vitality of lichens, mainly due to outdoor air infiltration which is associated with relative humidity levels.

Figure 4.2.3 shows the spatial distribution of the exposed lichens' electric conductivity in outdoor of Lisbon primary schools. Only the urban cluster was evaluated regarding

geospatial distribution since only this cluster gathered a sufficient number of samples to obtain a reliable spatial resolution of data (n = 14).

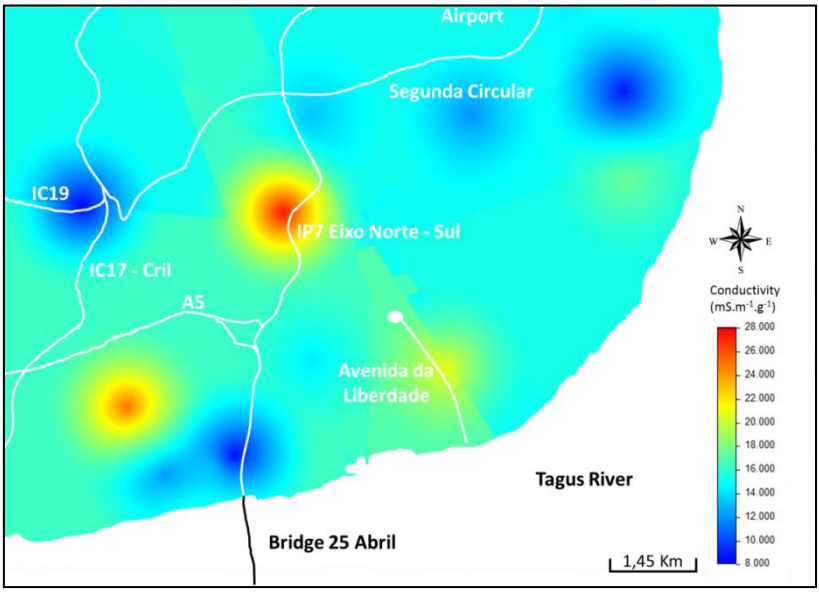

Figure 4.2.3 Spatial distribution of electric conductivity of biomonitors after exposure in urban cluster, Lisbon.

Figure 4.2.3 shows areas with high values of electric conductivity, which are associated with schools located nearby the main roads and avenues of the city, namely, school 2 at 130 m of Avenida da Liberdade, school 4 at 915m of highway A5, and school 14 at 117m of highway IP7 Eixo Norte-Sul. The outdoor of school 2 close to Avenida da Liberdade, which is one of the most polluted areas in Lisbon due to intensive traffic and characteristic topography (Borrego et al., 2000), presented the highest conductivity levels, confirming high levels of pollution already assessed through other studies (Almeida-Silva et al., 2011).

In the southwest region of Lisbon, it was possible to observe two more areas with high electric conductivities, which are located nearby the main highways (school 4 - A5 and school 14 - IP7 Eixo Norte-Sul). These highways are radial connections and part of the structural road network of the city, which serves to support it over long distances (CML, 2005).

4.2.4.2 Element accumulation

Tables A-1 and A-2 from Appendix section presents the chemical elements concentrations in exposed and unexposed lichens and for the studied environments (outdoor and indoor), and Figure 4.2.4 shows the exposed to control ratio (EC ratio), defined by Frati et al. (2005), which demonstrates accumulation of elements determined for all exposed lichen samples. The use of this ratio enables interpretation of changes in element content without assuming a linear or nonlinear model that describes element accumulation or release during the time of exposure (Godinho et al., 2009). EC ratio is also known as contamination factor (Fernández and Carballeira, 2001). The classification of EC ratio values refers to accumulation/loss during exposure and is divided in five classes: (i) 0 – 0.25: severe loss; (ii) 0.25-0.75: loss; (iii) 0.75-1.25: normal; (iv) 1.25-1.75: accumulation and (v) >1.75: severe accumulation.

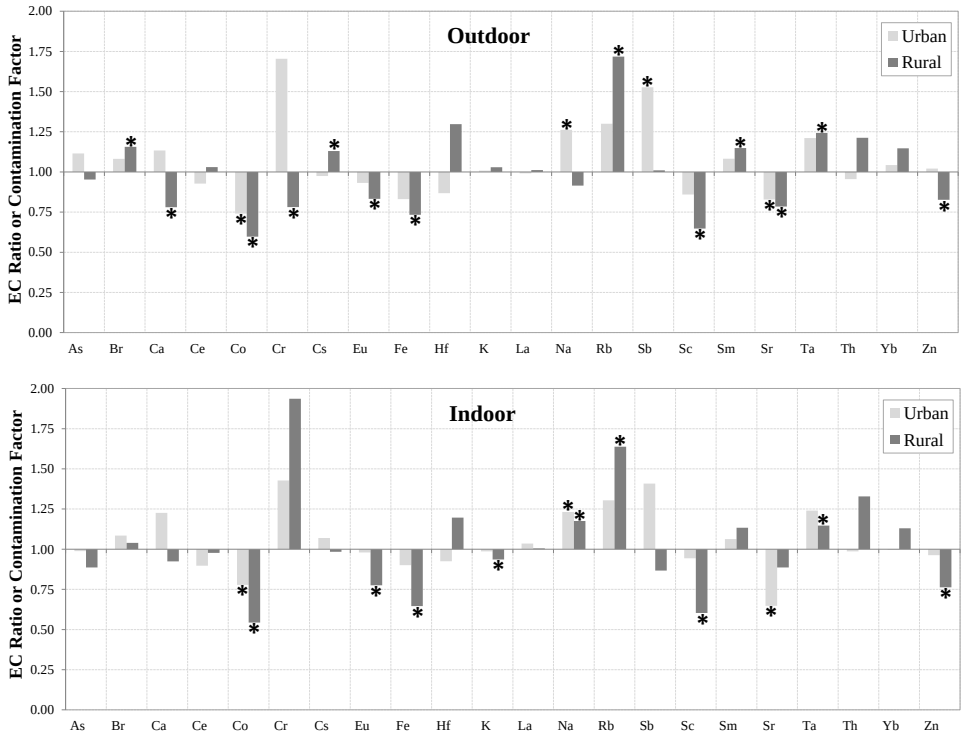

Figure 4.2.4 EC ratios or contamination factors of biomonitors after exposure period in both environments, indoor (up) and outdoor (down). * means a significant statistical difference (p-value below 0.050) between exposed and unexposed elemental content of lichens by a Mann-Whitney U Test.

Regarding the indoor environment, analysis of EC ratios allow one to conclude the existence of a loss with respect to the elements Co, Fe, and Sc in the rural cluster and Sr in the urban cluster with significant difference from unexposed values. Although in the normal range, Zn and Eu in the rural cluster and Co in the urban cluster presented values near the loss limit and were significantly different from unexposed levels. An accumulation for Cr, Rb, and Sb was found in the urban cluster that was not significantly different from unexposed samples, while in the rural cluster it was found an accumulation for Cr, Rb and Th, with Rb showing significant differences with unexposed values.

Concerning the outdoor environment, a significant loss of Co, Fe, and Sc for the rural cluster and a significant loss of Co for the urban cluster were detected. Close to the loss limit in the rural cluster were Ca, Cr, Eu, Sr, and Zn, while in the urban cluster only Sr presented values close to the loss limit. All elements were significantly different compared to unexposed values. An accumulation was found for Cr, Na, Rb, and Sb in the rural cluster, with Na and Sb showing significant differences, and for Hf and Rb in the urban cluster, with Rb presenting a significant difference.

The advantage of biomonitoring in relation to other passive methods that use filters (Canha et al., 2014a) is that biomonitoring enables parallel exposure of lichens indoors and outdoors, which contribute to a more complete understanding of outdoor contribution to indoors.

Figure 4.2.5 shows the relationship between indoor and outdoor concentrations of elements from exposed lichens. It is noteworthy that As, Ca, La, Sb, Sm, Zn, and Yb demonstrated significant correlations between indoor and outdoor concentrations.

This finding indicates the existence of common indoor and outdoor sources for these elements, which affirms the contribution of outdoor in indoor environment. Elements such as Ca, La, and Sm are usually associated with soil sources (Canha et al., 2012a), while As, Sb, Yb, and Zn are associated with anthropogenic sources such as traffic sources (Almeida-Silva et al., 2011; Calvo et al., 2013), namely, mechanical abrasion of tyres and brakes. Data showing no marked difference between indoor and outdoor concentrations were observed for all elements, indicating similar accumulation behaviour of biomonitors in both environments.

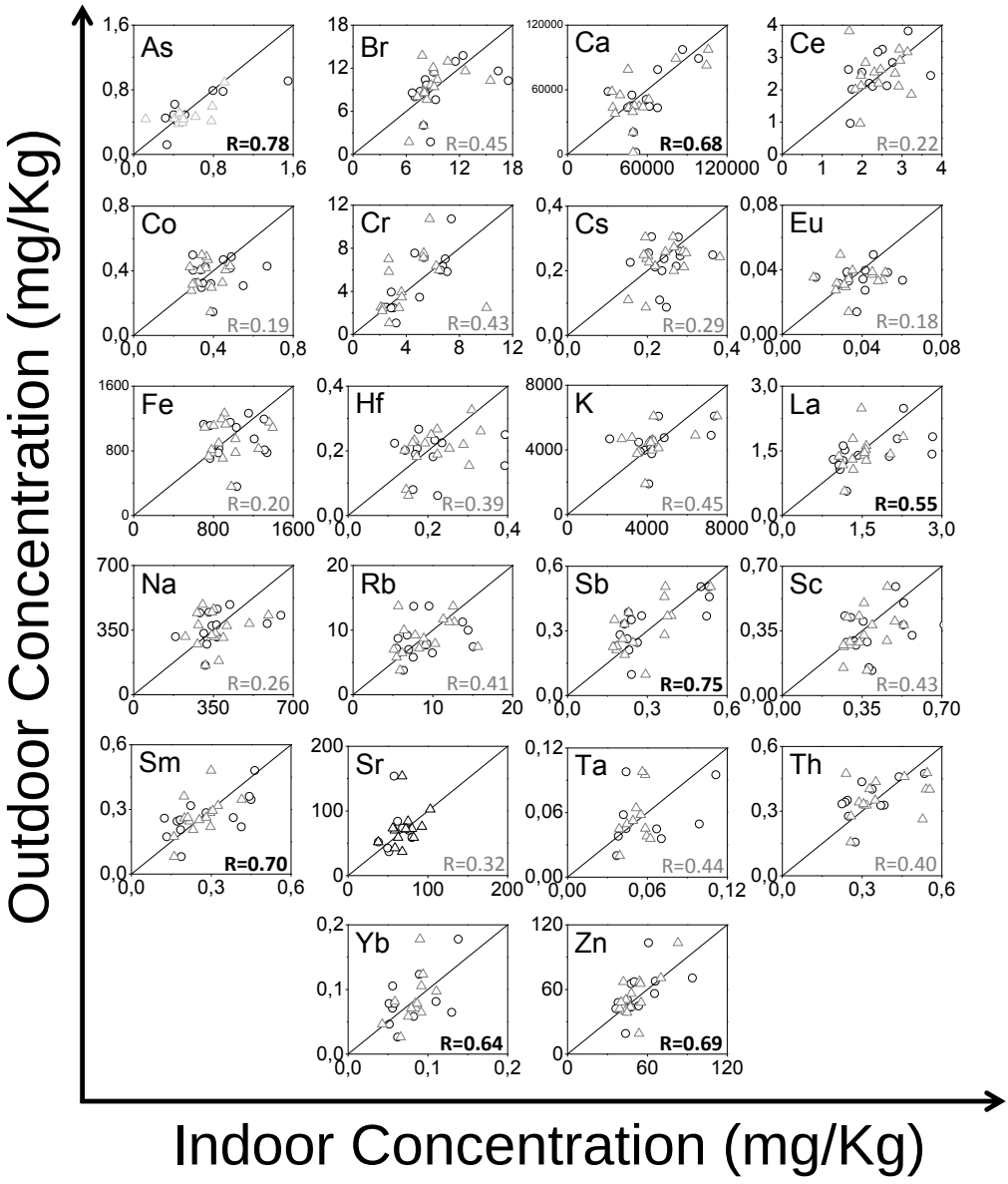

Figure 4.2.5 Relation of elemental concentrations in indoor environments (circle – classroom A and triangle – classroom B) and corresponding outdoor environment. R is the correlation coefficient between the mean of classrooms values and its outdoor (bold values are statistically significant: p-value < 0.050).

4.2.4.3 Crustal Origin of Elements

Crustal enrichment factors (EF) were determined to evaluate the strength of crustal and noncrustal origin of elements (Canha et al., 2010b). This parameter was calculated using Sc as a crustal reference element and Mason and Moore soil composition values (Mason and Moore, 1982). The EFs were calculated based on Equation 3.2.1 (Chapter 3.2.4.3) adapted for lichens instead PM..

Figure 4.2.6 shows the EFs of unexposed and exposed lichens at different environments. Enriched elements (EFs higher than 10) in unexposed lichens are (by decreasing order): Br > Ca > Sb > Zn > As > Sr > K. Usually, Zn and Sb are associated with anthropogenic sources such as combustion, incineration, and traffic (Almeida et al., 2009). This observation revealed that unexposed lichens were under some traffic influence, although they were collected in a rural area. However, enrichment of these elements in exposed lichens was always higher than the observed in unexposed samples.

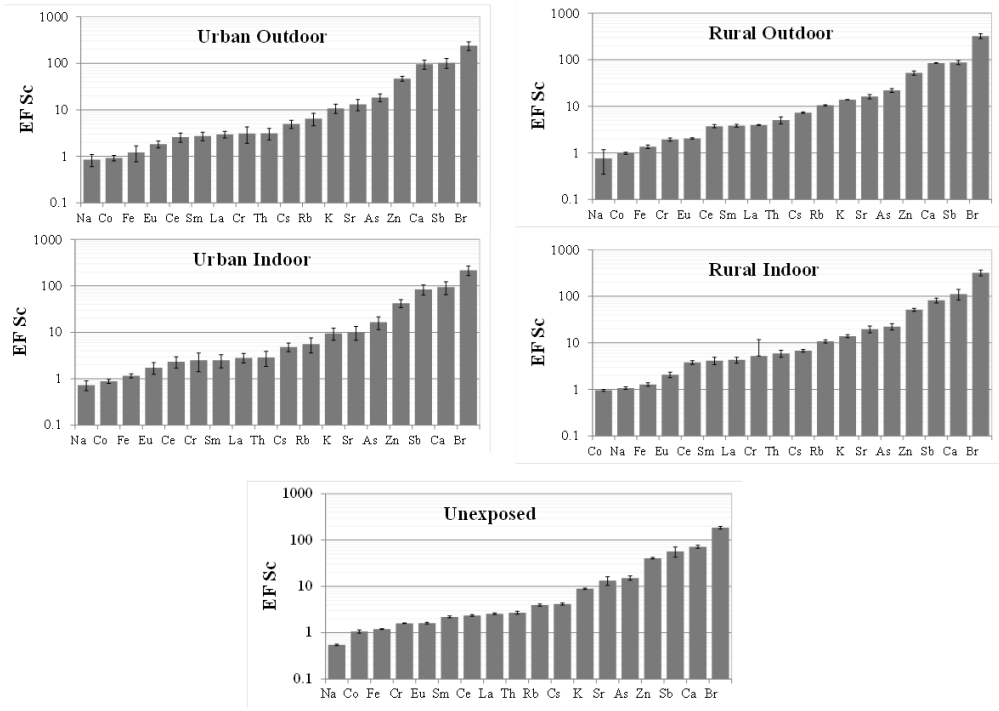

Figure 4.2.6 Enrichment Factors (EFs) for unexposed and exposed lichens samples at different environments.

For all types of environments, the five most enriched elements were Br, Ca, Sb, Zn, and As. The main difference was that for outdoor environment the order of enriched elements was Br > Sb > Ca > Zn > As (for both urban and rural clusters), while in indoor environment the enrichment was Br > Ca > Sb > Zn > As (for both clusters). In the outdoors, Sb is the element with the second highest enrichment due to traffic influence, while in indoors Ca is the element with the second highest enrichment, due probably to indoor sources (apart from some contribution from an outdoor soil source as seen previously), such as chalk (mainly Ca^{2+} and SO_4^{2-}, as reported by Canha et al., 2014a) used in blackboards that existed in all studied classrooms. Bromine, Sr, K, and Rb, found only in rural samples enrichment, are probably due to physiological characteristics of lichens.

4.2.4.1 Anthropogenic Elements

Four anthropogenic elements were considered enriched in the biomonitors, namely As, Sb, Zn, and Ca, which are known to act as tracers of specific pollution sources as previously shown. Therefore, Figure 4.2.7 illustrates the spatial variability of concentrations within clusters, environments, schools, and classrooms.

Overall, four urban schools presented higher values than all others (schools 1, 2, 4, and 10), which indicates that these classrooms have a higher accumulation rate of pollutants when compared with others. Schools 1, 5, 8, and 11 from the urban cluster and school 1 from the rural cluster presented higher indoor concentrations of calcium than outdoors, which indicates an indoor source for this element in these cases.

This biomonitoring study allows us then to identify which schools and classrooms have higher air pollutants concentration and therefore may have problems regarding indoor pollutants accumulation, which contributes to increasing child exposure and potentially adverse effects.

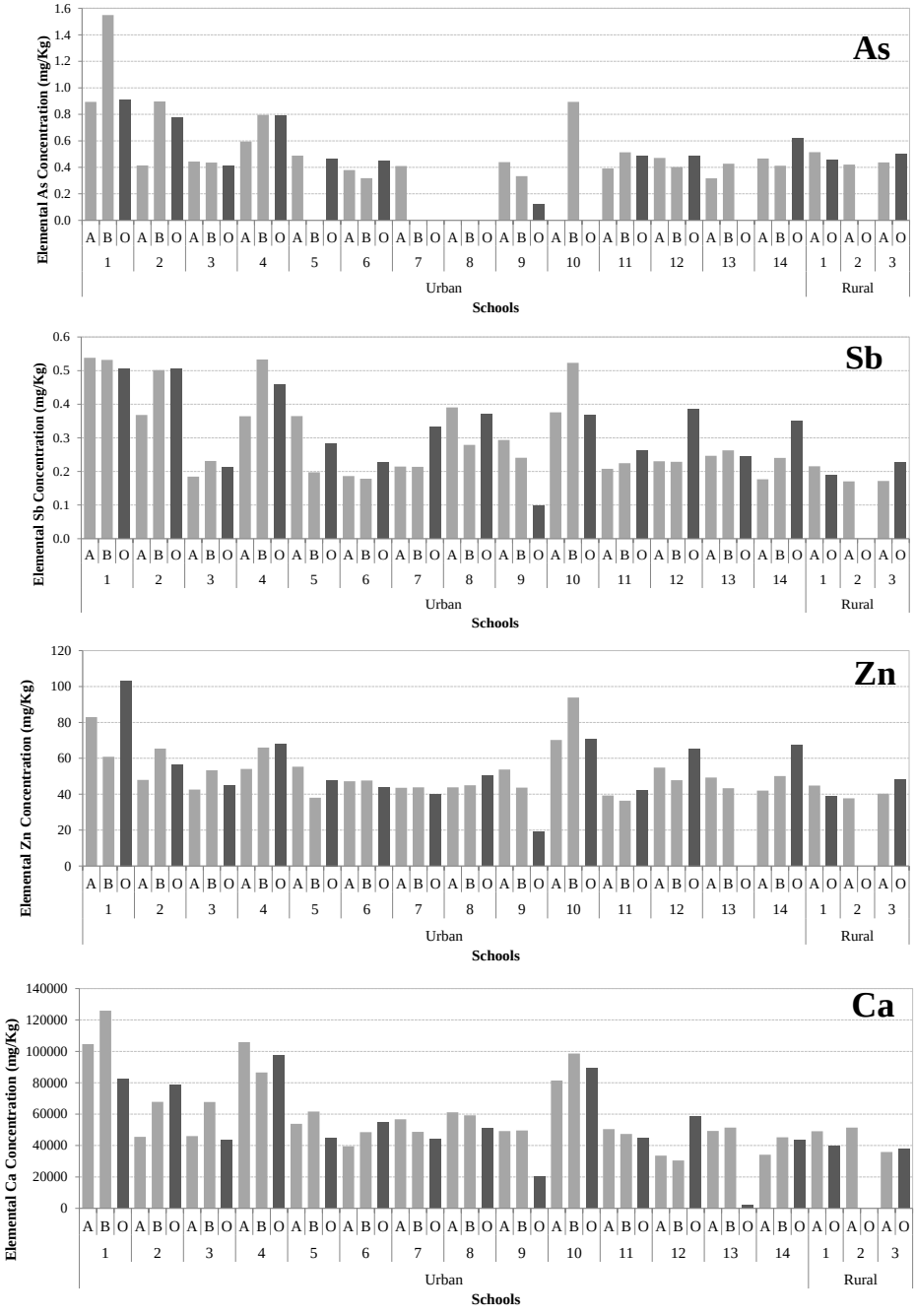

Figure 4.2.7 Variability of As, Sb, Zn and Ca elemental concentrations within clusters, environments, schools and classrooms.

4.2.5 Conclusions

A biomonitoring study with the lichen *Flavoparmelia caperata* was conducted in indoor and outdoor environments of primary schools to assess air quality and to evaluate possible sources of air contaminants. Elemental gain and losses were found in exposed lichens in both outdoor and indoor environments. This finding illustrates that the use of lichens is possible in indoor environments, despite the higher physiological stress that lichens are under in these types of environments, as evidenced by higher values of electric conductivity.

Electric conductivity seems to reflect differential patterns of ventilation habits used by teachers inside classrooms, since values differed within schools and classrooms where outdoor air infiltration may be the relevant player regarding relative humidity to maximize lichen vitality.

Enriched elements in lichens exposed both indoors and outdoors allowed assessment of outdoor sources such as soil and traffic that have an impact on indoor environments. An indoor source of Ca might be detected when analysing spatial variability of elements concentration within classrooms and schools. These results demonstrate that some classrooms and schools with higher accumulation of pollutants may have a possible indoor air problem.

Compared to PM sampling by passive methodology (using filters), biomonitoring study with lichens enabled study of both outdoor and indoor environments to understand contaminants sources and the impact of outdoor in indoor environment. When the goal is to assess IAQ of a larger number of sites for both outdoor and indoor environments simultaneously, a biomonitoring method with lichens appears as a reliable tool to supply qualitative information to indicate sites that may have potential air quality problems. This outcome can, afterwards, be used to apply mandatory sampling methods in problematic sites to assess IAQ in agreement with guidelines and to promote mitigation measures to reduce children exposure to air contaminants.

4.3 Overall conclusions

This chapter presents two different passive sampling methodologies to evaluate the indoor air quality of classrooms in order to overcome the constraints of active sampling methods of particulate matter.

The passive sampling of particulate matter using polycarbonate filters, which relies on the deposition of particles indoors, allows to identify classrooms with higher loads of indoor particles within a large set of classrooms and to understand which main sources are contributing for the indoor particles levels.

The use of biomonitoring with lichens in both indoor and outdoor environments of classrooms adds the advantage to study the outdoor influence over the indoor.

Both methodologies supply qualitative information about the air particulate matter of classrooms indoor since no air volume was sampled. Either way, the possibility to study a large number of classrooms simultaneously enables the identification of the classrooms with high concentrations of particulate matter and/or chemical elements present in the indoor air (in the case of the biomonitoring study). After this identification, active sampling methodologies can be aplied only to these specific classrooms to measure volumetric concentrations according to the regulatory legislation, in order to achieve the quantitative evaluation regarding the particulate matter.

Moreover, both passive sampling methods allow to identify sources that are contributing for the particulate matter in the classroom indoors. This information can be use to identify mitigation measures to improve indoor levels in classrooms in order to decrease the children exposure.

The passive and reference methods are based on different type of sampling exposures to PM. Reference methods are based on short sampling periods (from 8 to 24h, for instance) in order to avoid the clog of particles on the filter. The passive method relies on the passive deposition of particles on the filter and only after a longer period of, at least, 2 months is possible to obtain enough sample mass to perform follow up analysis (such as analysis of water soluble ions and chemical elements). Therefore, the passive method is focused on long term exposure to PM, while the reference methods are focused on short term exposure. Although being possible to perform a comparison study between methods in order to evaluate the quantitative validation, it would involve great financial needs since it would be necessary to perform the sampling with reference methods simultaneously with the passive method. Due to financial constraints, that comparison was not conducted and the comparison between methods was done qualitatively, regarding the sources contributing to the overall concentration of particles.

Overall, these passive sampling methodologies are simple, easy to handle, low cost and allows to perform spatial and temporal surveys of classrooms, when compared with the active sampling method.

5 Source Apportionment of Pollutants in Classrooms

5.1 Impact of Wood Burning on Indoor $PM_{2.5}$ in a Primary School in Rural Portugal

Based on article of same title:
Canha N, Almeida, SM, Freitas MC, Wolterbeek HT, Cardoso J,
Pio CA & Caseiro A
Atmospheric Environment (2014) 94:663 – 670.
DOI: 10.1016/j.atmosenv.2014.05.080

5.1.1 Abstract

A study concerning the chemical characterization of $PM_{2.5}$ sampled indoors of a primary school, which burns wood for classrooms' heating, was conducted in a rural area of Portugal. A Partisol sequential sampler was placed inside of a classroom, to collect $PM_{2.5}$ during the day, which corresponds to the occupied period, and during the night. The collected $PM_{2.5}$ was characterized by Instrumental Neutron Activation Analysis to determine the concentration of chemical elements and by Ion Chromatography to measure Water Soluble Ions. High $PM_{2.5}$ concentrations were found principally during the occupied periods (100 ± 71 μg m^{-3}). A source apportionment study was performed by means of Positive Matrix Factorization (PMF) analysis. Results showed that four factors contributed for $PM_{2.5}$ concentration whereas one factor was associated exclusively with a mixture of indoor sources: wood burning, re-suspension of soil and chalk. During classes, this indoor factor contributed for 60% of the total $PM_{2.5}$ concentration. This study showed that children are exposed to high levels of $PM_{2.5}$ and indicated the existence of an indoor air quality problem associated with specific indoor sources and poor ventilation.

5.1.2 Introduction

In recent years, the concern associated with the levels of particles in indoor environments has increased due to the awareness of a higher exposure of individuals in these specific

environments associated with the fact that people spend most of their time indoors (Almeida-Silva et al., 2014). Children are particularly sensible to indoor pollution due to their undeveloped airways, higher breathed air volumes (when compared to their body weight) and lower capability to deal with the pollutants (Schwartz, 2004). Therefore, indoor environments of primary schools have been widely studied to assess the children exposure to air pollutants and results showed that indoor air quality has negative impacts on health, performance and attendance of students (Mendell and Heath, 2005; Annesi-Maesano et al., 2013). Among the main causes of children's illness at school, which promote their absenteeism, there is the transmission of bacteria and virus (due to the close contact that children have among themselves) and also the chemical indoor air pollution, as reported by Park et al. (2002).

Moreover, children attending schools close to motorways with heavy traffic experienced more respiratory symptoms than did the children attending schools near motorways with low traffic, concerning mainly children with bronchial hyperresponsiveness, positive allergic sensitization to common allergens, or both (Janssen et al., 2003).

Due to the specific characteristics of indoor environment of schools, such as the children activities, particulate matter (PM) concentrations in classrooms are about six times higher than outdoor air (Oeder et al., 2012). Moreover, in some Portuguese schools, mainly in rural areas, the heating of classrooms in colder months is still done by wood burning (using fireplaces or slow combustion stoves). Although the negative impact of this heating system is known in residential indoor air quality, such as the increase of concentrations of carbon monoxide and airborne particle (Guo et al., 2008), similar studies have never been done in scholar environments in order to understand children's exposure level.

The present study aims to focus three issues that have been scarcely studied: 1) the chemical characterization of $PM_{2.5}$ collected in indoor of a primary school, 2) the impact of wood burning on classrooms' air quality and 3) the use of source apportionment tools, commonly used in outdoor environments, to identify emission sources.

5.1.3 Materials and Methods

5.1.3.1 Description of the Sampling Site and Equipment

Figure 5.1.1 shows the sampling site location that is placed in the Portuguese village of Foros de Arrão and is characterized as a rural area (39º10'43 N, 8º14'29 W). The village has about a thousand inhabitants and the main method used for house heating in the colder

months of the year (November – March) is through wood burning, mainly from *Quercus suber* L. (cork oak) and *Eucalyptus globulus* Labill. (eucalyptus). The study site was located at one primary school placed at the centre of the village, where a slow combustion stove was used for house heating (by means of wood burning). This school agreed to collaborate and it was chosen because it used wood burning for heating, which is a main indoor source pollution. The school is located in a residential area with low traffic and a working bakery nearby, at 110 m from the school building.

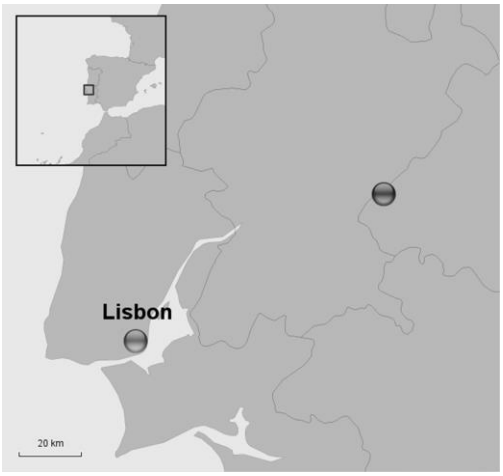

Figure 5.1.1 Location of the studied primary school described as a rural area (right dot) in mainland Portugal.

The studied classroom is located at the ground floor level, it has a volume of 159 m^3 and an occupancy of 19 students aged approximately 10 years old. The classroom has 3 windows (with an area of 3 m^2 each) and one door towards the outdoor of the school building. The sampling site is characterized by a flatland, surrounded by forest and it is located 100km away from the country capital, Lisbon.

The outdoor atmospheric conditions of the winter season in this area is characterized by a mean temperature of 8.2 ± 3.8 ºC (ranging from -1.4 to 19.2 ºC) and a mean relative humidity of 79 ± 18 % (ranging from 29 to 100%). The summer season is characterized by a mean temperature of 26.0 ± 5.7 ºC (ranging from 12.9 to 38.8 ºC) and a mean relative humidity of 43 ± 19 % (ranging from 11 to 96%). These data were collected from the Portuguese Sea and Atmosphere Institute, I. P. (IPMA, IP) and it regards the periods of 2009/2010 winter and 2010 summer.

A Partisol sequential sampler working at a rate of 16.7 L min^{-1} was placed inside the classroom to collect $PM_{2.5}$ in Teflon™ filters with a diameter of 47 mm. The sampler was located near the teacher's desk, near a closed window and in the opposite side of the classroom where the slow combustion stove was located (approximately 11 meters away). Particles were collected from 8 to 19 of March 2010 in two sampling periods: the occupied period (09h00-17h30) and the overnight period (17h30-09h00). The sampler also kept records of air temperature and relative humidity. The outdoor atmospheric conditions during the sampling period had a range of temperatures from 0.8 to 19.2 ºC (with a mean temperature of 9.3 ± 4.5 ºC) and a range of relative humidity from 29 to 97 % (with a mean relative humidity of 57 ± 16 %).

5.1.3.2 Gravimetric and Chemical Analysis

The filter loads were determined by gravimetry using a 0.1 µg-sensitivity balance in a controlled cleanroom (class 10000). The mass of the filter before and after sampling was obtained as the average of three measurements with observed variations of less than 5%.

Each filter was cut into two parts with a ceramic knife inside a Teflon™ box, without possibility of external contamination. For chemical identification, one half was analysed by Instrumental Neutron Activation Analysis (INAA) for the determination of the elements As, Br, Ce, Co, Cr, Fe, K, La, Na, Sb, Sc, Sm and Zn (De Corte, 1987). The other half was analysed by ion chromatography for the determination of the water soluble ions Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+} (Yu et al., 2004).

The INAA analysis was performed according to the procedure described in section "4.1.3.3.3 Chemical Element Content by Instrumental Neutron Activation". Figure 5.1.2 shows the quality assurance results for the reference material NIST-SRM-1633a 'Coal Fly Ash', with uncertainties at 95% confidence level.

The ratio data was acceptable and only Sb presented an average concentration below the expected value. However, the u-score (Dung et al., 2010) for this element was 0.07 which means that the results did not differ significantly from the certified ones.

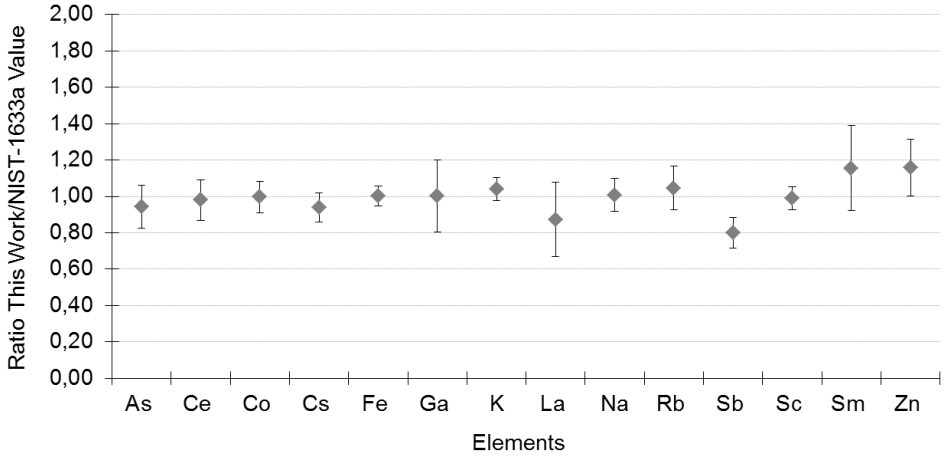

Figure 5.1.2 Ratios between the concentration results obtained in this work for the NIST-SRM-1633a (coal fly ash) and their consensus values (Roelandts and Gladney, 1998), with uncertainties at the 95% confidence level.

5.1.3.3 Statistical Analysis

The analysis of variance of results was performed by nonparametrics statistics for a significance level of 0.050: the Mann-Whitney for binary independent groups and Kruskal-Wallis for multiple independent groups. All the analyses were conducted using the software STATISTICA version 10.

Source apportionment was performed using Positive Matrix Factorization (EPA-PMF 3.0) that is a widely used receptor model for source apportionment studies and was developed by Paatero (1999). PMF can decompose the data matrix into two sub-data matrixes - the factor profiles and factor contributions - without detailed prior knowledge on source inventories. A selection of elements and ionic species was used, namely As, Br, Ce, Co, Cr, Fe, La, Sb, Sc, Sm, Zn, Cl-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+} and insoluble K, which was obtained by subtracting the soluble fraction concentration from the total concentration of the elements (Canha et al., 2012a). In this study, 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 at four times these geometric mean values.

The selection of the best PMF solution was performed following the procedure described by Comero et al. (2009).

5.1.4 Results and Discussion

5.1.4.1 Comfort Parameters

Figure 5.1.3 presents the mean values of temperature and relative humidity measured during the sampling campaign. During the day, a heating system based on the burn of wood was used. However, the main temperature during the occupied time varied between 15 and 20ºC and only two sampling days complied the optimal range of temperature established by the ANSI/ASHRAE Standard 55-2004 for the cold season (20-23ºC). These results indicate that the heating system, associated with a poor and ineffective insulation of the classroom, did not guarantee the comfort of the students. According with the same standard, the relative humidity measured inside the occupied classroom presented low values having varied between 24 and 53% in the occupied period when the acceptable relative humidity levels should range from 30 to 60%.

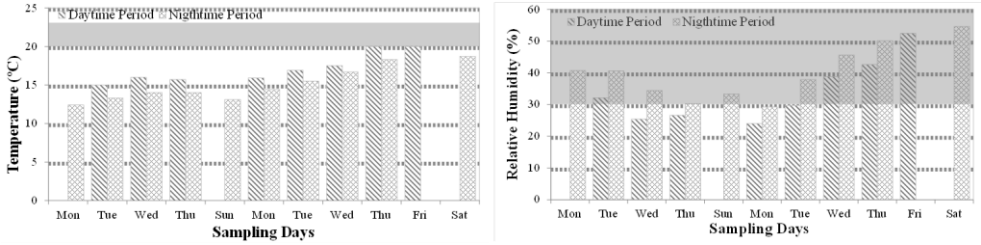

Figure 5.1.3 Temperature and Relative Humidity measured inside the classrooms during the sampling period. Grey area is the range of optimal ranges established by ANSI/ASHRAE Standard 55-2004.

5.1.4.2 $PM_{2.5}$ Total Mass Concentrations

Figure 5.1.4 presents the $PM_{2.5}$ concentrations obtained in each sampling period and shows that $PM_{2.5}$ collected during daytime and nighttime were significantly different between them (p-value of 0.03 by Mann-Whitney test). The average $PM_{2.5}$ concentrations were 100 ± 71 µg m^{-3} and 41 ± 28 µg m^{-3} for occupied and overnight periods, respectively. $PM_{2.5}$ measured during the occupied period presented on average 2.4 times higher concentrations than during the night.

The indoor guidelines for $PM_{2.5}$ are very variable within the few countries that already defined such regulation (Stranger et al., 2007). The limit value varies between 15 µg m^{-3} (averaged over one year) in Belgium (Decree of The Flemish Government, 2004), 25 µg m^{-3} (averaged over eight hours) in Portugal (Portaria n.º 353-A/2013 de 4 de Dezembro, 2013)

and 40 µg m^{-3} (averaged over one hour) in Canada (Health Canada, 1987). For $PM_{2.5}$ in the ambient air, WHO establishes the limit values of 10 µg m^{-3} and of 25 µg m^{-3} based on an annual mean and on 24 hours, respectively (WHO, 2006). $PM_{2.5}$ concentrations measured over the occupied period in this work indicate that the limit values were always exceeded regarding annual limit values of WHO and Belgium's guidelines. Regarding the daily WHO limit value, $PM_{2.5}$ concentrations were exceeded in 88% of the cases, as well for Portugal's guideline and 75% of the cases for Canada's guideline.

An analysis of the literature about $PM_{2.5}$ measured in indoor environments of schools showed that the levels obtained in this study were higher, especially during the daytime period when classes are in session.

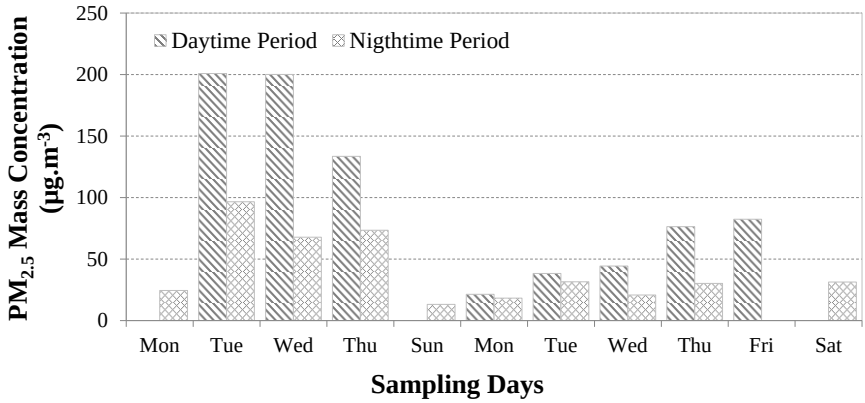

Figure 5.1.4 $PM_{2.5}$ concentrations measured inside the classrooms during the sampling period.

For example, John et al. (2007) studied the indoor air of three elementary schools located in different areas in U.S.A. and measured 24h $PM_{2.5}$ concentrations from Monday to Friday and mean $PM_{2.5}$ concentrations of 16 ± 13, 17 ± 14 and 16 ± 13 µg m^{-3} were registered in urban, suburban and rural classrooms, respectively. A study with 27 elementary schools was conducted at Antwerp, Belgium and showed that the average indoor $PM_{2.5}$ levels ranged from 54 to 72 µg m^{-3} (Stranger et al., 2008), on 12h samples (from 08:00 to 20:00). In Stockholm, a study of the chemical characterization of $PM_{2.5}$ in five elementary schools concluded that $PM_{2.5}$ concentrations in indoors ranged from 3.9 to 19 µg m^{-3} (Molnár et al., 2007), on 6h samples (sampled during 45 minutes every hour from 08:00 to 16:00) representing the occupied period.

Fromme et al. (2008) focused his study in the particulate matter of two classrooms of Munich and found mean $PM_{2.5}$ indoor values of 37 μg m^{-3}, which were sampled during the teaching hours (5 hours per day).

The higher concentrations of $PM_{2.5}$ measured in the present study can be associated with the existence of a working combustion stove in the classroom. In fact, the wood burning process inside the studied classroom is the main distinguishable factor and in the literature several studies confirmed that the biomass combustion is a major source of $PM_{2.5}$ (Reisen et al., 2013; Molnár et al., 2005).

5.1.4.3 $PM_{2.5}$ Chemical Characterization

Table 5.1.1 presents the statistics on the chemical elements and water-soluble ions contents measured in the collected $PM_{2.5}$. The chemical elements with higher concentrations were Na, Fe and K (570 ± 420, 880 ± 730 and 1700 ± 1500 ng m^{-3}, respectively) while Ca^{2+}, NO_3^-, SO_4^{2-} were the water soluble ions with higher contents (600 ± 340, 1100 ± 390, 1500 ± 980 ng m^{-3}, respectively).

The species Ce, Co, Fe, K, Na, Zn and Na^+ presented significantly higher concentrations in the occupied period when compared with the night period (p-value < 0.050).

The comparison between the levels measured in this rural school and the results obtained by Almeida et al. (2011) in urban schools shows that all elements presented higher concentrations in the current study, except Sb, probably due to the higher contribution of traffic in urban areas. Sb is a typical tracer of traffic, whose origin is mainly the brake wear (Almeida-Silva et al., 2011).

The ion concentrations measured in $PM_{2.5}$ in this study are comparable with others described in the literature. In fact, Fromme et al. (2008) reported that the ions with majors contributions to the indoor $PM_{2.5}$ in a classroom were, by decreasing order, $SO_4^{2-} > NO_3^- > NH_4^+ > Ca2^+$. In our study, the following order was obtained: $SO_4^{2-} > NO_3^- > Ca^{2+} > NH_4^+ \approx K^+$, where calcium ion has a higher contribution than ammonium ion and potassium ion has a similar concentration to ammonium, which probably is due to wood burning contribution to the indoor $PM_{2.5}$ since K^+ is a typical tracer of wood burning (Canha et al., 2012a).

John et al. (2007) described that sulfate ion was the largest component present in the $PM_{2.5}$ sampled in elementary schools from urban, suburban and rural areas, with mean concentrations ranging from 2.0 to 2.7 μg m^{-3}. This result agrees with the present study since it was also observed that the sulfate ion was the major water soluble ion in the

sampled $PM_{2.5}$, although with lower mean concentrations, (1.7 ± 1.1 μg m^{-3}). The major chemical elements in the indoor $PM_{2.5}$ were S, Si, Ca and Fe with values of 0.64, 0.32, 0.18 and 0.08 μg m^{-3}, respectively (John et al., 2007). In the present study, Fe had around 9 times higher mean concentration (1.2 ± 0.6 μg m^{-3}) and was also one of the major contributors to the sampled $PM_{2.5}$.

Table 5.1.1 Concentrations (ng m^{-3}) of the chemical elements and the soluble ions measured in the $PM_{2.5}$ collected in the classroom. *n* is the number of samples of each sampling period. *p*-value of the Mann-Whitney test between results of occupied and night periods.

	Mean concentration ± SD (ng.m^{-3}) (*n*)			
Element/Ion	**All day**	**Occupied Period**	**Night Period**	***p*-value**
As	0.92 ± 0.88 (17)	0.97 ± 0.61 (8)	0.87 ± 1.11 (9)	0.268
Br	4.7 ± 1.7 (18)	5.5 ± 1.8 (8)	4.1 ± 1.4 (10)	0.083
Ce	3.2 ± 3.0 (18)	4.9 ± 3.4 (8)	1.8 ± 1.8 (10)	**0.037**
Co	0.45 ± 0.35 (18)	0.64 ± 0.31 (8)	0.30 ± 0.31 (10)	**0.009**
Cr	9.3 ± 11.5 (18)	15 ± 15 (8)	4.6 ± 4.2 (10)	0.069
Fe	880 ± 730 (18)	1200 ± 600 (8)	630 ± 730 (10)	**0.046**
K	1700 ± 1500 (18)	2600 ± 1800 (8)	1000 ± 800	**0.037**
La	1.1 ± 1.0 (18)	1.5 ± 1.0 (8)	0.69 ± 0.81 (10)	0.069
Na	570 ± 420 (18)	870 ± 440 (8)	330 ± 200 (10)	**0.023**
Sb	0.38 ± 0.14 (18)	0.39 ± 0.08 (8)	0.37 ± 0.18 (10)	0.450
Sc	0.27 ± 0.27 (18)	0.36 ± 0.21 (8)	0.20 ± 0.29 (10)	0.083
Sm	0.20 ± 0.20 (18)	0.28 ± 0.21 (8)	0.14 ± 0.18 (10)	0.100
Zn	19 ± 12 (17)	24 ± 13 (8)	14 ± 10 (9)	**0.049**
Cl^-	250 ± 210 (17)	380 ± 260 (7)	170 ± 120 (10)	0.107
NO_3^-	1100 ± 400 (18)	1200 ± 400 (8)	1100 ± 400 (10)	0.505
SO_4^{2-}	1500 ± 1000 (18)	1700 ± 1100 (8)	1400 ± 900 (10)	0.564
Na^+	320 ± 230 (18)	460 ± 260 (8)	200 ± 130 (10)	**0.037**
NH_4^+	470 ± 260 (17)	430 ± 290 (7)	500 ± 250 (10)	0.526
K^+	460 ± 380 (18)	660 ± 480 (8)	300 ± 180 (10)	0.120
Mg^{2+}	70 ± 41 (18)	84 ± 41 (8)	58 ± 38 (10)	0.143
Ca^{2+}	600 ± 340 (18)	780 ± 380 (8)	450 ± 240 (10)	0.069

In Stockholm (Molnár et al., 2007), a study of the chemical characterization of $PM_{2.5}$ in five elementary schools concluded that Fe and K were among the elements with the largest

contribution to the aerosol, both presenting mean concentrations of 140 ng m^{-3}. Comparatively, the present study showed that Fe and K presented mean concentrations 9 and 19 times higher, respectively.

5.1.4.4 Enrichment Factors

To evaluate the strength of the crustal and non-crustal origin of the elements, the crustal enrichment factor method was applied to the set of the elemental concentrations, based on Equation 3.2.1 (Chapter 3.2.4.3). Figure 5.1.5 shows the EFs for the collected $PM_{2.5}$.

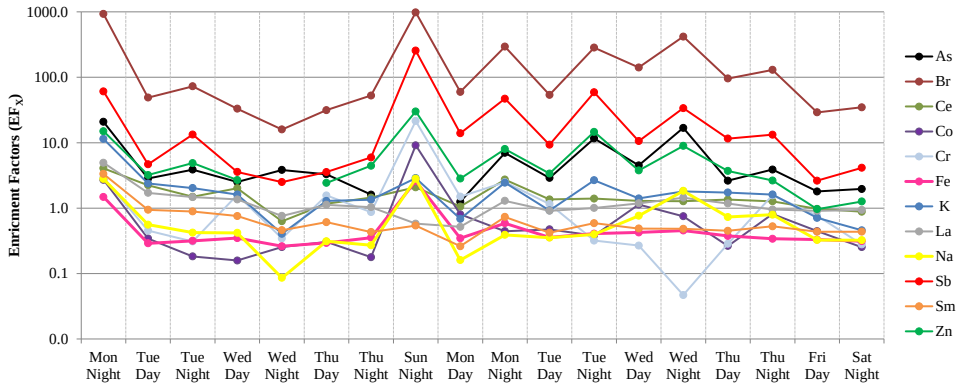

Figure 5.1.5 Enrichment factors using Sc as a reference element and Mason and Moore (1982) soil composition.

EFs indicated that Ce, Cr, Co, Fe, K, La, Na and Sm were associated with soil emissions since their values were below 10 (although Cr and K presented values of EFs higher than 10 for only one specific sampling period). These results agreed with source apportionment studies performed in the Lisbon region (Almeida et al., 2006a).

The strongly enriched elements (EFs > 10) were As, Br, Sb and Zn which can be associated with an anthropogenic origin, such as traffic and industrial emissions (Almeida-Silva et al., 2011). It is possible to observe a trend in the enrichment factors of the elements of anthropogenic origin, namely higher values during the night periods. This fact can be explained by the existence of a bakery industry nearby the studied primary school (at 110 meters) that is operating during the night periods.

5.1.4.5 Source Apportionment by Positive Matrix Factorization (PMF)

PMF identified 4 main chemical sources and their profiles, regarding concentrations and percentages, are presented in Figure 5.1.6.

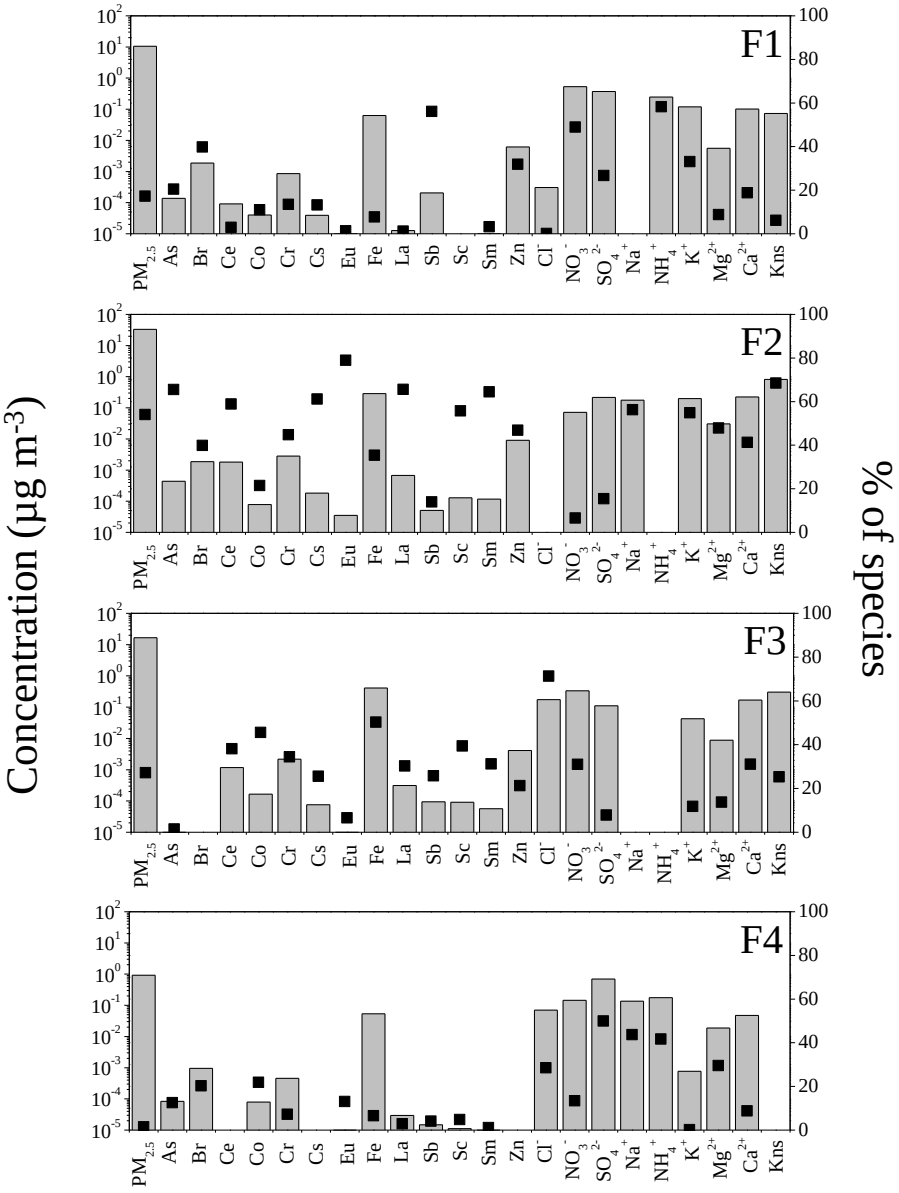

Figure 5.1.6 Source profiles for PMF solution in concentration (µg m^{-3}, columns) and percentage (%, black squares). (ns – non soluble)

Figure 5.1.7 shows that there was a very good agreement between $PM_{2.5}$ concentration calculated by PMF (modelled) and determined by gravimetry (r=0.94), except for the $PM_{2.5}$ concentrations peaks registered in the daytime of Tuesday and Wednesday of the first

week. This fact could be probably due to a more intensive use of the slow combustion stove in this week motivated by the lower outdoor temperatures (daily mean temperatures varied between 8.6 and 9.4 ºC in the first week, while in the second sampling week temperatures ranged between 14 and 16 ºC). This fact shows that the model developed by PMF was mostly accurate and gave a good representation of the real $PM_{2.5}$ concentrations.

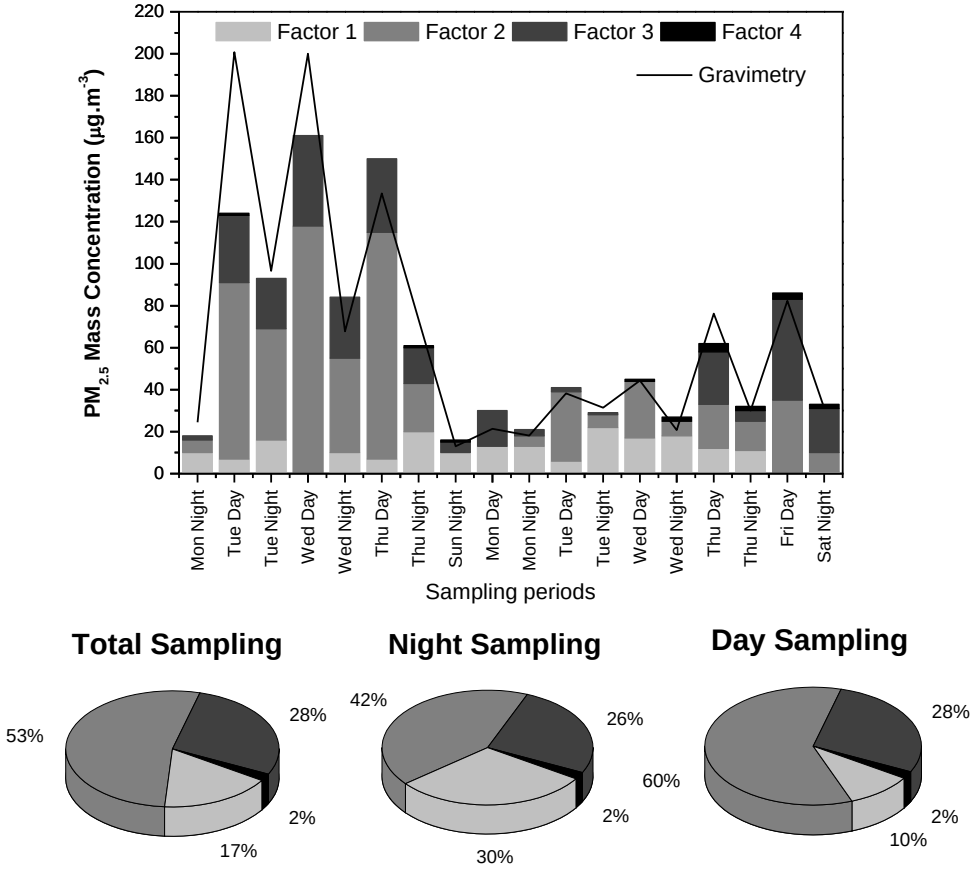

Figure 5.1.7 Real (line) and modelled (bars) $PM_{2.5}$ mass concentrations obtained by gravimetry and by PMF, respectively. Contribution of factors to the overall sampled $PM_{2.5}$ in different sampling periods by piecharts.

The first factor represents a wood burning process which was identified by a high association of K^+, Zn and Br, which are fingerprints of wood burning (Canha et al., 2012a, Molnár et al., 2005, Calvo et al., 2013). Arsenic and Sb also presented an important contribution for factor 1. The water soluble ions SO_4^{2-}, NH_4^+ and NO_3, that characterize the secondary aerosols (Almeida et al., 2006b), also presented a strong association with factor

1. Therefore, it is possible to conclude that the factor 1 is a mixture of a wood burning combustion source and secondary aerosols.

Factor 1 contributed on average for 12 μg m^{-3} of the overall $PM_{2.5}$ mass concentration (17%) and presented a higher contribution during the night (13 μg.m^{-3}, 30 %) and lower during the day (10 μg.m^{-3}, 10 %) (mean ratio Day/Night = 0.77). This fact indicates an association of this factor with a bakery industry which is located nearby the primary school. This industry is powered by wood burning and only works during the night.

The second factor represents a complex mixture of sources that could be identified as the following: 1) soil contribution associated with the re-suspension of settled dust or suspension of soil material brought in by the children's shoes (Almeida et al., 2011) that is defined by typical soil elements, such as Ce, Cr, Fe, La, Sc, Sm and non-soluble K (Canha et al., 2012a); 2) contribution of wood burning process identified by Br, K^+, Zn and As and 3) use of chalk defined by the high association of Ca^{2+} with this factor (Canha et al., 2014a).

Factor 2 contributed on average to 37 μg m^{-3} of the $PM_{2.5}$ mass concentration (53%) and presented statistically significant higher contribution (p-value < 0.050) during the day (61 μg m^{-3}, 60 %) than during the night (19 μg m^{-3}, 42 %) (mean ratio Day/Night = 3.3). This factor is a mixture of different sources (wood burning, soil re-suspension and chalk), which are all associated with indoor activities of the classroom.

The third factor is associated with the soil since a high association was found for typical soil elements, such as Ce, Cr, Fe, La, Sc, Sm and non-soluble K. Factor 3 contributed on average to 19 μg m^{-3} of $PM_{2.5}$ mass concentration (27%) and presented statistically significant higher contribution (p-value < 0.050) during the day (29 μg m^{-3}, 28 %) than during the night (12 μg m^{-3}, 26 %) (mean ratio Day/Night = 2.4). This factor is associated with re-suspension of settled dust or suspension of soil material brought in by the children's shoes and may be considered as an indoor source.

The main components defining the fourth factor are the element Br and the water soluble ions Cl^-, Na^+, SO_4^{2-} and Mg^{2+} which are associated with the sea salt contribution (Almeida et al., 2006a). This factor had the smaller contribution to the overall $PM_{2.5}$ concentration, contributing only with 1.3 μg m^{-3} for the total concentration (2%). Day and night contributions of factor 4 were not significantly different, being on average 1.8 μg m^{-3} (1.8%) and 1.0 μg m^{-3} (2.3%), respectively.

5.1.5 Conclusions

This study assessed the exposure level of children to $PM_{2.5}$ in the indoor of a primary classroom that is heated by wood burning. The results showed that children were exposed to high levels of $PM_{2.5}$ when attending classes, with a mean $PM_{2.5}$ concentration of 100 ± 71 μg m^{-3}. This value is greatly exceeding the limit value of $PM_{2.5}$ for indoor environments defined by several national guidelines. It was verified that the use of combustion stove in the classroom (associated with a poor and ineffective insulation of the classroom) neither provide adequate levels of comfort neither contributes for a healthy indoor air.

The source apportionment study revealed that 4 main factors were responsible for the $PM_{2.5}$ concentration in the classroom. The impact of the bakery industry nearby the primary school during the night period was represented by factor 1. In fact, $PM_{2.5}$ particles were found to be enriched for As, Br, Sb and Zn during the night period, which could be attributed to a bakery industry. Factor 2 represented an exclusively indoor and complex source characterized by wood burning process, soil re-suspension by children and chalk use. These are the main $PM_{2.5}$ sources that children were exposed when attending classes. Factors 3 and 4 represented the crustal and marine contributions to $PM_{2.5}$ concentrations, although in lower contributions than factors 1 and 2.

Overall, this study allowed to conclude that children were exposed to high levels of $PM_{2.5}$ and urgent mitigation and corrective measures are needed: 1) the replacement of combustion stove to other heating system that is able to supply comfort in classrooms without being a $PM_{2.5}$ source; 2) the improvement of the insulation of the classrooms; and 3) the improvement of ventilation rates to avoid indoor accumulation of pollutants.

5.2 Indoor air quality in primary schools

Based on article of same title:
Canha N, Martinho M, Almeida-Silva M, Freitas MC, Almeida SM, Pegas P, Alves A, Pio C, Trancoso M, Sousa R, Mouro F & Contreiras T

International Journal of Environment and Pollution (2012) 50 (1/2/3/4): 396 – 410.

DOI: 10.1504/IJEP.2012.051210

5.2.1 Abstract

The indoor air quality (IAQ) in classrooms is expected to play a key role in the assessment of the effects of the children's personal exposure to air pollution since they spend on average 7–11 h per weekday at school. A statistical treatment was conducted over a database of indoor air parameters and the primary schools where these parameters were sampled (urban area of Lisbon, Portugal). The aim of this study was to assess the associations between indoor air parameters with the schools' building characteristics, through the use of statistical methods. Several associations were found and allow pointing out from this study several recommendations to improve the classrooms IAQ. For example, some factors such as ventilation, cleanings and chalk use instead whiteboard pens, can reduce or increase specific contaminants inside the classrooms.

5.2.2 Introduction

Clean air is a basic requirement of life (WHO, 2000). The indoor air quality (IAQ) has been the object of several studies due to an increasing concern within the scientific community on the effects of IAQ upon health, especially as people tend to spend more time indoors than outdoors (Annesi-Maesano et al., 2013). The quality of air inside homes, offices, schools or other private and public buildings is an essential determinant of healthy life and people's well-being (WHO, 2010).

People can be exposed to contaminants by inhalation, ingestion and dermal contact. In the past, scientists have paid much attention to the study of exposure to outdoor air contaminants, because they have realised the seriousness of outdoor air pollution problems. However, each indoor microenvironment has unique characteristics, determined by the local outdoor air, specific building characteristics and indoor activities (Pegas et al., 2010). Indeed, hazardous substances are emitted from buildings, construction materials and indoor equipment or due to human activities indoors (Carrer et al., 2002).

Reports about buildings with air-related problems have received increasing attention since the 1970s (Spengler and Sexton, 1983). In an indoor environment, dust on floors and other surfaces contains minerals, metals, fibres from textiles, paper, and insulation material, particles from tobacco smoke, including polycyclic aromatic compounds (PAHs). For this reason, the indoor environment is cleaned to maintain an acceptable level of perceived cleanliness, to prevent surface degradation, to control potential risk of infection from microorganisms, and to control dust exposure in general. All of these pollutants could cause significant damage to health globally (WHO, 2010).

The IAQ in school buildings is expected to be a key role player in the assessment of the effects of the children personal exposure to air pollution as children spend at least a third of their time inside school buildings, that is, approximately seven or more hours a day in school (Almeida et al., 2011). Poor IAQ can affect scholarly performance and attendance (Mendell and Heath, 2005). Environmental asthma triggers commonly found in school buildings include respiratory viruses; cockroaches and other pests; mould resulting from excess moisture in the building; dander from animals in the classroom; and dander brought on the clothing from animals at home. Second-hand smoke and dust mites are other known environmental asthma triggers found in schools. Children with asthma may be affected by other pollutants from sources inside schools, such as unvented stoves or heaters and common products including chemicals, cleaning agents, perfumes, pesticides and sprays.

Indoor air quality problems in schools may be even more serious than in other categories of buildings, due to higher occupant density and insufficient outside air supply, aggravated by frequent poor construction and/or maintenance of school buildings (Pegas et al., 2010). Schools are seen as particularly likely to have environmental deficiencies because chronic shortages of funding contribute to inadequate operation and maintenance of facilities. Previous studies showed the poor indoor environmental quality at schools may be explained by:

1) Insufficient ventilation in schools, especially in winter
2) Infrequently and not thoroughly cleaned indoor surfaces
3) A large number of students in relation to room area and volume, with constant re-suspension of particles from room surfaces (Janssen et al., 1999).

The effects of air pollution on children have been growing (Khan et al., 2007) and one of the consequences is the increase of the prevalence of allergic rhinitis (ISAAC, 1998).

The aim of this study was to assess the associations between indoor air parameters (measured inside classrooms of primary schools) with the schools' building characteristics, through the use of statistical methods. Improving the understanding of the sources of the

indoor air pollutants in schools, this study will contribute to identify what sort of additional actions should be taken to enforce an effective improvement of IAQ in schools.

5.2.3 Experimental

5.2.3.1 Sampling site and schools description

This study was carried out in Lisbon, which is the largest city of Portugal, and data on the characteristics of classrooms and indoor air were collected in 14 primary schools in Lisbon. Figure 4.1.1 shows the location of these 14 primary schools in the urban area of Lisbon.

For each school, data were collected in two classrooms, named for reference purposes as classroom 'a' and classroom 'b'. The information concerning the classrooms' characteristics is already described elsewhere (Freitas et al., 2011). All schools have natural ventilation, which means that no forced ventilation or air conditioning system in use (ventilation is done by opening doors and windows).

The data studied here is part of a larger study, which has been described and analysed in previous research (Almeida et al., 2011; Canha et al., 2010a, 2011; Pegas et al., 2010, 2011).

5.2.3.2 Sampling and chemical analysis

The sampling passive method described in Chapter 4.1 was used to perform the total particulate matter (TPM) sampling and a total of three sampling campaigns were conducted: spring (May–June 2009, total of 34 days), autumn (October–December 2009, total of 62/68 days) and winter (January–March 2010, total of 76/78 days).

Sampling of VOCs and carbonyls was performed in the same periods but only for 14 consecutive days within the studied season. Although there are results for all the campaigns and measured parameters, only the campaigns and measured parameters which have results for the two classrooms of all 14 schools were considered in this study. The sampling and analysis methods used for the studied parameters were already fully described elsewhere (Freitas et al., 2011). All the values of the parameters were normalised to the day.

The indoor analysed parameters were: VOCs, carbonyls and TPM (masses concentrations, chemical elements and water-soluble ions's content).

5.2.3.3 Statistical analysis

Wilcoxon signed rank tests (Hollander and Wolfe, 1973) were used to test differences between seasonal concentrations of the studied parameters, since this type of test is a non-parametrical statistical test for testing hypothesis on median. The statistical significance of a result describes the degree to which the result is representative of the population. The p-value represents a decreasing index of the reliability of a result which means the probability of error that is involved in accepting an observed result as valid, that is, as representative of the population. For example, a p-value of 0.050 indicates that there is a 5% probability that the relation between the variables found in the studied sample is a fluke (Statsoft, 2012).

To investigate the association between independent variables (classroom characteristics) and dependent variables (measured parameters), for each dependent variable a linear model was first applied using all the ten independent variables characterising the classrooms. The independent variables considered are: 1) level of classroom, 2) number of student per m^3, 3) number of windows and doors opened, 4) type of board, 5) floor material, 6) ceiling material, 7) presence of heating device, 8) dusty surfaces, 9) number of cleanings per day, and 10) view from classroom.

The 31 dependent variables analysed are part of one of the following groups: 1) total particle mass, 2) chemical element mass, 3) mass of water soluble ions, 4) VOCs, and 5) carbonyls.

Then, the independent variables were taken out from the model, one by one, in order to select the best model. The best model selected was the one that minimised the AIC (Akaike, 1974; Hollander and Wolfe, 1973) and had all terms significant. This analysis was conducted in the statistics package R. All selected models have all terms significant at 5%. The multiple R-squared refers to the fraction of variance explained by the model and was calculated for all selected models.

5.2.4 Results

5.2.4.1 Seasonal Variability

The seasonal variation of TPM is resumed in Figure 5.2.2. The results of the Wilcoxon signed rank tests indicated that the concentration of total particles in the air is lower in the spring than in the autumn ($p = 0.001$) and in the winter ($p < 0.001$). On the other hand, the

tests showed no evidence to suggest a difference in the concentration of total particles in the air between the autumn and the winter ($p = 0.76$).

Concerning to Cr, K, Sb, Sc and Zn concentrations in autumn and winter in 28 classrooms of the 14 schools, an evidence was found which suggest that the air concentration is smaller in the winter than in the autumn for Cr ($p < 0.001$), K ($p = 0.03$) and Sb ($p = 0.016$). On the contrary, there is no evidence supporting a difference between autumn and winter in the concentrations of Sc ($p = 0.11$) and Zn ($p = 0.22$).

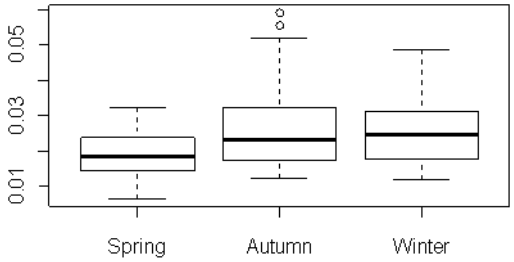

Figure 5.2.2 Boxplot of TPM mass, in mg day^{-1}, in three seasons in 28 classrooms of 14 primary schools.

About VOCs and carbonyls, the statistical tests suggested that the air concentrations are larger in the winter than in the autumn for pentane ($p < 0.001$), isooctane ($p < 0.001$) and acetone ($p < 0.001$).

The test results supported that the concentration of benzene in the air is lower in the spring than in the autumn ($p < 0.001$). There is also evidence that the concentration is smaller in the autumn than in the winter ($p < 0.001$). The results indicated no difference in the concentration of toluene between the spring and the autumn ($p = 0.20$), but suggested that the concentration is smaller in the spring than

5.2.4.2 Association of the Classroom/School Characteristics with IAQ parameters

The results obtained are summarised and fully described in a work already published (Freitas et al., 2011). The effects (i.e., regression coefficients) are shown for variables with significant effects. Figure 5.2.3 illustrates the relation of some of these variables in boxplot charts.

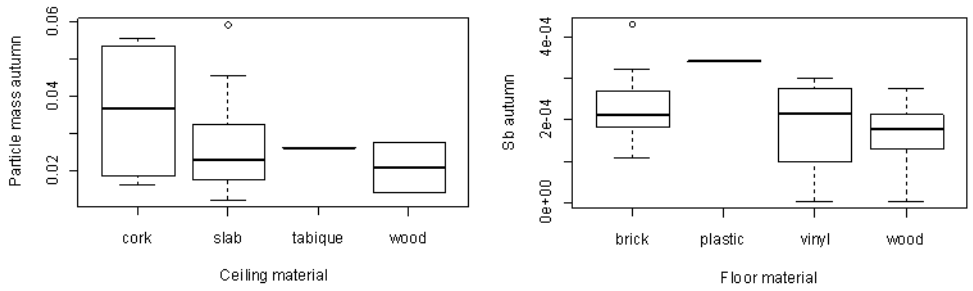

Figure 5.2.3 Boxplot for significant parameters (selected examples).

5.2.4.2.1 Mass of TPM

In autumn and winter, 73% and 67% respectively of the variability across classrooms of the particle mass indoor is explained by classroom characteristics. There are negative significant associations with the number of windows opened ($p < 0.010$ in autumn; $p < 0.050$ in winter) and the existence of heating device ($p < 0.001$ in autumn; and $p < 0.050$ in winter). Classroom facing the street – as opposed to an inner patio – are associated with lower concentrations of particle mass indoor in both autumn and winter ($p < 0.001$ in autumn and $p < 0.010$ in winter). The ceiling material ($p < 0.001$ in autumn and $p < 0.010$ in winter) has also a significant effect, with the results suggesting that wood may be associated with lower levels of particle mass indoor and false ceilings with higher levels of particle mass indoor. Regarding the particle mass in spring, none of the variables is significant at 5%.

5.2.4.2.2 Chemical Elements in TPM

Available measurements for the chemical elements refer all to the autumn season. The classroom characteristics considered in this study explained 57% of the variability of Cr. Significant effects were found for:

1) The ceiling material ($p < 0.050$), with a positive association with wood ceilings;

2) The existence of a heating device ($p < 0.050$) with lower Cr when devices are present.

According to the value of the multiple R^2, the floor and ceiling materials explain together 52% of the variation of the Sb in particle mass indoor. The significant effects of floor material ($p < 0.050$) and the ceiling material ($p < 0.010$) suggest lower Sb amount in classrooms with vinyl floors and slab ceilings.

For Sc in particle mass, 57% of its variation is explained by:

1) the number of windows/doors opened ($p < 0.050$), which is negatively associated to Sc; 2) the use of whiteboard with pen ($p < 0.010$), which is associated to higher Sc amount; 3) the ceiling material ($p < 0.050$), with slab associated to lower levels of Sc in the classroom; and 4) the classroom facing the streets as opposed to an inner patio, the former being negatively associated to the Sc amount in the classroom ($p < 0.050$).

With 55% of the variability explained, the Zn in particle mass displays significant effects for: 1) the number of students per m^3 (positive relation, $p < 0.010$); 2) the existence of a heating device in the classroom (negative relation, $p < 0.050$); 3) the dust present in the classroom (negative relation, $p < 0.010$); and 4) the number of cleanings per day (negative relation, $p < 0.001$).

5.2.4.2.3 Water Soluble Ions in TPM

All data on ions were collected in the winter season. The classroom characteristics appear to explain a large part of the variability across classrooms of Cl^-, Mg^{2+} and Na^+ ions (multiple R^2 equals 0.81, 0.77 and 0.68, respectively). On the contrary, few variations have been explained for the SO_4^{2-} and Ca^{2+} ions, as the multiple R^2 are relatively low (0.18 and 0.25, respectively). This suggests that other factors, not included in this study, may have responsibility for the variability of these ions.

For example, the sodium and chloride ions present significant associations with almost the same group of variables. Namely, both ions present significant associations with the floor level of the classroom ($p < 0.050$) suggesting lower concentrations in the ground and first floors. The floor and the ceiling materials also have significant effects on these two ions with wooden floors and ceilings presenting the lowest coefficient and thus associated with lower concentrations. In addition, the number of cleanings per day also has a significant negative effect (Na^+: $p < 0.050$; Cl^-: $p < 0.001$). The results indicate that the use of whiteboard with pen – as opposed to blackboard with chalk – is associated with higher levels of the soluble ion Cl^- indoor ($p < 0.010$) and the number of windows/doors opened is associated with lower levels of Na^+ indoors.

Results for the water soluble ions K^+, F^-, NO_3^- and PO_4^{3-} are described elsewhere (Freitas et al., 2011).

5.2.4.2.4 VOCs

For example, toluene and isooctane both collected in autumn, present significant effects for the same variables: floor level ($p < 0.001$ and $p < 0.010$, respectively), ceiling material ($p <$

0.001), heating device ($p < 0.001$) and classroom facing street/inner patio ($p < 0.010$). These variables explain 92% and 80% of variability of these pollutants, respectively. For both VOCs, higher concentrations are associated with classrooms in the basement, facing inner patios or without heating devices. Classrooms with wooden ceilings are associated with higher levels of toluene while classrooms with cork ceilings are associated with higher levels of isooctane. Lower concentrations of both are associated with classrooms on the ground floor, with heating devices, facing the street. Classrooms with slab ceilings are associated with lower levels of toluene and those with wooden ceilings are associated with lower levels of isooctane.

Benzene was measured in spring, autumn and winter, but only the autumn and winter measurements show significant effects with variables considered in this study, which explained 82% and 53%, respectively, of the variation of those measurements. For the autumn measurement, significant effects were found for floor level ($p < 0.010$), floor material ($p < 0.050$), presence of heating device ($p < 0.001$), dust in surfaces ($p < 0.010$) and classroom facing the street/inner patio ($p < 0.001$).

The concentration of benzene in winter was shown to be significantly larger from that in the autumn and the set of variables with significant effects is also different: type of board ($p < 0.010$), the ceiling material ($p < 0.050$), dust ($p < 0.050$) and the number of cleanings per day ($p < 0.050$).

Results for m+p xylene, n-hexane, acetone, 2-methylpentane, cyclohexane, ethanol and isopropanol, which variation is between 78% to 50% and it is explained by one or more schools' characteristics, are described elsewhere (Freitas et al., 2011). For all other VOCs and carbonyls, the multiple R^2 is less than 50% and the selected models contain at most two variables with significant effects.

5.2.5 Discussion

In this study, models were applied to several components of the air to investigate associations with classrooms' characteristics. Some patterns emerged across these analyses:

1) Classrooms facing a street seem to have lower air concentrations of several components than those facing an inner patio. This could be linked to ventilation issues as inner patios may generate less air movement and consequent accumulation of some components. Classrooms facing the inner patios are associated with higher concentration of Sc, PO_4^{3-}, F^-, isooctane (autumn), acetone, benzene (autumn) and toluene, as well as TPM mass with less particle mass in the autumn and winter.

2) Classrooms with higher number of windows/doors opened were associated with less particle mass, K, Sc, acetone and Na^+ in the air, possibly due to increased ventilation.

However, a larger number of opened windows/doors were also associated with more o-xylene and ethanol, which suggest outdoor sources for these two components.

3) Crowded classrooms (high density of students per m^3) seem to lead to increased concentrations of several components, such as, Zn, 2-methylpentane, methanol, isooctane (winter) and benzene – (autumn).

4) Classrooms located in basements seem to suffer from accumulation of several components, perhaps due to lack of ventilation. The results indicated that the air of the classrooms in the basement tended to have more particle mass, cyclohexane, ethanol, isooctane, acetone, benzene, toluene, Na^+ and Cl^-.

5) Cleanings appear to contribute to a decrease in several air components, but to an increase of others. It is possible that some components of the cleaning products pass into the air. Classrooms with higher number of cleanings a day were associated with higher concentrations of acetaldehyde but reduced concentrations of Zn, several ions (Na^+, Cl^-, K^+, NO_3^-, F^-, Mg^{2+}), 2-methylpentane, methanol and benzene (winter).

6) Chalk and whiteboard pens are expected to liberate distinct substances. The use of whiteboard pens was associated with higher concentrations of Sc, benzene (winter), Cl^-, PO_4^{3-}, NO_3^- and F^-.

7) Different construction materials appear to impact on specific elements. Overall, wood seems to lead to a reduced concentration of several elements. Wooden ceilings in particular were associated with lower concentrations of particle mass, K, Sc, cyclohexane, isooctane (autumn) and acetone; wooden ceilings and floors were associated with lower concentrations of Na^+, Cl^-, Mg^{2+} and K^+. Plastic floors on the contrary were associated with higher concentrations of several components, including Sb; VOCs such as n-hexane, n-heptane, ethylbenzene, m+p xylene and o-xylene; and several ions, like Cl^-, Mg^{2+} and NO_3^-. These results support evidence on the emissions of hazardous substances from buildings and construction materials (WHO, 2010; Carrer et al., 2002), but must be interpreted with caution as there is only one classroom with plastic floor and one school (two classrooms) with wooden ceilings. The significant effects observed could be associated with other factors presented in that particular classroom/school.

Few components in this study were measured for more than one season. The seasonal analysis, albeit limited, suggested higher concentrations in winter as compared to spring of

particle mass and of two VOCs, benzene and toluene. Spring being the season when windows tend to be open due to higher temperatures; these results suggest that these components get trapped in classrooms for lack of ventilation. The concentrations of isooctane, acetone, benzene and toluene seem to be higher in winter than in autumn. For some elements, namely Cr, K and Sb, the concentrations seem, on the contrary, to be higher in autumn than in winter.

5.2.6 Conclusions

This study shows the importance of considering cleaning and ventilation practices as well the construction materials when studying the IAQ in schools. It is known for example than benzene has adverse health effects. The results obtained here suggest that lower concentrations of benzene may be obtained with less crowded and better ventilated classrooms, frequent cleanings and by avoiding the use of whiteboard pens.

Overall, the conclusions of this study point to the following recommendations:

1) Classrooms should face streets rather than patios and should not be located in basements;

2) Density of students can affect the indoor environment and should be limited;

3) Wooden materials appear to have advantages as building materials due to a lower input of contaminants.

In particular, in this work, wood did not contribute to an increase of the VOCs, as reported in previous research (Norback et al., 1995). Other factors, like ventilation, cleanings and use chalk versus whiteboard pens, can reduce or increase specific contaminants inside the classrooms. Therefore, caution is suggested when deciding on building materials for schools and on school practices, such as cleaning and boards, as these may affect the indoor air which children will breathe for long periods of the day.

5.3 Overall conclusions

This chapter presents two different approaches to assess sources that contribute to the indoor air quality of classrooms.

The source apportionment technique PMF, that is applied nowadays only to outdoor air studies, was applied with success for the first time in indoor environments. This technique enabled to assess different factors contributing to the overall $PM_{2.5}$ concentration in classrooms' indoors, one of them exclusively related to the indoor environment. This

indoor source is characterized by a complex mixture of sources such as soil re-suspension, indoor generated pollutants or specific indoor activities.

The use of statistical methods to evaluate the relationship between IAQ parameters and buildings'characteristics of the classrooms, along with users' habits (ventilation or cleaning), allowed to understand which are the main parameters affecting the pollutants' concentrations.

This information can be used to promote mitigation measures or to estabilish good practices in order to minimize the children exposure to these pollutants.

6 General Discussion

This thesis was set in the context of IAQ in schools and aimed to contribute to a better understanding on how is the quality of the air that children breathe in classrooms, how it can be characterized and which are the sources contributing to its degradation.

The main factors that influence the IAQ in classrooms are the emission of indoor sources, the infiltration of outdoor air pollution and the ventilation. All these issues were addressed in this thesis which started with the characterization of ventilation conditions in classrooms and with the characterization of indoor pollutants levels, developed new passive sampling methodologies to evaluate IAQ and finally assessed indoor and outdoor sources by different methods.

6.1 Overview

Chapter 2 characterized the ventilation patterns of different types of classrooms, regarding two types of ventilation: natural and mechanical. Naturally ventilated classrooms, typically from southern European countries, do not gather the minimum ventilation rates required by the international and national guidelines while the mechanical ventilation type, typical from north European countries, promoted ventilation rates greatly above the established guidelines.

A low ventilation rate implicates an insufficient renewal of the indoor air, the accumulation of indoor pollutants and, consequently, a higher exposure of children attending the classrooms. Mainly in winter, due to the outdoor atmospheric conditions, naturally ventilated classrooms may have serious IAQ problem that requires intervention to solve it.

Usually, the type of ventilation featured in the classrooms depends on the economical and climatic conditions of the countries. Mechanical ventilation systems are effective but expensive to implement and to maintain due to their energy and maintenance needs. In countries with good climatic conditions, natural ventilation is typically used but do not provide the minimum ventilation rates to assure a good IAQ. If it is not possible to upgrade the ventilation system, good practices to improve the natural ventilation should be provided to the teachers in order to overcome this problem.

This work presented the first published results of the use of a computerized tool to determine the ventilation rates, based in the build-up phase of the CO_2 emitted by the occupants, which is used as a tracer gas. This tool was developed under a WHO survey program on IAQ in schools and proved to be an easy method to assess the ventilation rates using the CO_2 monitoring data.

Chapter 3 provided an overview on multi-pollutant assessment of IAQ in schools using classical methodologies, which in case of particles were based on active sampling methods. Ventilation was also characterized in a large set of classrooms using four different indicators: CO_2 concentrations, air exchange rates, ventilation rates and ICONE, which is an air stuffiness index. All the indicators supplied different information on the ventilation conditions of the classrooms and results showed that they may be complementary used. Once again, the type of ventilation used in the classrooms showed to have a significant impact in the ventilation conditions of the classrooms, with mechanically ventilated classrooms presenting ventilation rates two times higher than naturally ventilated classrooms.

The influence of the ventilation indicators on the IAQ parameters of the classrooms was studied and results showed that low ventilation rates were associated with high indoor concentrations of 1,4-dichlorobenzene, acetaldehyde, formaldehyde, hexaldehyde and $PM_{2.5}$.

Due to the known negative impact that PM has on human health, a detailed study was conducted to characterize this pollutant, namely fine particles ($PM_{2.5}$) along with coarse particles ($PM_{2.5-10}$) in classrooms in order to assess the children exposure levels. High concentrations of coarse particles were found indoors with mean values of 73 $\mu g\ m^{-3}$, while $PM_{2.5}$ had mean indoor values of 10 $\mu g\ m^{-3}$. The chemical characterization of the collected particulate matter allowed to identify particles re-suspension due to the children activities, chalk, detritions of the building materials and traffic influence as the main sources of particulate matter in classrooms. However, this study confirmed one of the main disadvantages of using the classical active particles' sampling methods in classrooms since, due to the interference of the samplers with the classrooms activities due to the noise of the equipments, teachers refused to continue with the study in their classrooms. Along with this issue, the applicability of this method on a spatial and temporal survey is highly limited regarding the need of extra equipments, specialized personel and power.

Chapter 4 proposed new sampling methodologies to overcome these constraints. A passive sampling method to collected particulate matter indoors using filters and based on the passive deposition of particles was developed, applied and allowed to assess exposure levels. Through a chemical characterization of the collected particles it was possible to assess the main sources contributing to the indoor particulate matter. The same sources found in Chapter 3 for the active sampling of particulate matter, were found by the passive sampling methodology.

Due to the inapplicability of this passive method at outdoors, a biomonitoring study using lichens was performed in indoor and outdoor environments of the classrooms, in order to study the influence of the outdoor in the classrooms. Usually this technique is only used in outdoor studies but this work showed the feasibility of this technique in indoor environments and allowed to understand the impact of outdoor sources, such as soil and traffic in the classrooms.

Both proposed methods do not supply volumetric concentrations but allow to provide valuable qualitative information that can be used to support decision making and to focalize further studies using classic sampling methodologies only on classrooms that show higher concentrations by these methods, saving time, effort and money when a great number of schools are under evaluation.

Chapter 5 focused on methods to identify the sources affecting the indoor air of classrooms. The use of Positive Matrix Factorization on $PM_{2.5}$ data of a classroom allowed to identify the main sources affecting the indoor air and, as observed before, a complex indoor source was found that gathered soil re-suspension, chalk and wood burning processes (specific of this sampling site).

The inventory of the classroom and school characteristics when analysed with the indoor air pollutants through statistical methods also allowed to understand which are the major factors contributing to the increase or decrease of the pollutants. The information regarding the pollution sources affecting indoor air allows to propose mitigation measures to promote the decrease of emissions from these sources in order to provide an indoor air with lower levels of exposure to occupants.

6.2 Final Remarks

This thesis exposed the reality of natural ventilation in classrooms, which are often crowded. Natural ventilation does not supply enough ventilation rates to provide good IAQ to their occupants. Especially when natural ventilation is the most commom type of ventilation used, a IAQ monitoring program should be carry out to evaluate the exposure levels of children, which can conditionate their health and performance.

Nowadays, in developed and wealth countries, surveys on IAQ in schools are being conducted and it is an issue of great importance for the national authorities and local school management. However, IAQ surveys are not conducted in the majority of the countries.

National programs to evaluate IAQ in classrooms should be undertaken to understand exposure levels and actual conditions, in order to identify corrective measures to improve IAQ by means of a better ventilation or by limiting the emission sources. The new passive sampling methods proposed in this thesis may constitute valuable tools in this context since they allow the IAQ characterization for a great number of classrooms, with substantial lower financial needs than traditional methods.

Good practices regarding IAQ, which should gather issues such as ventilation and type of materials used inside, should be supplied to teachers in order to provide them simple, but effective tools to improve IAQ. Moreover, the design and construction of a classroom should be carefull though considering the IAQ that the occupants will be exposed to.

Indoor air quality should be understood as a dynamic system of several different factors that can have a great influence on the learning process and health of the children, which should not be devalued.

6.3 Future Research

IAQ in classrooms is an issue of great importance and a continuous effort should be conduct to provide a healthier air to children in these microenvironments.

Emerging pollutants should be studied in these microenvironments, such as indoor chemistry products or ultrafine particles, regarding their composition to understand their sources and their health impact on children. Focus on low emission materials/products and good practices (cleaning, decoration) should be evaluated *in situ* through intervention studies.

Complete surveys regarding IAQ in classrooms, health and performance of students should be conducted during several years (follow ups) to understand the impact and evolution of IAQ on physical and academic development of the children.

List of abbreviations

Chapter 1

DALY - Disability Adjusted Life Years
IAQ - Indoor Air Quality
ICONE - Air stuffiness index
PM – Particulate Matter
$PM_{2.5}$ - Particulate Matter with an aerodynamic diameter of 2.5 micrometers
PMF - Positive Matrix Factorization
SBS - Sick Building Syndrome
UFP - Ultrafine particles
VR - Ventilation Rates
WHO - World Health Organization

Chapter 2

AER – Air Exchange Rate (h^{-1})
ASHRAE - American Society of Heating, Refrigerating and Air-Conditioning Engineers
C(t) - CO_2 concentration (ppm) at time t (h)
C_a, C_b, C_c - CO_2 concentrations (ppm) at equally spaced times a, b and c during the buildup
C_0 - CO_2 concentration (ppm) at the beginning (t = 0)
C_t - CO_2 concentration (ppm) at time t
CO_2 – Carbon dioxide
C_r - CO_2 concentration in the replacement air (ppm(v))
C_{ss} - Steady-state concentration (ppm(v)) at the final equilibrium
CS – Slow combustion stove
EN - European Standard
FP - Fireplace
G - CO_2 generation rate (mL/h)
IAQ – Indoor Air Quality
MV – Mechanical Ventilation
n - Number of occupants of the room
NV – Natural Ventilation
Q – Ventilation Rate ($m^3.h^{-1}$)
VR - Ventilation Rate per Person (L/s per person)
REHVA - Federation of European Heating, Ventilation and Air-conditioning Associations
t – Time (h)
THL – National Institute for Health and Welfare (Kuopio, Finland)
V – Room volume (m^3)
WHO – World Health Organisation

Chapter 3

AD – Aerodynamic diameter
AER - Air exchange rates, h^{-1}
APM – Air Particulate Matter

C - Classrooms
CO_2 – Carbon dioxide
CSTB - Scientific and Technical Building Centre
EF_X - Enrichment factor of element X
f_1 - Proportion of CO_2 values between 1000 and 1700 ppm
f_2 - Proportion of CO_2 values above 1700 ppm
IAQ - Indoor Air Quality
ICONE - Air stuffiness index
INAA - Instrumental Neutron Activation Analysis
LV – Limit Value
MV – Mechanically Ventilated
n_0 - CO_2 values < 1000 ppm
n_1 - CO_2 values between 1000 and 1700 ppm
n_2 - CO_2 values > 1700 ppm
NIST - National Institute of Standards and Technology (USA)
NV – Naturally Ventilated
OQAI - French Observatory of Indoor Air Quality
P – Percentiles
$PM_{2.5}$ – Particulate Matter with an aerodynamic diameter of 2.5 µm
$PM_{2.5-10}$ – Particulate Matter with an aerodynamic diameter between 2.5 and 10 µm
PM_{10} – Particulate Matter with an aerodynamic diameter of 10 µm
PN – Particle Number
RH – Relative Humidity
RSDT - Règlement Sanitaire Départemental Type
S - Schools
SD – standard deviation
VOCs – Volative Organic Compounds
VR – Ventilation Rate, L/s per person
WHO – World Health Organization

Chapter 4

A - Autumn
CO - Carbon Monoxide
CO_2 - Carbon Dioxide
CRM - Certified Reference Materials
EF_X - Enrichment factor of element X
ELDS - Einstein-Lioy Deposition Sampler
EPA - US Environmental Protection Agency
IC - Ion Chromatography
INAA - Instrumental Neutron Activation Analysis
FAAS - Flame Atomic Absorption Spectrometry
HNO_3 - Nitric acid
PM - Particulate Matter
$PM_{2.5}$ - Particulate Matter with an aerodynamic diameter of 2.5 µm
$PM_{2.5-10}$ - Particulate Matter with an aerodynamic diameter between 2.5 and 10 µm
PM_{10} - Particulate Matter with an aerodynamic diameter of 10 µm
n - Number of samples

N - Number of studied classrooms
NO_2 - Nitrogen Dioxide
r - Coefficient of Linear Correlation
R^2 - Coefficient of Determination
n - Number of Replicates
n.a. - Not Available
NIST - National Institute of Standards and Technology (USA)
R - Rural cluster
RPI-ITN - Portuguese Research Reactor
SD - Standard Deviation
Sp - Spring
SO_2 - Sulfur Dioxide
Su - Summer
SRM - Standard Reference Materials
TPM - Total Particulate Matter
U - Urban cluster
W - Winter

Chapter 5

AIC - Akaike Information Criterion
EF_X - Enrichment factor of the element X
IAQ - Indoor Air Quality
INAA - Instrumental Neutron Activation Analysis
ISAAC - International Study of Asthma and Allergies in Childhood
LOQ - Limit of quantification
n - Number of samples
ns - Non soluble
NIST - National Institute of Standards and Technology (USA)
PAH - Polycyclic aromatic compounds
$PM_{2.5}$ - Particulate Matter with an aerodynamic diameter of 2.5 µm
PMF - Positive Matrix Factorization
QC - Quality Control
SD - Standard deviation
SRM - Standard Reference Materials
TPM - Total Particulate Matter
VOCs - Volatile Organic Compounds
WHO - World Health Organization

Chapter 6

CO_2 - Carbon Dioxide
IAQ - Indoor Air Quality
ICONE - Air stuffiness index
$PM_{2.5}$ - Particulate Matter with an aerodynamic diameter of 2.5 µm
$PM_{2.5\text{-}10}$ - Particulate Matter with an aerodynamic diameter between 2.5 and 10 µm
WHO - World Health Organization

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Summary

The context for this thesis is the concern that exposure to indoor air pollutants could cause adverse effects in health, performance and attendance in children attending classrooms. Despite the increased awareness of this subject and scientific effort in the last decade to characterize these micro-environments, standardized and practical methodologies, along with strategies to understand how to minimize this exposure, are needed in order to promote healthier environments for children's learning process. Therefore, the primary aim of this thesis is to characterize the exposure to indoor air pollutants in classrooms focusing in ventilation conditions and IAQ parameters, to develop practical sampling methodologies and to study source apportionment techniques in indoor environments.

Chapter 1 summarises some of the most important issues in indoor air quality in schools.

Chapter 2 evaluates the ventilation conditions of classrooms from different countries that use different ventilation systems, namely, natural and mechanical ventilations. A new method to assess ventilation rates, which is based on a computerized tool that relies on the build-up phase of indoor generated CO_2, was used. This information allows to understand the exposure level of children attending to those classrooms.

Chapter 3 describes IAQ assessment by classical methodologies centered on ventilation indicators, a wide range of IAQ parameters and, later, focused on particulate matter.

Chapter 4 describes the development, applicability and evaluation of new passive sampling methodologies for the indoor air of classrooms. Passive sampling of indoor particles and biomonitoring with lichens indoor and outdoor of classrooms were fully characterized.

Chapter 5 focus on methods of source apportionment in classrooms indoor to identify pollution sources in these environments. PMF, a traditional method used in outdoor studies was applied for the first time in indoors. Later, associations between indoor air parameters with the schools' building characteristics, through the use of statistical methods, were evaluated.

Chapter 6 provides an overall summary and conclusions for the thesis.

Samenvatting

De context van dit proefschrift is de bezorgdheid dat blootstelling aan inhuizige verontreinigingen negatieve effecten kunnen hebben op de gezondheid, prestaties en concentratie van kinderen in het klaslokaal.

Ondanks de verhoogde bewustwording ten aanzien van dit onderwerp, en de wetenschappelijke inspanningen over de laatste 10 jaar om deze (micro)-omstandigheden te karakteriseren, zijn gestandaardiseerde en praktische methoden nodig om te begrijpen hoe blootstelling kan worden geminimaliseerd en hoe te komen tot betere en meer gezonde omstandigheden voor kinderen in hun leeromgeving. Dit proefschrift is daarom gericht op het karakteriseren van de blootstelling aan inhuizige verontreinigingen in klaslokalen, met een focus op ventilatiecondities en IAQ (Indoor Air Qualiy) parameters, om praktische sampling methoden te ontwikkelen en tot bronprofielherkenning te komen in inhuizige omstandigheden.

Hoofdstuk 1 vat enige van de meest relevante issues samen ten aanzien van de inhuizige luchtkwaliteit in scholen.

Hoofdstuk 2 evalueert de ventilatiecondities in klaslokalen van verschillende landen, waarin diverse ventilatiesystemen worden toegepast, waaronder zowel natuurlijke- als mechanische ventilatie. Een nieuwe methode is gebruikt om ventilatiesnelheden te bepalen, gebaseerd op een gecomputeriseerde aanpak op grond van de opbouw van inhuizig gegenereerde CO_2 niveaus. Deze informatie maakt het mogelijk de blootstelling van kinderen in klaslokalen beter te begrijpen.

Hoofdstuk 3 omschrijft de vaststelling van IAQ via klassieke methoden, gebaseerd op ventilatieindicatoren, een grote range aan IAQ parameters, en, uiteindelijk, richt zich op vaste deeltjes (particulate matter).

Hoofdstuk 4 omschrijft de ontwikkeling, de toepasbaarheid en de evaluatie van nieuwe passieve bemonsteringsmethoden voor de inhuizige lucht in klaslokalen. Passieve bemonstering van inhuizige deeltjes en biomonitoring met korstmossen, zowel binnen als buiten klaslokalen, werden volledig gekarakteriseerd.

Hoofdstuk 5 richt zich op methoden voor bronherkenning in klaslokalen om tot identificatie van verontreigingsoorzaken te komen. Daaropvolgend, met behulp van statische methoden, werd geevalueerd of inhuizige lucht parameters konden worden gecorreleerd aan de schoolgebouw-karakteristieken.

Hoofdstuk 6 geeft een algemene discussie, samenvatting en conclusies van het proefschrift.

Acknowledgments

The work now presented has the contribution of many during the most recent years of my scientific and personal life.

First of all, I would like to express my gratitude to my supervisors that guided me through this process and from whom I have learned so much. To Dr. Maria do Carmo Freitas for receiving me in her research group in 2009, for believing in my work and for all the research opportunities. Thank you for the pragmatic view and for teaching how to live science. To Prof. Dr. Bert Wolterbeek for accepting the supervision of my thesis, for his challenging mind and pertinent comments through the process. To Dr Marta Almeida for all the support, availability, pragmatism and the important discussions in the last years that brought us here today. Thank you all for the opportunity.

I am very grateful to all the schools and their staff, along with teachers and students, that allowed to perform this work.

Along the way, several international opportunities have arisen to improve my scientific skills, knowledge and horizons. Therefore, I am thankful for the opportunity of working with Prof. Otto Hänninen (in Kuopio, Finland) and with Corinne Mandin (and all her team!) from the French Observatory of Indoor Air quality (in Paris, France). My perspectives of the scientific world greatly improved!

One special thank you for the friends/colleagues of our research group (former NANE). Thank you for your support, questions, discussions or help whenever it was needed. Thanks to Catarina Galinha, Marina Almeida-Silva, Carla Ramos, Joana Lage, Alexandra Silva, Ana Cruz, along with all the others that passed by during this time. A special thank you also to Isabel Dionísio and Teresa Fernandes for their help.

These years had dark times within and I am honestly grateful to all people that touch my path and brought me back: friends, ex-friends, not friends at all.

I would like to express my gratitude to my family for their support during this process. Special thank you to my mum, Maria do Céu, for always believing in me and for always being there despite the distance between us. Thank you as well to my brother and nephews (Daniel and Marco), godmother, godfather and grandmother for all the support.

A special thank you to Pedro for everything.

Curriculum Vitae

Nuno Canha was born on the 9th January 1982 in Abrantes, Portugal. He holds a bachelor and a MSc in Chemistry from the Instituto Superior Técnico of University of Lisbon, Portugal. His Master thesis was entitled "Determination of oxidative stability of biodiesel and its relationship with the operation conditions".

In 2009, he joined the research group NANE at Instituto Tecnológico e Nuclear under the supervision of Dr Maria do Carmo Freitas, as a junior researcher working on the Portuguese research project "Impact of atmospheric indoor aerosol in human health - PTDC/SAU-ESA/65597/2006". His work focused on indoor air quality assessment in primary classrooms of the urban area of Lisbon, mainly particulate matter and bioaerosols.

In the past years, he perfomed several short and long scientific visits in several research centers in Europe, such as, French Observatory of Indoor Air Quality (at CSTB – in Paris, France), Unit of Assessment and Modelling (at Finnish National Institute for Health and Welfare – in Kuopio, Finland), Institute of Isotopes (at KFKI - in Budapest, Hungary) and FRMII reactor (in Munich, Germany).

Nuno Canha published 32 scientific articles in international peer-reviewed scientific journals, one chapter book and 7 proocedings in international conferences. He also performed 7 oral presentations and 8 poster presentations in international conferences, as main author. His main research interests are indoor air quality, air pollution, source apportionment and biomonitoring.

In 2011, he engaged a PhD in Environmental Sciences at Delft University of Technology, where his main research area was indoor air quality in scholar environments. The results of his research are presented in this book.

List of Publications

Journal articles

Canha, N., Almeida, S.M., Freitas, M.C., Wolterbeek, H.T., 2014. Indoor and Outdoor Biomonitoring using Lichens at Urban and Rural Primary Schools. *J Toxicol Env Heal A* 77 (14-16), 900-915.

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Book Chapter

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Appendix

Table A-1. Concentrations (in mg kg^{-1}) of elements of lichens after exposure in both clusters and different sites.

	Urban						Rural					
	Classrooms			Outdoor			Classrooms			Outdoor		
Element	Mean	SD	Range	Mean	SD	Range	Mean	SD	Range	Mean	SD	Range
As	0.51	0.24	[0.28 – 1.60]	0.58	0.26	[0.12 – 1.50]	0.46	0.09	[0.36 – 0.62]	0.49	0.04	[0.46 – 0.53]
Br	9.4	2.9	[6.2 – 20.4]	9.4	3.1	[1.7 - 16.2]	9.1	0.9	[8.0 – 10.8]	10.1	1.3	[9.3 – 12.1]
Ca	60000	24000	[29000 – 135000]	56000	26000	[2000 – 144000]	45000	8000	[35000 – 60000]	38000	1000	[37000 – 40000]
Ce	2.4	0.7	[1.2 – 4.9]	2.5	0.8	[0.7 – 4.2]	2.6	0.5	[1.7 – 3.1]	2.7	0.3	[2.3 – 3.0]
Co	0.39	0.09	[0.28 – 0.74]	0.37	0.10	[0.13 – 0.56]	0.27	0.03	[0.22 – 0.30]	0.30	0.02	[0.26 – 32]
Cr	4.3	1.8	[1.7 – 7.6]	5.2	2.9	[0.8 – 12.8]	5.9	7.6	[2.0 – 25.7]	2.4	0.2	[2.0 – 2.7]
Cs	0.25	0.07	[0.15 – 0.48]	0.23	0.06	[0.08 – 0.32]	0.23	0.04	[0.18 – 0.27]	0.27	0.01	[0.25 – 0.28]
Eu	0.036	0.012	[0.011 – 0.063]	0.034	0.009	[0.013 – 0.054]	0.028	0.006	[0.017 – 0.034]	0.030	0.001	[0.029 – 0.031]
Fe	1000	260	[670 – 2000]	940	260	[300 – 1600]	730	120	[560 – 870]	830	90	[700 – 910]
Hf	0.21	0.07	[0.12 – 0.44]	0.20	0.06	[0.06 – 0.29]	0.28	0.07	[0.17 – 0.36]	0.30	0.08	[0.17 - 0.36]
K	4300	1500	[2000 – 11000]	4400	1400	[1600 – 8900]	4100	400	[3400 – 4700]	4500	100	[4400 – 4600]

Table A-1 (cont.). Concentrations (in mg kg^{-1}) of elements of lichens after exposure in both clusters and different sites.

	Urban						Rural					
	Classrooms			Outdoor			Classrooms			Outdoor		
Element	Mean	SD	Range	Mean	SD	Range	Mean	SD	Range	Mean	SD	Range
La	1.5	0.5	[0.8 – 3.3]	1.5	0.5	[0.5 – 3.0]	1.5	0.2	[1.0 – 1.7]	1.5	0.0	[1.4 – 1.5]
Na	360	120	[180 – 840]	370	120	[130 – 680]	340	30	[300 – 400]	270	140	[10 – 360]
Rb	8.8	3.2	[4.8 – 18.0]	8.7	3.0	[3.3 – 14]	11	1	[8 – 13]	12	0	[11 – 12]
Sb	0.30	0.12	[0.14 – 0.62]	0.33	0.14	[0.08 – 0.82]	0.19	0.03	[0.16 – 0.24]	0.22	0.02	[0.19 – 0.24]
Sc	0.39	0.11	[0.26 – 0.76]	0.36	0.14	[0.12 – 0.95]	0.25	0.03	[0.21 – 0.29]	0.27	0.01	[0.25 – 0.28]
Sm	0.27	0.11	[0.10 – 0.59]	0.27	0.11	[0.06 – 0.55]	0.28	0.05	[0.19 – 0.36]	0.29	0.02	[0.26 – 0.30]
Sr	61	16	[20 – 100]	43	29	[29 – 240]	83	10	[69 – 100]	74	5	[70 – 82]
Ta	0.055	0.022	[0.026 – 0.125]	0.054	0.028	[0.016 – 0.117]	0.051	0.004	[0.047 – 0.058]	0.055	0.008	[0.048 – 0.064]
Th	0.36	0.14	[0.16 – 0.79]	0.35	0.11	[0.12 – 0.69]	0.49	0.11	[0.28 – 0.59]	0.45	0.09	[0.29 – 0.51]
Yb	0.079	0.027	[0.026 – 0.16]	0.082	0.042	[0.024 – 0.19]	0.089	0.019	[0.067 – 0.13]	0.091	0.015	[0.071 – 0.108]
Zn	52	14	[34 – 120]	55	26	[16 – 180]	41	4	[36 – 49]	44	5	[38 – 50]

Table A-2. Concentrations (in mg kg^{-1}) of elements of lichens before exposure (unexposed lichens).

	Unexposed Lichens		
Element	Mean	SD	Range
As	0.52	0.04	[0.45 – 0.57]
Br	8.7	0.2	[8.3 – 8.9]
Ca	49000	1000	[47000-51000]
Ce	2.7	0.1	[2.6 – 2.8]
Co	0.50	0.03	[0.48 – 0.56]
Cr	3.0	0.2	[2.8 – 3.3]
Cs	0.24	0.0	[0.23-0.25]
Eu	0.037	0.003	[0.032 – 0.041]
Fe	1100	40	[1100 – 1200][
Hf	0.23	0.02	[0.20 – 0.25]
K	4400	100	[4300 – 4500]
La	1.5	0.0	[1.4 – 1.5]
Na	290	10	[280 – 300]
Rb	6.7	0.1	[6.6 – 6.9]
Sb	0.21	0.05	[0.17 – 28]
Sc	0.42	0.02	[0.39 – 0.45]
Sm	0.25	0.01	[0.25 – 0.26]
Sr	94	16	[77 – 110]
Ta	0.045	0.005	[0.038 – 0.053]
Th	0.37	0.01	[0.36 – 0.39]
Yb	0.079	0.009	[0.062 – 0.085]
Zn	54	1	[52 – 56]

ISBN: 978-94-6295-050-4