Universidade de Aveiro Departamento de Ambiente e Ordenamento
Ano 2012

PRISCILLA NASCIMENTO PEGAS

QUALIDADE DO AR INTERIOR EM ESCOLAS DO 1º CICLO DE LISBOA E AVEIRO

INDOOR AIR QUALITY IN ELEMENTARY SCHOOLS OF LISBON AND AVEIRO

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Tese apresentada à Universidade de Aveiro para cumprimento dos requisitos necessários à obtenção do grau de Doutor em Ciências e Engenharia do Ambiente, realizada sob a orientação científica da Doutora Célia dos Anjos Alves e sob co-orientação da Doutora Margarita Evtyugina, Investigadoras Auxiliares do Centro de Estudos do Ambiente e do Mar, Departamento de Ambiente e Ordenamento, da Universidade de Aveiro.

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o júri

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Prof. Doutora Célia dos Anjos Alves
investigadora auxiliar do CESAM - Centro de Estudos do Ambiente e do Mar da Universidade de Aveiro. (Orientadora)

Prof. Doutora Margarita Guennadier Evtyugina
investigadora auxiÌiar do CESAM - Centro de Estudos do Ambieitete do Mar da Universidade de Aveiro. (Coorientadora)

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palavras-chave qualidade do ar interior, COVs, carbonilos, NO_2, CO_2, PM_{10}, escolas

Resumo

Tem havido uma preocupação crescente com a qualidade do ar interior (QAI) nas escolas em muitos países. Muitos estudos epidemiológicos têm encontrado diferenças regionais entre ambientes interiores. Apesar da elevada incidência de asma e rinite na população infantil, praticamente nada se sabia sobre a QAI em escolas portuguesas. A percepção dos problemas de QAI é crucial para avaliar os riscos para a saúde e rendimento dos estudantes, e para sugerir meios de reduzir a exposição a poluentes indesejáveis. Neste estudo procurou-se obter as concentrações de poluentes de interesse em estabelecimentos de ensino do 1º ciclo de Lisboa e Aveiro, estimar o estado atual de casos de asma e rinite em escolas primárias da capital, avaliar a influência de diferentes materiais das salas de aula/construção e hábitos escolares na QAI, identificar potenciais fontes de poluentes nos interiores e exteriores das salas de aula e propor medidas mitigadoras. Catorze escolas de Lisboa foram visitadas para obter a caracterização física das construções em termos de estrutura, ventilação, materiais de acabamento, produtos de limpeza, densidade de ocupação e potenciais fontes interiores de poluição. Os estudantes foram questionados sobre os seus hábitos e sintomas respiratórios através de inquéritos do modelo ISAAC (*International Study of Asthma and Allergies in Childhood*). Durante a primavera, outono e inverno (2008-2010), nas salas de aula e pátios, foram monitorizados, por amostragem passiva, compostos orgânicos voláteis (COVs), carbonilos e dióxido de azoto (NO_2). Foram também medidos parâmetros de conforto e níveis de microrganismos. Duas escolas localizadas, uma no centro da cidade e outra na região suburbana, em Aveiro foram estudadas em 2010. Parâmetros de conforto, microrganismos, COVs, NO_2, material particulado (PM_{10}) foram medidos no interior e no exterior de ambas escolas. Os iões solúveis, carbono orgânico e elementar (OC e EC), e compostos orgânicos presentes no material particulado foram subsequentemente analisados em laboratório. Uma medida mitigadora - fitoremediação - foi avaliada na escola do centro da cidade de Aveiro em 2011. Os resultados do estudo mostraram que a QAI é pior do que a do ar exterior. Em geral, os níveis de CO_2 e dos bioaerosóis excederam os níveis máximos aceitáveis para o conforto dos ocupantes estipulado pelas regulamentações portuguesas. Quase todos os COVs e carbonilos identificados mostraram razões interior/exterior (I/E) maiores que uma unidade, o que demonstra a importante contribuição de fontes interiores em todas as escolas. As razões I/E das concentrações de NO_2 nunca excederam a unidade. Os níveis interiores diários de PM_{10} foram sempre maiores que os exteriores, exceto nos fins de semana. Após a colocação de plantas numa das salas de aula, observou-se uma redução estatisticamente significativa nos níveis de CO_2, COVs, carbonilos, PM_{10}, OC, e dos iões nitrato, sulfato, amónia, cálcio e carbonato. A possível redução dos níveis de poluentes no interior após a colocação de plantas pode representar uma solução de baixo custo para reduzir a exposição a muitos compostos, melhorar o rendimento e aumentar o bem estar dos alunos e professores em sala de aula.

Keywords indoor air quality, VOCs, carbonyls, NO_2, CO_2, PM_{10}, school

Abstract

There is a growing concern about indoor air quality (IAQ) in schools in many countries. Most epidemiological studies have found significant differences among indoor environments from different regions. Despite the high incidence of asthma and rhinitis in children, virtually nothing was known about the IAQ in Portuguese schools. The perception of IAQ problems is crucial to assess health risks and students' performance, and to suggest ways to reduce the exposure of children to undesirable pollutants. The main purpose of this study was to obtain the concentrations of pollutants of interest in Lisbon and Aveiro schools, to estimate the actual state for asthma/rhinitis in Lisbon's primary school population, to evaluate the influence of outdoor environment on indoor air, to evaluate the influence of different classroom/building materials and school habits on IAQ, to evaluate the relevance of both indoor and outdoor air quality to the incidence of respiratory symptoms and students' performance, to identify potential outdoor/indoor pollutant sources, and to propose mitigation measures. Fourteen schools of Lisbon city were visited to obtain the physical characterisation of the buildings in terms of structure, ventilation, furniture materials, cleaning products, occupant density, and potential indoor pollutant sources. Students were questioned about habits and respiratory symptoms through ISAAC (*International Study of Asthma and Allergies in Childhood*) surveys. During spring, autumn and winter seasons (2008-2010), classrooms and playgrounds were monitored by volatile organic compound (VOC), carbonyl and nitrogen dioxide (NO_2) passive sampling. Comfort parameters and microorganisms were also measured. Two schools located in Aveiro, one at the city centre and another on the outskirts of the city, were the target of the study in 2010. Comfort parameters, microorganisms, VOCs, NO_2 and particulate matter (PM_{10}) were measured inside and outside of both schools. The soluble ions, organic and elemental carbon (OC and EC) and organic compounds in particulate matter were subsequently analysed in the laboratory. A mitigation measure – phytoremediation - was evaluated at the city centre Aveiro school in 2011. The results of this study showed that IAQ is worse than outdoor air. Generally, the CO_2 and bioaerosol levels were higher than the acceptable maximum values stipulated by the Portuguese regulations. Almost all identified VOCs and carbonyls showed indoor/outdoor (I/O) ratios higher than one, which denotes an important contribution from indoor sources at all schools. In general, the I/O NO_2 ratios never exceeded the unity. The daily indoor PM_{10} levels were always higher than those outdoors, except on weekends. After the placement of potted-plants in one classroom, a statistically significant reduction in the levels of CO_2, VOCs, carbonyls, PM_{10}, organic carbon, and ions (nitrate, sulphate, ammonia, calcium, and carbonate) was observed. The use of plants may represent a low-cost solution to reduce exposure to many compounds and lifetime risk, and to further improve performance, attendance and welfare of students and teachers in classrooms.

Index

Table and Figure List:

List of publications

This thesis is based on the work contained in the following papers:

I. Pegas, P.N., Alves, C.A., Scotto, M.G. , Evtyugina, M., Pio, C.A., Freitas, M.C., 2011. Risk factors and prevalence of asthma and rhinitis among primary school children in Lisbon. Revista Portuguesa de Pneumologia, 17, 109-116.

II. Pegas, P.N., Evtyugina, M.G., Alves, C.A., Nunes, T., Cerqueira, M., Franchi, M., Pio, C., Almeida, S.M., Freitas, M.C., 2010. Outdoor/Indoor air quality in primary schools in Lisbon: a preliminary study. Química Nova, 33, 1145-1149.

III. Pegas, P.N., Alves, C.A., Evtyugina, M., Nunes, T., Cerqueira, M., Franchi, M., Pio, C., Almeida, S.M., Canha, N., Freitas, M.C., 2011. Indoor air quality in elementary schools of Lisbon in spring. Environmental Geochemistry and Health, 33, 455-468.

IV. Pegas, P., Alves, C.A., Evtyugina, M., Nunes, T., Cerqueira, M., Franchi, M., Pio, C., Almeida, S.M., Cabo Verde, S., Freitas, M.C., 2011. Seasonal evaluation of outdoor/indoor air quality in primary schools in Lisbon. Journal of Environmental Monitoring, 13, 657-667.

V. Pegas, P.N., Nunes, T. Alves, C.A., Silva, J.R., Vieira, S.L.A., Caseiro, A., Pio, C.A., 2012. Indoor and outdoor characterisation of organic and inorganic compounds in city centre and suburban elementary schools of Aveiro, Portugal. Atmospheric Environment 55, 80-89.

VI. Pegas, P.N., Alves, C.A., Nunes, T., Bate-Epey, E.F., Evtyugina, M., Pio, C.A., 2012. Could houseplants improve indoor air quality in schools? Journal of Toxicology and Environmental Health, Part A [ISSN: 1093-7404] 75, 1371-1380.

Abbreviations

ACGIH - American Council of Governmental Industrial Hygienists

AIRMEX - European Indoor Air Monitoring and Exposure Assessment Project

ASHRAE - American Society of Heating, Refrigerating, and Air-Conditioning Engineers

B[a]P - Benzo[a]pyrene

BiBa - Binnenlucht in Basisscholen (Dutch acronym for indoor air in primary schools)

BSTFA - *N*,*O*-bis(trimethylsilyl)-trifluoroacetamide

BTEX - Benzene, Toluene, Ethylbenzene and Xylenes

Ca^{2+} - Calcium

CFU m^{-3} - Colony-Forming Units per Cubic Metre of Air

Cl^- - Chlorides

CO - Carbon Monoxide

CO_2 - Carbon Dioxide

CO_3^{2-} - Carbonate

COSHR - Canadian Occupational Safety and Health Regulations

CRBA - Chloramphenicol Rose Bengal Agar

CS_2 - Carbon Disulfide

DCM - Dichloromethane

DNPH - 2,4-Dinitrophenylhydrazine

EC - Elemental Carbon

EC – Elemental Carbon

EI - Electron Impact

EPA - Environmental Protection Agency

GC-FID - Gas Chromatography coupled to Flame Ionisation Detector

GC-MS – Gas Chromatographic coupled to a Mass Spectrometry

H_3PO_4 - Phosphoric Acid

HCl - Hydrochloric Acid

HESE - Health Effects of Schools Environment

HITEA - Health Effects of Indoor Pollutants: Integrating Microbial, Toxicological and Epidemiological Approaches

HPLC - High-Performance Liquid Chromatography

IAQ - Indoor air quality

IARC - International Agency for Cancer Research

ISAAC - International Study of Asthma and Allergies in Childhood Program

K^+ - Potassium

LARES - Large Analysis and Review of European housing and health Status

LOD - Limit of Detection

Mg^{2+} - Magnesium

Na^{+} - Sodium

NAAQS - National Ambient Air Quality Standards

NaOH - Hydroxide Sodium

NDIR - Non-Dispersive Infrared sensor

NEDA - N-1-naphtilene diamine

NIOSH - National Institute for Occupational Safety and Health

NO_2 - Nitrogen Dioxide

NO_3^- - Nitrates

O_3 - Ozone

OC - Organic Carbon

OSHA - Occupational Safety and Health Administration

PAHs - Polycyclic Aromatics Hydrocarbons

PC - Pyrolysed Organic Carbon

PERC - Perchloroethylene

PID - Photo-Ionisation Detector

PM_{10} - Particle Matter < 10µm

$PM_{2.5}$ - Particle Matter < 2.5 µm

PVC - Polyvinyl Chloride

RH - Relative Humidity

RRF - Relative Response Factor

RSECE - *Regulamento dos Sistemas Energéticos de Climatização de Edifícios*

SaudAR - Health and The Air We Breathe

SBS - Sick Building Syndrome

SEARCH - School Environment and Respiratory Health of Children

SINPHONIE - Schools Indoor Pollution and Health: Observatory Network in Europe

SO_4^{-2} - Sulphates

TCE - Trichloroethylene

TEA – Triethanolamine

TMCS - Trimethylchlorosilane Groups

TSA - Tryptic Soy Agar

TVOCs – Total Volatile Organic Compounds

VOCs - Volatile Organic Compounds

WHO - World Health Organisation

WSII - Water Soluble Inorganic Ions

Chapter 1

1. INTRODUCTION

1.1 Indoor air quality

Indoor air quality (IAQ) in enclosed spaces depends on several factors, including thermal, acoustic and visual comfort. Both physical and perceptual parameters are important in defining a good indoor environment. The IAQ may have a significant influence on health, welfare and comfort of occupants, which may impact the performance and productivity (Daisey et al., 2003; Paevere et al., 2008; Simoni et al., 2010; Viegi et al,. 2004). The IAQ is determined by a constant interaction of factors that affect the types, levels and importance of pollutants inside the building. In closed environments, IAQ can be related to several causes either chemical (e.g. carbon oxides, environmental tobacco smoke, formaldehyde, and volatile organic compounds) (Bakke et al., 2008; Dales et al., 2008; Giulio et al., 2010; OSHA, 2011) or physical (ventilation rate, dampness, temperature, and non-ionising and ionising radiation) (Bakke et al., 2008; Giulio et al., 2010; OSHA, 2011). In addition, IAQ is also related to bioaerosols (bacteria, virus, fungi, and toxins from microbial metabolism) (Douwes et al., 2003; Giulio et al., 2010; OSHA, 2011).

Indoor air pollution is the second most important environmental risk factor, after unsafe water. It accounts for twice the number of deaths reported from urban outdoor air pollution (Singh and Jamal, 2012). An acceptable IAQ is defined as air without contaminants at harmful levels and where the majority of people are satisfied. The IAQ depends on both the outdoor air quality and on the emissions of indoor sources. Thus, it is necessary an entrance of tempered outdoor air and a sufficient quantity of clean air (Amissah, 2005). However, each indoor microenvironment is uniquely characterised, and it depends on the outdoor air, specific buildings characteristics and indoor activities (Giulio et al., 2010; Stranger et al., 2007).

The U.S. Environmental Protection Agency (1999) has classified IAQ among the top five environmental risks to public health. The IAQ is characterised by physical factors

(ambient temperature, humidity, ventilation rate, for example), air pollutant factors (pollutant levels and exposure times) and human factors (activities and health status) (Bakke et al., 2008; Dales et al., 2008; Giulio et al., 2010; OSHA, 2011; Paevere et al., 2008). Other factors that contribute negatively to IAQ are poor cleaning practises, poor moisture control (water leaks or damp surfaces), human occupancy (odours, respiration) and poor building maintenance (Mi et al., 2006; OSHA, 2011; Paevere et al., 2008; Salonvaara et al., 2004; U.S. Environmental Protection Agency, 1999). The modern construction with better insulation may result in warmer buildings, but more humid houses with poorer availability of fresh air by the ventilation (Järnström et al., 2006; Jones, 2000). Low ventilation rates have been associated with several health problems, respiratory allergies and asthma, like sick building syndrome (SBS) symptoms (Daisey et al., 2003; Fraga et al., 2008; Godwin and Batterman, 2007; Griffiths and Eftekhari, 2008; Kim et al., 2007a; Mi et al., 2006; Seppanen et al., 1999; Shaughnessy et al., 2006; Yang et al., 2009). SBS is a situation in which occupants experience health effects (of mucosal, skin, and general symptoms) that seem to be linked to time spent in a building, but no specific illness or cause can be identified. The complaints may be localised in a particular room or zone, or may be widespread throughout the building. These symptoms include headaches, eye, nose, and throat irritation, a dry cough, dry or itchy skin, dizziness and nausea, difficulty in concentrating, fatigue, and sensitivity to odours. SBS reduces work performance and may also decrease the attendance (Burge, 2004; Daisey et al., 2003; Fang et al., 2004; Li and Yang, 2004; Rashid and Zimring, 2008; Syazwan et al., 2009; U.S. Environmental Protection Agency, 1999; WHO, 2009).

In recent years there has been increased interest in indoor pollutants because citizens spend more time (about 90%) inside buildings and many studies have showed higher levels inside than outside (Godoi et al., 2009; Jo and Seo, 2005; Kotzias et al., 2009; Lee and Chang, 2000; Lee et al. 2001, 2002, Li et al. 2001; Pegas et al., 2010; Pegas et al., 2011a,b; Yang et al., 2009)

Indoor pollution sources are the primary cause of a bad IAQ. Insufficient ventilation can exacerbate the IAQ problems, since there is not adequate air renewal to dilute the indoor pollutant concentrations and there is not a removal of indoor pollutants to the outside (Daisey et al., 2003; Griffiths and Eftekhari, 2008; Mi et al., 2006). High

temperatures and humidity may also increase levels of chemical compounds and bioaerosol (Burge, 2004; Li and Yang, 2004; U.S. Environmental Protection Agency, 2008).

The main indoor sources include combustion sources (oil, gas, kerosene, coal, wood, and tobacco products), building materials and furniture (both new and deteriorated), asbestos (used in insulation), carpet, hardwood, plywood, wall paneling, particleboard, fiberboard, paints, paint strippers, and other solvents, wood preservatives, aerosol sprays, cleansers and disinfectants, moth repellents and air fresheners, stored fuels and automotive products, hobby supplies, dry-cleaned clothing, central heating and cooling systems and humidification devices (Cerón et al., 2007; Daisey et al., 2003, Guo et al., 2004, Mendell, 2007; Ugucione et al., 2009; U.S. Environmental Protection Agency, 2008). In some cases, the age of a specific source and its conservation status may increase or decrease emissions and pollutants that are emitted (Järnström et al., 2006; Yang et al., 2009). Moreover, the emissions are variable in length over time. For example, building materials, architectural finishes and furniture release pollutants more or less continuously, while cleaning and hobby activities, kerosene and gas space heaters, woodstoves, fireplaces, and gas stoves release pollutants intermittently. Changes in construction designs in order to conserve energy (higher heat and sound insulation, for example) and the increasing application of synthetic products have contributed to the enhancement of the number of complaints about IAQ at several environments (Järnström et al., 2006; Sundell et al., 1994; Yang et al., 2004). The application of insulation and energy efficiency measurements has a negative effect on air renovation causing the accumulation of harmful compounds to human health (Agência Portuguesa do Ambiente, 2009; Brickus and Aquino-Neto, 1999).

Health effects from a poor IAQ may be experienced during exposure or, possibly, years later. Most pollutants to which people are exposed indoors constitute an additional risk factor in the development of several pathologies (Daisey et al., 2003; Mendell, 2007; Simoni et al., 2010; Singh and Jamal, 2012; Sundell et al., 1994). Immediate effects include eyes, nose, and throat irritation, allergic rhinitis, flu-like symptoms, headaches, difficulty in concentration, fatigue, dry or itchy skin, difficulty in breathing and nausea feeling sick. Symptoms of some diseases, including asthma, wheezing, rhinitis and hay fever, may be aggravated by exposure to pollutants (Daisey et al., 2003; Mendell, 2007; U.S. Environmental Protection Agency, 2008). Long term-effects include respiratory

diseases, heart disease, and cancer, which can lead to death (Bernstein et al., 2008; Guieysse et al., 2008; Jie et al., 2011; Rios et al.; 2009; Samet and Spengler, 2003).

1.2 Guidelines for indoor air quality

Many of the regulations for IAQ are incomplete and fragmented. Some institutions or groups have introduced general specifications and/or guidance notes addressing IAQ issues. This section tries to summarise some recommendations for acceptable indoor air quality levels for the main indoor pollutants, such as carbon dioxide (CO_2), carbon monoxide (CO), particle matter < 2.5 µm ($PM_{2.5}$), particle matter < 10µm (PM_{10}), ozone (O_3), nitrogen dioxide (NO_2), microorganisms, volatile organic compounds (VOCs), formaldehyde, and polycyclic aromatics hydrocarbons (PAHs).

In the United States of America, the Occupational Safety and Health Act of 1970 created both the Occupational Safety and Health Administration (OSHA) and the National Institute for Occupational Safety and Health (NIOSH). OSHA was created to assure safe and healthful working conditions. The standards were developed through a formal rule-making process, and the limits can only be changed by reopening this process. It does have standards about ventilation and standards on some of the air contaminants that can be involved in IAQ problems. NIOSH is the federal agency responsible for researches and recommendations for the prevention of work-related injury and illness. It helps to assure safe and healthful working conditions for working men and women by providing research, information, education, and training in the field of occupational safety and health. It recommended maximum exposures for industrial environments, but these recommendations are not reviewed regularly, and in some cases levels are set above those needed for health reasons, because commonly available industrial hygiene practices do not reliably detect substances at lower levels. Also created in 1970 in the USA, the Environmental Protection Agency (EPA) is an organisation of the federal government which was created with the purpose of protecting human health and the environment by writing and enforcing regulations. EPA does not have regulations or standards related to IAQ, but has been developing guidance documents. The National Ambient Air Quality

Standards (NAAQS) developed by EPA have standards for outdoor air quality, but they are also applicable to indoor air contaminant levels. The concentrations are set conservatively in order to protect the most sensitive individuals, such children, the elderly, and those with asthma. The American Society of Heating, Refrigerating, and Air-Conditioning Engineers (ASHRAE) in its documents "Ventilation for Acceptable Indoor Air Quality" (ASHRAE 62-2001) and "Thermal Environmental Conditions for Human Occupancy" (ASHRAE 55-2004) promulgated standards, which are currently adopted not only in the USA, but also in other regions of the world. The American Council of Governmental Industrial Hygienists (ACGIH) is a member-based organisation dedicated to the industrial hygiene and occupational health and safety industries. Their guidelines are applicable for normal industrial working conditions (40 hours per week), and for single contaminant exposure. These recommendations are guidelines, rather than enforceable standards, and are not selected to protect the most sensitive people. These guidelines were developed in 1987 and updated in 1999. They are intended for application to both indoor and outdoor exposures, but are guidelines rather than an enforceable standard. The Canadian Occupational Safety and Health Regulations (COSHR) established requirements for maintaining a healthy and safe working environment. COSHR requires that indoor contaminant concentrations be kept within the limits set by the ACGIH. The World Health Organisation (WHO) Office for Europe, based in Denmark, developed guidelines to be used in non-industrial settings.

The Portuguese Legislation lays on some rules for IAQ, defined by the National System for Energy and Indoor Air Quality Certification of Buildings (*Regulamento dos Sistemas Energéticos de Climatização de Edifícios* - RSECE, Decree-Laws 78/2006 and 79/2006). This set of laws establishes a technical note with the methodology to the audit of IAQ in buildings. To perform an audit, the following tasks are necessary: i) gathering all relevant information about the building (plans, description of the ventilation system, special areas, number of occupants, registration of complaints and symptoms); ii) preliminary visit to the building (verify the accuracy and update the information given by the owner, gather additional information, interviews with occupants); iii) check the CO_2 levels inside and outside the building (near the air intakes, like windows, balconies or external openings of the ventilation system); and iv) pre-assessment of hygiene and maintenance of heating, ventilation and air conditioning (HVAC) system, when it exists (RSECE, 2006).

PM_{10} represent particles of any substances that are less than or equal to 10 micrometres diameter. Particles in this size range make up a large proportion of dust that can be drawn deep into the lungs. Respirable particulate matter is released from a wide range of biogenic and anthopogenic sources. Continuous exposure to PM_{10} contributes to the risk of developing cardiovascular and respiratory diseases, as well as of lung cancer (Sloan et al., 2012). The World Health Organisation has set a guideline of 20 μg m^{-3} for the annual mean. A threshold of 150 μg m^{-3} for indoor PM_{10} without a temporal base has been established by the Portuguese Legislation (RSECE, 2006).

Indoor CO_2 levels are an indicator of the adequacy of outdoor air ventilation relative to indoor environment. The National System for Energy and Indoor Air Quality Certification of Buildings establishes an acceptable maximum value of 1800 mg m^{-3} of CO_2 for buildings in Portugal (RSECE, 2006). This measurement is useful to know if the confined space meets reference concentration to ensure the welfare of the occupants and comply with the ventilation rates recommended by RSECE (8.33 l s^{-1} per person). The minimum value recommended by the ANSI/ASHRAE Standard 62-1999 is only 2.5 l s^{-1} per person.

Acute exposure to CO, a pollutant resulting from combustion processes, is related to reduction of exercise tolerance and increase in symptoms of ischaemic heart disease (WHO, 2009). At lower levels of exposure, CO causes mild effects that are often mistaken for the flu. These symptoms include headaches, dizziness, disorientation, nausea and fatigue. The effects of CO exposure can vary greatly from person to person depending on age, overall health and the concentration and length of exposure. While the WHO has sets limits for CO concentrations in accordance with the exposure period, RSECE only establishes an acceptable maximum value.

Ozone at ground level is formed by the reaction in the presence of sunlight (photochemical reaction) of pollutants such as nitrogen oxides (NOx) from vehicle and industry emissions and biogenic VOCs or emitted by vehicles, solvents and industry. The highest levels of ozone pollution occur during periods of sunny weather. High ozone concentrations may cause breathing problems, trigger asthma, reduce lung function and cause lung diseases (WHO, 2010). The Portuguese legislation establishes a limit of 200 μg m^{-3} without specifying further conditions for ozone exposure.

Formaldehyde is, in general, the most abundant carbonyl compound in indoor air. This volatile compound is released from a variety of sources, including building materials, consumer products and furniture. It is classified as a human carcinogen by the International Agency for Cancer Research (IARC). Exposure to moderate levels of formaldehyde (hundreds of ppb or greater) can cause a number of irritant symptoms, including temporary burning of the eyes or nose, and a sore throat. RSECE has set a limit of 0.1 mg m^{-3} without further information about the duration of exposure (RSECE, 2006). The formaldehyde guideline (30 min average) recommended by WHO was target in order to prevent effects on lung functions, as well as nasopharyngeal cancer and myeloid leukaemia (WHO, 2009).

Among all VOCs, benzene, toluene, ethylbenzene and xylenes (BTEX) are of particular interest due to their known carcinogenic effects. It has been demonstrated that vehicular emissions and industrial sources are the major sources of ambient BTEX, while the indoor sources are quite numerous (e.g. combustion by-products, cooking, construction materials, furnishings, paints, varnishes and solvents). Benzene is a genotoxic carcinogen in humans and, according to WHO, no safe level of exposure can be recommended. The risk of toxicity from inhaled benzene would be the same whether the exposure were indoors or outdoors. Thus there is no reason that the guidelines for indoor air should differ from ambient air guidelines (WHO, 2010). RSECE establishes a target of 600 μg m^{-3} for total VOCs in indoor environments (RSECE, 2006).

Also among VOCs, chlorinated compounds (e.g. trichloroethylene and tetrachloroethylene) have received increasing attention. Trichloroethylene (TCE) is primarily used as a solvent to remove grease from metal parts. As a solvent or as a component of solvent blends, it is used in adhesives, lubricants, paints, varnishes, paint strippers, carpet shampoos and waterproofing agents. Consumers may be exposed to trichloroethylene when using products containing the substance, especially if there is not good ventilation. Because TCE is used in many consumer products, short-term indoor concentrations may be elevated above the levels considered safe. Exposure to moderate amounts of TCE may cause headaches, loss of balance, and tremors. Larger exposures will cause dizziness or sleepiness, and at very high levels may cause unconsciousness. Very large exposures may cause irreversible cardiac problems, nerve and liver damage, and death. TCE is mildly irritating to the eyes, nose and throat. Chronic (long-term) exposures

to TCE have been shown to cause nausea, intolerance to fatty foods, respiratory irritation, renal (kidney) toxicity, and immune system depression (DSEWPC, 2001). IARC has classified TCE as a probable human carcinogen. WHO (2010) reported an unit risk estimate of 4.3×10^{-7} per μg m^{-3}. The concentrations of airborne TCE associated with an excess lifetime cancer risk of 1:10 000, 1:100 000 and 1:1 000 000 are respectively 230, 23 and 2.3 μg m^{-3} (WHO, 2010). Tetrachloroethylene, also known as perchloroethylene (PERC), is used in the dry-cleaning industry. It can be added to solvent soaps, printing inks, adhesives, sealants, polishes, lubricants and silicones. Consumers may be exposed to PERC when using consumer products containing the compound, by spending time in dry-cleaning facilities or by bringing dry-cleaned clothes into their homes. In high concentrations, in air, with closed or poorly ventilated areas, single exposures to PERC may cause central nervous system effects (DSEWPC, 2001). PERC was classified as a probable human carcinogen by IARC. Carcinogenicity was not selected by WHO as the end-point for setting the guideline value for three reasons: the epidemiological evidence is equivocal, the animal tumours detected are not considered relevant to humans, and there are no indications that PERC is genotoxic. Based on studies of dry cleaning workers, the lowest level for which adverse effects on kidneys are observable after long-term exposure was considered to be 102 mg m^{-3}, while a minimal risk level of 0.28 mg m^{-3} has been estimated for chronic inhalations (WHO, 2010). Based on these outcomes, WHO set an annual average of 0.25 mg m^{-3}. Naphthalene is the most volatile PAH. Most airborne emissions result from combustion, and key sources include industry, open burning, tailpipe emissions, and cigarettes. The second largest source is off-gassing, specifically from naphthalene's use as a deodoriser, repellent and fumigant. Exposure to naphthalene has been linked to a number of adverse health effects. The major non-cancer endpoints are hyperplasia and metaplasia in respiratory and olfactory epithelium, respectively, and the cancer endpoint of concern are nasal tumors (Jia and Batterman, 2010). Is has been classified as possibly carcinogenic to humans by IARC. A guideline of 0.01 mg m^{-3} (annual average) has been recommended by WHO. This value was assumed to prevent potential malignant effects in the airways.

PAHs are combustion products that constitute a large group of organic compounds with two or more benzenic rings. Low-molecular-weight PAHs (two and three rings) occur predominatly in the vapour phase, whiles five or more ringed PAHs are largely bound to

particles. Benzo[a]pyrene (B[a]P) is often used as a marker for total exposure to carcinogenic PAHs, as the contribution of B[a]P to the total carcinogenic potential is high. According to WHO (2010), no threshold can be determined and all indoor exposures are considered relevant to health. The unit risk for lung cancer for PAH mixtures is estimated to be 8.7×10^{-5} per ng m^{-3} of B[a]P. The corresponding concentrations for lifetime exposure to B[a]P producing excess lifetime cancer risks of 1/10 000, 1/100 000 and 1/1 000 000 are approximately 1.2, 0.12 and 0.012 ng m^{-3}, respectively.

NO_2 is a pollutant associated with combustion sources. It is an irritant gas and can increase susceptibility to airway infections and impair lung function in exposed populations. Short-term human controlled exposure experimental studies indicated minor changes in pulmonary function in people with asthma exposed to 560 μg m^{-3} nitrogen dioxide for up to 2½ hours. Small increases in airway reactivity to a range of stimuli in asthmatics at repeated short exposures to 500 μg m^{-3} were also observed. Meta-analysis of studies on association of lower respiratory illness in children showed that an increase in indoor nitrogen dioxide of 28 μg m^{-3} above the background of ca. 15 μg m^{-3} can be associated with a 20% increased risk of lower respiratory illness in children (WHO, 2010). A 1-hour indoor nitrogen dioxide guideline of 200 μg m^{-3} was recommended by WHO. No standard is provided in the Portuguese legislation.

Bacteria found in indoor environments typically come from human sources (skin and respiration) or from the outdoors. Like mould, most of the bacteria found in the air in buildings are saprobes, meaning they grow on dead organic matter. As far as building envelopes are concerned the primary preoccupation is about bacteria colonies that may grow in damp areas. Exposure to bacterial and mould may cause allergic reactions, asthma, and other respiratory complaints, excluding pathogenic bacteria that trigger specific diseases. The Portuguese legislation establishes an indoor limit of 500 colony forming units per cubic meter (CFU m^{-3}) for the levels of both bacterial and fungal populations (RSECE, 2006).

A summary of IAQ guidelines for selected pollutants comparing RSECE, WHO/Europe, NAAQS/EPA, OSHA/ASHRAE, NIOSH, ACGIH and COSHR. is shown in **Table 1.1**.

Table 1.1. Summary of IAQ guidelines for selected pollutants: RSECE, WHO/Europe, NAAQS/EPA, OSHA/ASHRAE, NIOSH, ACGIH and COSHR.

Parameters	Guidelines						
	RSECE	WHO/Europe	NAAQS/EPA	OSHA/ASHRAE	NIOSH	ACGIH	COSHR
Total particulates				15 $\mu g\ m^{-3}$			refers readers to ACGIH recommendations
Particulate matter <2.5µm ($PM_{2.5}$)			15 $\mu g\ m^{-3}$ (1 year), 65 $\mu g\ m^{-3}$ (24 h)	5 $mg\ m^{-3}$		3 $mg\ m^{-3}$	
Particulate matter <10µm (PM_{10})	0.15 $mg\ m^{-3}$	20 $\mu g\ m^{-3}$	50 $\mu g\ m^{-3}$ (1 year), 150 $\mu g\ m^{-3}$ (24 h)			10 $mg\ m^{-3}$	
CO_2	1800 $mg\ m^{-3}$	-		5000 ppm	5 ppm, 30000 ppm (15 min)	5 ppm, 30000 ppm (15 min)	
CO	12.5 $mg\ m^{-3}$	7 $mg\ m^{-3}$ (24 h), 10 $mg\ m^{-3}$ (8 h), 35 $mg\ m^{-3}$ (1h), 100 $mg\ m^{-3}$ (15 min)	9 ppm or 35 ppm (1 h)	50 ppm	35 ppm	25 ppm	
O_3	0.2 $mg\ m^{-3}$	120 $\mu g\ m^{-3}$ (8 h)	0.12 ppm (1 h)	0.1 ppm	0.1 ppm	0.05 ppm -heavy work, 0.08 ppm - moderate work, 0.1 ppm -light work, 0.2 ppm – any work (2 h)	
Formaldehyde	0.1 $mg\ m^{-3}$	0.1 $mg\ m^{-3}$ (30 min)	0.4 ppm	0.75 ppm, 2 ppm (15 min)	0.016 ppm, 0.1 ppm (15 min)	0.3 ppm	
Total Volatile organic compounds (VOCs)	0.6 $mg\ m^{-3}$	-					
Benzene	-	no safe level of exposure can be recommended		32 $mg\ m^{-3}$		2 $mg\ m^{-3}$	
Trichloroethylene	-	until risk estimate of 4.3 x 10^{-7} per $\mu g\ m^{-3}$		538 $mg\ m^{-3}$		269 $mg\ m^{-3}$	
Tetrachloroethylene	-	0.25 $mg\ m^{-3}$ (24 h)		679 $mg\ m^{-3}$		170 $mg\ m^{-3}$	
Polycyclic aromatic hydrocarbons (PAHs)	-	no threshold can be determined and all indoor exposures are considered relevant to health					
NO_2	-	200 $\mu g\ m^{-3}$ (1 h average), 40 $\mu g\ m^{-3}$ (annual average)	0.05 ppm (1 year)		1 ppm (15 min)	3 ppm, 5 ppm (15 min)	
Naphtalene	-	0.01 $mg\ m^{-3}$ - annual average					
Bacteria and Mould	500 CFU m^{-3}	-					
Legionella	100 CFU l^{-1} water	-					

1.3 Indoor air quality in schools

The increased traffic and industrial emissions caused an increased concern about outdoor air quality in the last 50 years. At the same time, studies have shown that citizens spend most of their time in buildings and are far more exposed to pollution indoors than outdoors (Blondeau et al., 2005; Rodrigues, 2008; Yu et al., 2009). Schools constitute a particular indoor environment because children represent a special susceptible group of the population (Geller et al., 2007). In an extensive review work, Mendell and Heath (2005) concluded that school IAQ need to be studied with the aim of finding connections between pollutants and performance or attendance, due to two main reasons: schools normally have environmental deficiencies since chronic shortages of funding contribute to inadequate operation and maintenance of facilities; and children have greater susceptibility to pollutants than adults because they breathe higher volumes of air relative to their body weights and their organs are actively growing. Moreover, children are less likely than adults to comprehend and clearly communicate their symptoms.

Levels of specific contaminants in indoor air may be significantly higher than outdoors. Contaminants found at increased levels indoors include formaldehyde, VOCs, moulds and bacteria, PM, CO, CO_2 and NO_2 (Godish, 1989). Many indoor sources can contribute to indoor air pollution in a school, as shown in **Figure 1.1**.

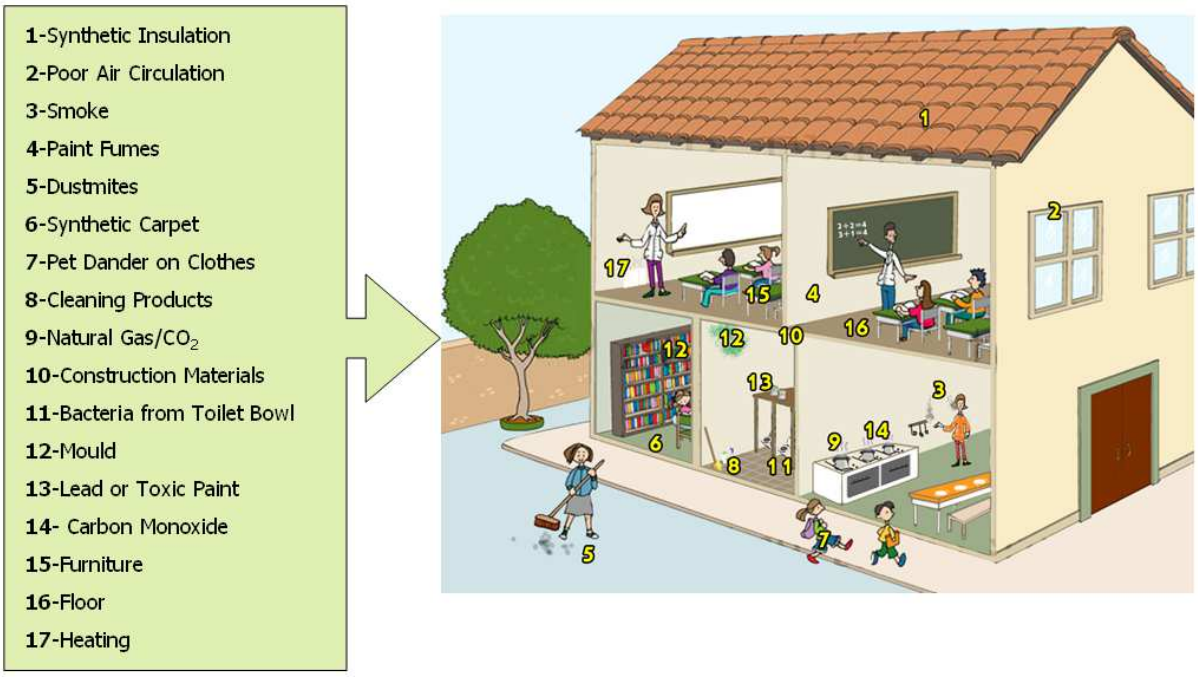

Figure 1.1. Examples of indoor pollutant sources in a school.

Students, teachers, and other staff members need a healthy and comfortable indoor environment in schools, because poor IAQ may lead to discomfort or illness, which may reduce productivity, attendance and academic performance. The control of IAQ in a school is a special problem due to the fact that students and teachers often work more closely together in classrooms than people in typical office buildings. In addition, approximately four times more people may occupy a given area of floor in a school classroom as than in an office (U.S.EPA, 1999). Thus, there is a growing concern about IAQ in schools in many countries.

Most studies in schools have been performed in northern Europe (Kim et al., 2007a,b; Zhao et al., 2006), USA (Godwin and Batterman, 2007; Shaughnessy et al., 2006) and China (Kim et al., 2007b, Mi et al., 2006; Zhao et al., 2006). Significant differences among indoor environments from different regions have been found (Mi et al., 2006; Zhao et al., 2006). Data are needed on air quality in schools, since children are assumed to be more vulnerable to health hazards and spend a large part of their time in classrooms (Bayer et al., 2000).

Daisey et al. (2003) compiled information about IAQ and health problems in schools. Generally, the CO_2 concentrations in schools indicated inadequate air exchange rates, since the CO_2 measurements (above 1000 ppm) do not meet the ASHRAE Standard 62-1999 for minimum ventilation rate (Blondeau et al., 2005; Brennan et al., 1991; Casey et al., 1995; Fisher et al., 1994; Fromme et al., 2007; Griffiths and Eftekhari, 2008; Lee and Chang, 2000; Madureira et al., 2009; Menzies et al., 1993; Milton et al., 2000; Nielsen et al., 1984; Norback, 1995; Smedje et al., 1996, 1997; Thorne, 1993; Turk et al., 1987, 1989, 1993; Willers et al., 1996). Fromme et al. (2007) performed a study in 64 schools in Munich and a neighbouring district outside the city boundary during the winter of 2004 and 2005 and found correlations between high CO_2 levels, inadequate ventilation, occupancy rates and poor IAQ. The accumulations of pollutants and poor ventilation rates have been related to asthma and allergies commonly reported by students and teachers (Bornehag et al., 2004, 2005; Seppanen et al., 1999; Sundell et al., 1994). Wargocki et al. (2000) observed that increasing ventilation decreased the percentage of subjects dissatisfied with the air quality and the intensity of odour, and increased the perceived freshness of air. It also decreased the sensation of dryness of mouth and throat, eased difficulty in thinking clearly and made subjects generally better.

Chaloulakou and Mavroidis (2002) investigated indoor and outdoor CO concentrations in Greek schools. The outdoor CO levels were higher than indoors. However, indoor CO concentrations were higher during winter than during summer, showing a variation dependent on the season. Rundell et al. (2006) and Ali and Athar (2008) studied schools in different traffic locations and also found higher CO levels outdoor. On the other hand, Chen et al. (2000) reported an increase of 3.79% absence rate for increases of 1 ppm in indoor CO concentrations, in elementary schools (Chen et al., 2000).

Persuasive evidence links higher indoor NO_2 concentrations to reduced school attendance (Ali and Athar, 2008; Brunekreef et al., 1997; Janssen et al., 2001, 2003; Mi et al., 2006; Peacock et al., 2003; Pénard-Morand et al., 2005; Piloto et al., 1997; Singer et al., 2004; Van Roosbroeck et al., 2007; Wargocki and Wyon, 2007). A well-designed study on the effects of emissions from gas heaters in both school and home settings reported a

significant dose-response relationship with increasing NO_2 exposure for increased rates of sore throat, colds and absences from school (Pilotto et al., 1997).

Few measurements of speciated VOCs in schools are reported in the literature. Most studies have been focused on total VOCs (Bayer and Dowing, 1992; Black and Worthan, 1995; Casey et al. 1995; Cavallo et al., 1993; Norback, 1995; Smedje et al., 1996). Black and Worthan (1995) reported total VOC concentrations of 0.45 and 0.2 mg m^{-3} under occupied and unoccupied conditions for a school in Washington State. In two US schools with humidity and mould problems, the total VOC levels ranged from 1 to 23 mg m^{-3} (Bayer and Dowing, 1992). A cross-sectional study in Swedish secondary schools performed by Smedje et al. (1996) reported a loss in student performance due to IAQ problems related to multiple indoor exposures and conditions, including the high concentrations of total VOCs. Huang et al. (2008) measured indoor and outdoor concentration of 82 VOCs in one elementary school in Beijing. They found that total VOCs were higher inside the school than at playgrounds. The chemical speciation of indoor VOCs was similar to the outdoor air. The most common species of VOCs found were isopentane, benzene, propanal, propene and dichloromethane. Madureira et al. (2009) characterised the IAQ in Oporto schools to evaluate cases of health symptoms reported by teachers and to study the impact of pollutants on the prevalence of these symptoms. The results showed that schools near heavy traffic roads had higher concentrations of benzene and toluene. In Turkish schools, Sofuoglu et al. (2011) evaluated VOCs indoors and outdoors. Benzene and toluene were the most abundant compounds, followed by naphthalene and xylenes.

Two controlled exposure studies evaluated the effects of a mixture of 22 VOCs on sick-building syndrome patients relative to asymptomatic controls (Kjaergaard et al., 1991; Mølhave et al., 1986). Along with increasing symptom reports of irritation with increasing VOC exposure (0, 5, 25 mg m^{-3}), Mølhave et al. (1986) reported reduced performance on digit span among SBS subjects. This finding was not replicated, however, when this study was conducted with young, healthy male subjects. Kjaergaard et al. (1991) also found impaired digit span performance in SBS-sensitive subjects but not among non-SBS subjects with exposure at 25 mg m^{-3} VOC mixture, which is roughly equivalent to 7 ppm toluene. Otto et al. (1992) suggested that differential effects may be due to differential

sensitivity of the subject groups as well as relative insensitivity of many of the current neurobehavioural methods. Nasal swelling, congestion, inflammation, irritant symptoms (nose, throat, eyes and skin) and other symptoms typical of SBS are related to VOC exposure (Gyntelberg et al., 1994; Madureira et al., 2009; Mølhave et al., 1986; Sundell et al., 1993; Willers et al., 1996).

The first measurements of formaldehyde in schools were reported by Olsen and Dossing (1982). They measured formaldehyde in 10 Danish daycares centres. The average formaldehyde concentration for mobile buildings was 0.35 ppm, while the level for permanent buildings was 0.065 ppm. Health symptoms were three times more frequent among the staff in the mobile buildings than permanent buildings. Black and Worthan (1995) reported formaldehyde concentrations of 0.01 ppm e before and during occupancy in a complaint school of Washington State after the adoption of mitigation measures. Formaldehyde concentrations for 10 schools in Milan, Italy (Cavallo et al., 1993) and 10 schools in Paris, France (Laurent et al., 1993) were at or near 0.05 ppm. Both studies reported a relationship between irritation and formaldehyde exposure. High concentrations of formaldehyde were related to a significant prejudice in mental performance in 627 Swedish secondary school students (Smedje et al., 1996). Sodré et al. (2008) evaluated the main carbonyls at indoor public spaces, including 6 classrooms. Formaldehyde levels ranged from 12.4 to 1034 mg m^{-3}. Levels were above the threshold limit of OSHA in 49 of the 50 analysed samples. Acetaldehyde and acetone were below the limits in all samples. Formaldehyde was one of the most abundant pollutants measured indoors and outdoors of three Turkish schools during spring, autumn and winter (Sofuoglu et al., 2011). Formaldehyde was either the highest concentration compound among those measured in this study or was at comparable levels with toluene and benzene. The mean and median concentrations were all close and ranged from 19 to 55 μg m^{-3}. The most pronounced difference among the three schools in formaldehyde concentrations were observed in fall campaign (the difference between two of the schools was 36 μg m^{-3}), while the gap was not as wide in winter (14 μg m^{-3}) and spring (8 μg m^{-3}). Health outcomes like lung inflammation, nasal, throat, eyes, skin irritations, SBS symptoms and cancer are related to formaldehyde exposure (Franklin et al., 2000; Norback et al., 2000; Pazdrak et al., 1993; Samet et al., 1988; Sundell et al., 1993; Wantke et al., 1996).

Several studies have reported that exposure to bioaerosol (diverse variety of agents from biological sources) in indoor environment is often associated with allergies, asthma, rhinitis, hypersensitivity pneumonitis and SBS symptoms (Beaumont, 1988; Dales et al., 1991; Li and Hsu, 1997; Meyer et al., 2002; Norback et al., 2000; Roponen et al., 2002; Siersted and Gravensen, 1993; Sigsgaard et al., 2002). Reported microbiological contaminants included allergens in deposited dust, fungi, and bacteria. Levels of specific allergens were sufficient to cause symptoms in allergic occupants (Norback et al., 2000; Roponen et al., 2002; Sigsgaard et al., 2002). There is evidence that low ventilation rates, occupant density, and high humidity level can lead to increased airborne microorganisms in classrooms (Brundage et al., 1998; Fisk et al., 2001; Smedje et al., 1996). Many studies report airborne bacteria measurements ranging from 7 to 19500 CFU m^{-3} (Bates and Mahaffy, 1996; Black and Worthan, 1995; Cousins and Collett, 1989; Gallup et al., 1993; Maroni et al., 1993; Meklin et al., 1996; Mouilleseaux et al., 1993; Thorne, 1993).

The studies investigating causal relationships between health symptoms and exposures to specific pollutants suggest that such symptoms in schools are related to bad ventilation and exposures to allergens, VOCs, formaldehyde, moulds and microbial VOCs (Mi et al., 2006; Taskinen et al., 2002).

Little is known about the characterisation of PM found inside the classrooms. The increased PM concentrations in schools could be from the students' physical activity that contributes to a constant process of resuspension of sedimented particles, from their owner class activities, from skin desquamation or clothing, and from outdoor sources (Brunekreef et al., 1997; Diapouli et al., 2008; Ekmekcioglu and Keskin, 2007; Fromme et al., 2007; Janssen et al., 2003; Lee and Chang; 2000; Peacock et al., 2003; Pénard-Morand et al., 2005;. Richmon-Bryant et al., 2009; Van Roosbroeck et al., 2007). Brunekreef et al. (1997) studied 13 schools located 35 – 645 m from a motorway. The PM_{10} levels ranged from 6.73 to 20.8 μg m^{-3} in schools farthest from the road, and from 9.20 to 32.8 μg m^{-3} in schools nearest from the road. Lee and Chang (2000) found PM_{10} concentrations above the acceptable maximum values stipulated by the local legislation at five schools in Hong Kong. Branis et al. (2005) studied the effects of outdoor air and human activities in PM_{10}, $PM_{2.5}$ and PM_1 concentrations in Prague schools. The results confirmed that human activities are an important factor for high indoor particulate levels and that outdoor

concentrations influence the indoor environment. Five elementary schools in Istanbul, Turkey, showed PM_{10} levels varying from 27.9 to 289 μg m^{-3} according to the traffic intensity (Ekmekcioglu and Keskin, 2007). In 64 schools in Munich, Fromme et al. (2007) observed indoor PM concentrations lower in the summer and twice higher during the winter. The high occupants' number associated with the small size of classrooms and poor ventilation contributes to increased concentrations of PM in the winter. Seven primary schools in Athens, Greece, have been reported to present higher indoor PM_{10} (229 μg m^{-3}) than outdoor levels (166 μg m^{-3}) (Diapouli et al., 2008).

Mejía et al. (2011) compiled information about data collection, analysis and health effects of air pollutants in school children. The compilation has demonstrated that indoor normally exceed outdoor levels and that IAQ is affected by the penetration of outdoor pollutants, wall absorption, emissions from furniture and other materials, level and length of occupancy, quality of ventilation, and resuspension by children movement around during their school day. The study also points to the fact that there is strong evidence that low socioeconomic level is highly correlated with the proximity of the school to pollution sources.

An increase in the prevalence of asthma and rhinitis has been documented in the last decades in Europe. For many reasons shown before, school population is a susceptible group, and there are evidences on the potential detrimental role to health of a variety of indoor pollutants that can be found in classroom environments. Recently, many European projects have been carried out to characterise indoor and outdoor environments, possible pollutant sources and relationships between pollutants and health in schools.

Various IAQ problems in schools from European countries, a lack of standardised methodologies, and an absence of studies on consequences to health or on the effect of different local policies regarding school buildings were reported by the European Federation of Allergy and Airways Diseases Patients Associations (EFA, 2002).

Several common IAQ problems in schools were detected by a preliminary study conducted by the HESE ("Health Effects of Schools Environment") project, mainly inadequate ventilation (Ciarleglio et al., 2006a; Norback et al., 2006). This study also encountered a lack of preparation of educators and officials to deal with environmental

issues and health problems of more sensitive students, such as asthmatics and allergy-suffers (Ciarleglio et al., 2006b).

In 2008, the “European Indoor Air Monitoring and Exposure Assessment Project” (AIRMEX) evaluated the exposure to indoor air chemicals and possible health risks, mainly the effect of VOCs (aromatics, carbonyls, and terpenoids) on human health. Many measuring campaigns were performed in public buildings (town halls, guild halls), schools and kindergartens in various cities from Southern and Central Europe. It was concluded that personal exposure concentrations are higher than the indoor (generally twice times) or outdoor (significantly higher) concentrations (Geiss et al., 2011; Kotzias, 2005; Kotzias et al., 2009). In most cases, indoor pollutant concentrations were higher at homes than at public buildings and school/kindergartens, probably because there are stronger indoor sources at dwellings (Geiss et al., 2011; Kotzias et al., 2009). From investigations using microarray-based gene expression profiling (toxicogenomics), it was concluded that toluene, benzene and other single aromatic compounds in indoor air enhance non-carcinogenic responses, such as inflammation (Kotzias et al., 2009). Key findings highlight the need for further research to assess the burden of indoor air pollution at schools and kindergartens in Europe.

The “School Environment and Respiratory Health of Children” (SEARCH) constituted a research project implemented within the international frameworks of the EU Action Plan on Environment and Health; and the World Health Organisation's Children’s Environment and Health Action Plan for Europe. The first phase of the SEARCH project (2006–2009) led to the creation of a comprehensive environment and health database through assessments in selected European countries. Stakeholders and experts requested a follow-up project to continue the valuable research activities. SEARCH II was developed in order to expand the monitoring of children’s health and air quality. This follow-up project included the design of environment and health capacity-building programmes for school staff and training for local implementation strategies. Four new countries, Belarus, Kazakhstan, Tajikistan and Ukraine, have joined the SEARCH I participants Albania, Bosnia and Herzegovina, Hungary, Italy, Serbia and Slovakia. The project contributed to the European legal and policy framework for sustainability in schools, since children’s health and educational potential depend on the quality of the school environment.

Classrooms painted with water-resistant paints presented great levels of benzene, xylenes and ethylbenzene, and the occupants of these classrooms showed more prevalence of allergies. The presence of new furniture was related to high ethylbenzene and xylene concentrations. Classrooms with carpets on the floor showed increased VOC and NO_2 levels, which were related to students woken by wheezing at night. Schools located near heavy traffic and/or industry areas had an adverse effect on children exposure. An elevated number of students in a classroom were associated with higher CO_2 and PM_{10} levels. Insufficient ventilation during the class period was related to increased levels of CO_2 and formaldehyde and a high number of chronic bronchitis and asthma cases (Csobod et al., 2010). Recommendations were made for improving the school environment, buildings and energy consumption based on an analysis of data from the 10 countries.

The "Binnenlucht in Basisscholen" – BiBa project (Dutch acronym for indoor air in primary schools) evaluated IAQ in classrooms of thirty Flemish primary schools. The assessment included classroom inspections, measurements of ventilation rates, relative humidity, temperature, and medical tests for respiratory function in more than 1500 children, and measurement of exposure to chemical pollutants, such as $PM_{2.5}$, PM_x, benzene, toluene, tetrachlorethene, ethylbenzene, xylenes, 1,2,4-triethylbenzene, total VOCs, formaldehyde, acetaldehyde, and total other aldehydes. A very high variability in concentrations among classrooms was observed, BiBa concluded that concentrations of many chemicals were much higher indoors than outdoors. Formaldehyde, benzene, total VOCs, CO_2 and other parameters often exceeded the Flemish indoor environment guidelines (Stranger et al., 2010).

The project "Health Effects of Indoor Pollutants: Integrating Microbial, Toxicological and Epidemiological Approaches" (HITEA) has been studying the relationship between the role of biological agents present in indoor air and long term respiratory, inflammatory and allergic health impacts among children and adults. HITEA focused on many indoor exposures and factors, like allergens, chemicals, cleaning agents, traffic exhaust and poor ventilation, but the main objective focused on microbial exposures due to dampness and moisture problems of buildings. Other important objective of this project was to propose new approaches to characterise indoor biological exposures, by using novel methods to measure airborne exposure and by characterising the house dust for

its in vitro toxicity, inflammatory properties and microbial toxin content. The HITEA has already tested if exposure to endotoxin could be associated with increased respiratory symptoms and injury in lung function in adults. Bakolis et al. (2012) found endotoxin levels varying from 0.1 to 402.6 EU mg^{-1}. However, there was no evidence of cause-effect of endotoxin exposure and lung function problems.

The "Large Analysis and Review of European housing and health Status" (LARES) project evaluated relationship between housing and health focusing indoor air pollution, the effect of cold homes and dampness, noise effects, and domestic accidents. The LARES project achieved a more comprehensive understanding of housing and health in the WHO European region. The WHO/LARES concluded that the main features of housing impacting health were often related to thermal comfort, indoor air quality (dampness, moulds, indoor emissions, infestations, and others), noise, home safety, and social and physical quality of the housing (WHO, 2007). This study corroborates the importance of studying the indoor school environment since it is the second place where children spend more time, after their homes.

The project "Schools Indoor Pollution and Health: Observatory Network in Europe" (SINPHONIE) is currently ongoing with a special focus on schools and childcare centres. Thirty-eight environment and health institutions from 25 countries have been involved in SINPHONIE tasks. This study aims at capitalising on the existing knowledge and information and taking this opportunity to extend the spectrum of information available covering the new and some assessing countries through a standardised procedure in order to be able to produce a set of policies, guidelines and good practices manual that assure the best indoor environment for children in schools within the European Union. In Portugal, six elementary schools and two kindergartens has been studied in Aveiro and Oporto cities.

In Portugal, the "Health and The Air We Breathe" (SaudAR) studied the relation between outdoor and indoor air quality and human health in Viseu city. The study region was characterised in terms of air quality, economical and social development and population health. Two different populations of children with wheezing symptoms were compared, but no differences were found concerning the prevalence of wheezing (Neuparth et al., 2006). The SaudAR project pointed out that state of buildings and

ventilation are one of the major problems in schools. In the frame of SaudAR study, Valente (2010) evaluated IAQ at 4 schools in the city of Viseu, Portugal, during the summer and winter of 2006 and 2007. The PM concentrations ranged according to the season. Values were higher in summer. PM concentrations were higher indoors than outdoors. The low levels observed during weekends suggested that higher PM concentration during week days are related to human activities.

Portugal participated in the International Study of Asthma and Allergies in Childhood Program (ISAAC) in 1993. The ISAAC program was created in 1991 with the aim to assess the prevalence and progression of asthma and allergic diseases, using a standardised written questionnaire, translated and adapted to several languages, including Portuguese (Asher et al., 1995). The survey questionnaire was distributed to students between 13 and 14 years old in five geographic areas (Lisbon, Oporto, Coimbra, Funchal and Portimão). In Lisbon, Funchal and Portimão, 6 and 7 years old children were also questioned (Pinto et al., 2006; Trindade, 1999). This study pointed to significant regional differences in terms of prevalence of respiratory symptoms, recommending further studies to define evolutionary trends and identify risk factors. Khan et al. (2007) applied an adapted version of the ISAAC questionnaire to 995 children in 2006. This survey study was compared with the results, interpretations and correlations obtained in the ISAAC 2002 programme, which questioned 2484 children from 6 to 7 years of age from the basic schools of Lisbon, fromNovember 2002 till March 2003. It was observed a decrease for wheeze and rhinitis and an increase for asthma between the ISAAC studies in 2002 and 2006.

Fraga et al. (2008) evaluated the association between the IAQ in Oporto schools and the prevalence of allergic and respiratory symptoms in adolescents. High CO_2 concentrations were associated with greater respiratory symptoms. Madureira et al. (2009) characterised the IAQ in Oporto schools to evaluate cases of health symptoms reported by teachers and to study the impact of pollutants on the prevalence of these symptoms. CO_2 concentrations exceeded the reference values and the increasing of PM concentrations was associated with the use of chalk.

As far as it is known, an extended characterisation of the IAQ in elementary schools in Lisbon and Aveiro has not been performed before. Besides contributing to

understand regional differences, the evaluation of IAQ in Portuguese institutions is a critically important aspect of creating and maintaining school facilities, helping to resolve or alleviate problems of contaminated air if they do arise, seeking to eliminate potential sources of contamination that originate from outdoors as well as indoors, and taking steps to ensure a safe and healthy working environment for staff and students. It also constitutes an opportunity to develop and apply routine methodologies of evaluating IAQ and making a reflection on the necessity of updating or reviewing the applicable legislation.

1.4 Objectives

The urban inhabitants spend about 90% of their days in indoor environments, such as homes, workplaces, schools, universities, shopping centres and vehicles. Epidemiological studies have shown that a poor IAQ is associated with adverse health effects, including higher rates of chronic disease and mortality due to cardiovascular and respiratory diseases. Studies on IAQ in schools found in scientific literature have demonstrated that school environment usually presents higher levels of pollutants than outdoor environments. It is observed that the health problems caused by indoor environments with low ventilation and high levels of pollutants may reduce the performance of the occupants. However, little is known about the specific composition and characterisation of indoor air in schools.

The main purpose of this study is to evaluate the IAQ in elementary schools of Lisbon and Aveiro. Specific goals were:

- to measure the physical parameters and chemical and biological pollutants of indoor (and related outdoor) air in schools;

- screening of conditions that could be the cause for poor IAQ in schools, identifying potential outdoor/indoor pollutant sources and evaluating the influence of different classroom/building materials and school habits on the air quality indoors;

- to get the actual state for asthma/rhinitis in primary school population in Lisbon;

- to propose possible mitigation measures;

- to test the use of houseplants as a mitigation measure in a school indoor environment.

1.5 Description of locations covered in the study

Lisbon is located at the mouth of the Tagus river (38º42'49.75"N, 9º8'21.79"W) and is the westernmost capital of Europe. It is the largest city of Portugal with a population of 547,631 within its administrative limits on a land area of 84.8 km^2. However, the Lisbon metropolitan area extends on an area of 958 km^2 with about 3 million people. The climate is characterised by mild winters and warm to hot summers. The average annual temperature is 21ºC during the day and 13ºC at night. In January, the coldest month, the maximum temperature typically ranges from 10 to 18ºC during the day, while the minimum values range from 4 to 12ºC at night. In August, the warmest month, the maximum temperature ranges from 27 to 33ºC during the day, while the minimum temperature ranges from 18 to 22ºC at night.

The elementary schools involved in this study are located at different civil parishes: Santa Maria de Belém (I), Ajuda (J), Alcântara (H), Santo Condestável (M), São José (C), Benfica (G), Campolide (L), São João de Brito (B), Alvalade (N), Marvila (F) e Santa Maria dos Olivais (A, D and E) (**Figure 1.2**).

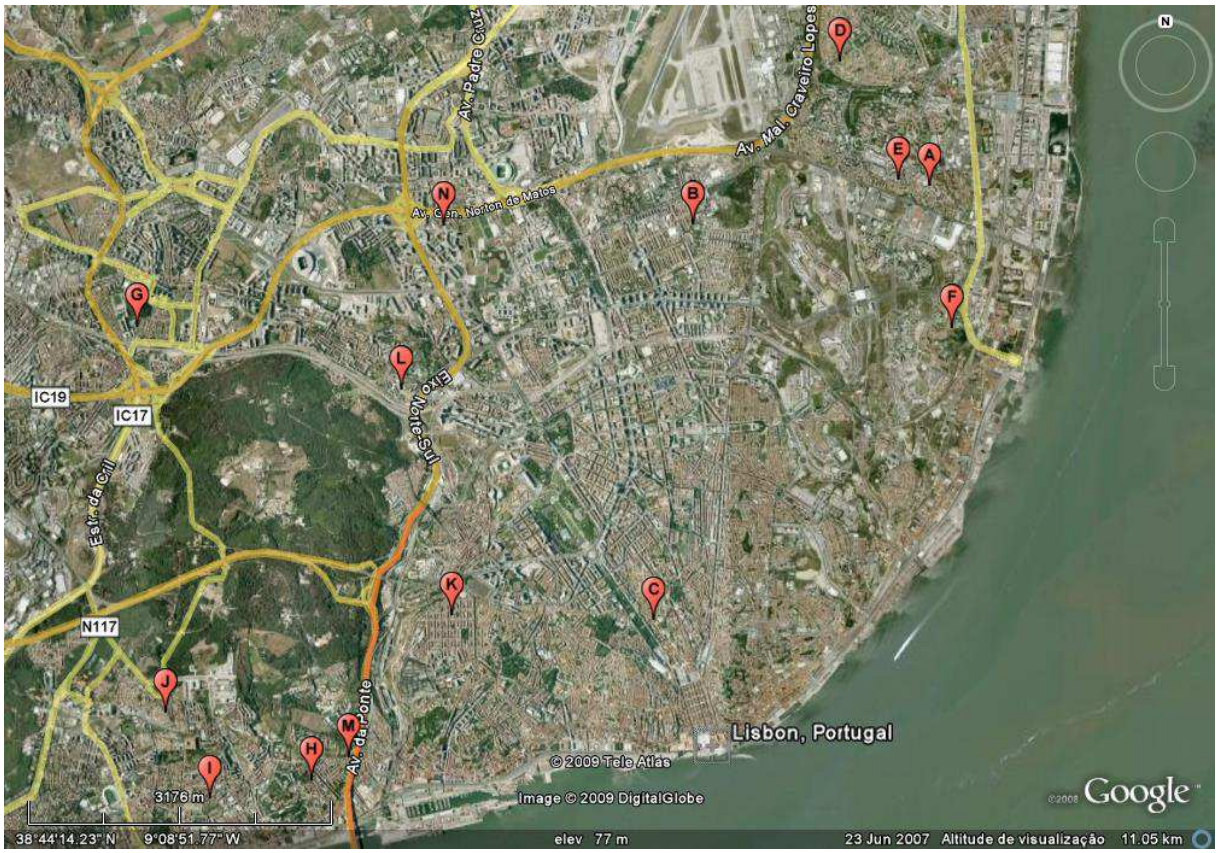

Figure 1.2. Location of schools involved in the study in the city of Lisbon.

Aveiro is located at 40º43'23"N, 8º31'44"W, in the central coastal region of Portugal. The city extends on an area of 199.9 km^2 with a population of 78,450. The average annual temperature is about 18ºC during the day and 11ºC at night. In January, the coldest month, the mean maximum temperature is 13.4ºC during the day, and the mean minimum temperature is 6.4ºC at night. In August, the warmest month, the mean maximum temperature is 21.9ºC during the day, whereas the mean minimum temperature is 15ºC at night.

The two elementary schools of this study are located at different civil parishes: Glória (A) and Vera Cruz (B) (**Figure 1.3**).

Figure 1.3. Location of the two involved in the study in the city of Aveiro.

1.6 General overview of the work performed

Parents of the students from the Lisbon schools were invited to answer a questionnaire similar to that of the International Study of Asthma and Allergies in Childhood Program (ISAAC) between October and December 2008 (Chapter 2). The survey aimed at identifying children with respiratory problems (wheezing, asthma and rhinitis), and assessing the nutrition habits, environmental aspects and housing conditions.

Indoor and outdoor air samples were collected at three schools in Lisbon in December 2008. These schools were located in the city centre and were previously considered representative of all the elementary-level educational institutions for the preliminary study (Chapter 3). VOCs, formaldehyde and NO_2 were passively monitored over a two-week period. Bacterial and fungal colony-forming units and comfort parameters were also monitored at classrooms and playgrounds. This campaign was important to define methodologies that were subsequently used at all 14 schools in Lisbon.

Chapters 4 and 5 evaluated the indoor and outdoor levels of NO_2, speciated VOCs and carbonyls at fourteen primary schools in Lisbon during spring, autumn and winter. Three of these schools were also selected to be monitored for comfort parameters, such as temperature and relative humidity, CO_2, CO, total VOCs, and both bacterial and fungal colony-forming units per cubic metre. The three monitoring campaigns enabled carrying out a seasonal evaluation of outdoor and indoor air quality at Lisbon schools.

Chapter 6 investigated pollutant concentrations inside and outside school buildings at different locations (city centre and suburban) in Aveiro, between April and June 2010. The aim was to evaluate simultaneously comfort parameters (temperature, CO_2 and CO) and indoor and outdoor concentrations of VOCs, NO_2, PM_{10} and bioaerosol. PM_{10} samples were analysed and characterised, for the first time, for the water soluble inorganic ions (WSII), organic carbon (OC), elemental carbon (EC), carbonates, and detailed organic speciation.

To evaluate the efficacy of a possible mitigation measure, Chapter 7 presents the effect of using common houseplants on the indoor air quality in a classroom of a school in Aveiro. Based on previous test-chamber studies carried out in the USA, the three species chosen were *Dracaena deremensis "Janet Craig"* (Janet Craig), *Dracaena marginata* (Marginata) and *Spathiphyllum "Mauna Loa"* (Peace lily). Indoor and outdoor concentrations of VOCs, carbonyls, and PM_{10} (inorganic ions, OC and EC) were measured in the absence and presence of plants and the IAQ between both periods was compared.

1.7 Details of experimental work carried out

1.7.1 Comfort parameters

Continuous measurements of temperature, relative humidity (RH), CO_2 and total VOCs were performed with an automatic portable Indoor Air IQ-610 Quality Probe (GrayWolf® monitor) at schools (**Figure 1.4**).

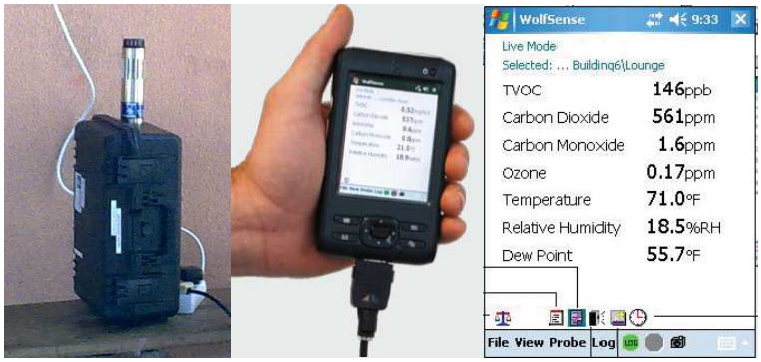

Figure 1.4. Indoor air quality monitor IQ-610 - GrayWolf®.

This IAQ monitor includes a Pt100 probe for measuring temperature in a range from 5º to 160ºF (-15ºC to +70ºC) with accuracy of ± 0.3ºC; and a capacitance probe to sense RH in a range from 0 to 100% with accuracy of ± 2% RH for values under 80% (± 3% RH for values above 80% RH). The monitor also includes a CO_2 non-dispersive infrared sensor (NDIR) in a range from 0 to 10,000 ppm with accuracy of ± 3% rdg ± 50 ppm, and an electrochemical sensor to measure CO in a range from 0 to 500 ppm with accuracy of ± 2 ppm under 50 ppm, and ± 3% rdg above 50 ppm. To track total VOCs over time, the monitor encompasses a photo-ionisation detector (PID) operating in the 5-20,000 ppb range with resolution of 1 ppb and a limit of detection under 5 ppb. It is possible to select TVOCs units among ppb, ppm, µg m^{-3} and mg m^{-3}. The PID sensor does not respond to VOCs with ionisation potentials above 10.6, such as ethane, methane or formaldehyde. However, it responds to the vast majority of VOCs. All sensors exhibit an extremely fast response; most reading are registered in less than 1 minute. It displays measurements in real time allowing logged data to be downloaded to the WolfSense® PC software for analysis. The operating range is 0 to 90% RH at -15 to 60ºC for VOCs, and 0 to 98% RH at -15 to 70ºC for other sensors. The equipment was supplied with a factory calibration certificate, but it is checked prior to next use with appropriate calibration kits (**Figure 1.5**). For the calibration of VOCs, it is recommended to use isobutylene in a known concentration. To make the zero point for VOCs, CO_2 and CO, it is recommended to use nitrogen gas. For correction of the CO calibration straight line, a certified cylinder containing this gas at a concentration of 330 ppm was used. For the correction of the CO_2

calibration, CO_2 gas at 350 ppm for the lower point and 1,000 ppm for the higher point was employed.

Figure 1.5. Gas calibration hood and certified cylinders used with the air quality monitor.

1.7.2 Microorganisms

Taking into account that the National System for Energy and Indoor Air Quality Certification of Buildings (DL 79/2006, RSECE) restricts the bioaerosol measurements to bacterial and fungal colony-forming units per cubic metre of air (CFU m^{-3}), only viable and culturable fungi and bacteria were quantified. Viable microorganism levels were monitored by liquid impinger sampling (May and Harper, 1957) in the classrooms and playgrounds. The liquid impinger was first described by Greenburg and Smith (1922) as a dust cloud sampler. More recently, the device has come into wide use for bioaerosol sampling, as it is often very convenient for this purpose both in laboratory and in the field. The positive aspects that were decisive in choosing the method were: it is compact and inexpensive; the sample fluid can be plated out simultaneously on different culture medium, thus ensuring optimum growth conditions for organisms of interest; an extreme range of airborne concentrations can be accommodated by the serial dilution technique; the particle retention efficiency is very high (all particles down to about 0.5 µm are effectively trapped in the impinger fluid); it gives a measure of the number of individual viable

organisms (colony-forming units), it acts as its own constant flow metering device; and, it is unaffected by the repeated autoclaving of the material.

The apparatus used for the liquid impinger sampling is shown in **Figure 1.6**. The sampling train was composed of an impinger flask, a vacuum pump, a calibrated flow meter and a flow control valve. May and Harper (1957) concluded that sonic velocity impingement has a lethal effect on the more sensitive types of bacterial cells. The recommended optimum impingement velocity is of roughly 3.0 - 2.5 l min^{-1}. Sampling took one hour at each sampling place, totalising samples of 180 l and 150 l of air.

Figure 1.6. Liquid impinger sampling in classroom and at playground.

To capture bioaerosols, 0.1% peptone water was used. This solution is used for the capture and/or the cultivation of microorganisms. It is a minimal growth medium, containing peptone as a source of carbon, nitrogen, vitamins and minerals. Sodium chloride maintains the osmotic balance. The peptone water solid formula was dissolved in the needed amount of purified water, mixed thoroughly, separated at doses of 60 ml for each sample in Schott bottles, and autoclaved at 121ºC for 15 minutes.

A non-selective and a selective culture media were used for microorganisms' growth. Tryptic soy agar (TSA) is a general purpose culture medium for cultivation and isolation of microorganisms or for maintenance of stock culture. The TSA composition is casein peptone (pancreatic), soya peptone (papainic), sodium chloride and agar. To prepare

this medium, 40 g of dehydrated media were suspended in 1 l of purified water. The medium was sterilised at 121ºC for 15 minutes, cooled to 45-50ºC, mixed gently and dispensed into sterile Petri dishes. Chloramphenicol rose bengal agar (CRBA) is used for the selective isolation and enumeration of yeasts and moulds. CRBA is composed of mycological peptone, dextrose, monopotassium phosphate, magnesium sulphate, rose bengal, chloramphenicol, and agar. To prepare this medium, 32.15 g were suspended in 1 l of purified water, boiled to dissolve the medium completely, and sterilised by autoclaving at 121°C for 15 minutes. It was mixed thoroughly and dispensed into sterile Petri plates. The peptone water bottles and the TSA and CRBA Petri dishes were storage at 4-8ºC after the preparation.

After sampling, over a flame to avoid contamination, the amount of 60 ml of peptone water was immediately filtered (**Figure 1.6**) or storage under refrigeration. The amount of 60 ml was used to have enough sampled solution for all the replicates and pipette washing. Five replicates of 10 ml of solution were filtered under vacuum through a membrane filter with porosity of 0.45 μm (Millipore), which retained bacteria cells and fungal spores. The membrane was placed on a selective culture medium (TSA for bacterial and CRBA for fungal) contained in a Petri dish (**Figure 1.6**). Before each filtration, the solution was agitated for homogenisation of peptone water with microorganisms. After filtration, the Petri dishes were incubated for 5 and 7 days for bacterial and fungal, respectively, in dark boxes with constant ambient temperature (25^{o}C) (**Figure 1.7**). The Petri dishes were observed and the colonies formed on the membrane were counted every day.

Figure 1.7. Filtration of peptone water through a Millipore membrane and microorganism's growth in Petri dishes during the incubation period.

1.7.3 NO_2

For sampling and quantification of NO_2, passive samplers based on absorption of ion nitrite by triethanolamine (TEA) were used. These devices are small, lightweight, reusable, relatively cheap and efficient since they are not noisy and do not need a power source. Their operation is based on the principle of molecular diffusion. The pollutant is diffused from the zone with higher concentration (open end) to the absorbent that is placed at the opposite side of the tube. The samplers were exposed in the classroom and at playgrounds during an extended period (2 weeks) to provide the average concentration of the pollutant. A drawback of passive samplers is the impossibility of providing information on maximum levels. So passive sampling is less suitable for compliance checking.

The NO_2 passive samplers consist of a cylindrical acrylic tube of 7.1 cm in length and 1.1 cm internal diameter, with two polyethylene lids that fit perfectly in each end. Two wire meshes are placed in one lid to hold up the absorption solution (TEA). The tubes are placed on polyvinyl chloride (PVC) supports in vertical position to avoid ingress of rain, with the impregnated cap at the top and without cap at the opposite end. Together with 3 replicate tubes, a blank (double side capped) was collected at each sampling point. The concentration of NO_2 was calculated based on the average value of the three tubes exposed, subtracting the blank value (Bhugwant and Hoareau, 2003).

The preparation of the tubes involved the placement of two stainless steel mesh juxtaposed in one of the lids of each tube to which 30 µl of triethanolamine in acetone

(1:1) solution were directly added (Gair et al., 1991; Heal et al., 1999). For the identification, the lid with impregnated mesh was marked abroad.

The analytical procedure followed that described in Methods for the Determination of Indoor Pollutants (Winberry et al., 1993) with some modifications adopted in most British laboratories (Atkins and Lee, 1995). For calibration, a set of seven standard solutions were prepared with different concentrations (0 to 0.00035 mg ml^{-1}) from a sodium nitrite stock solution (1,725 g l^{-1}).

After the exposure, the samples were stored in a refrigerator and analysed within 24 to 48 hours. For each sample, the lid without mesh was removed and 5 ml of a combined reagent were added into the tube. This reagent is composed of 20 parts of 1% sulphanilamide solution in 2.5% phosphoric acid and one part of 0.14% N-1-naphtilene diamine (NEDA) solution. The tube was closed and agitated. After 20-30 minutes, the absorbance of the solutions was read in a spectrophotometer at 540 nm in a 1 cm cell.

Figure 1.8 depicts at a glance the steps from sampling to analysis.

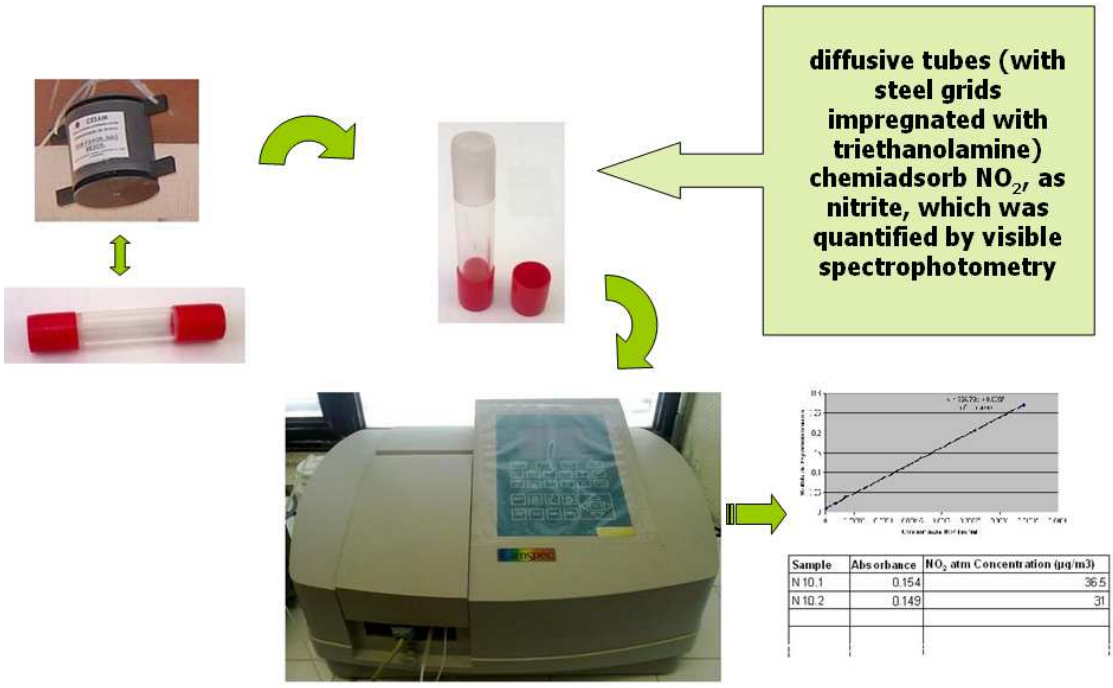

Figure 1.8. PVC holders, NO_2 diffusive tubes, spectrophotometer, and an example of calibration line to calculate the concentrations in each sample.

1.7.4 VOCs

Passive samplers for VOCs from Radiello® were used to obtain a screening of heavy and light molecular weight compounds. Indoor passive samples were collected at a height of about 1.5 m above the floor. They were positioned at a distance that should exceed 1 m from a window or a door. Outdoor passive samples were collected at heights of about 2 m above the ground.

One of the techniques recommended for analysis of these VOCs samples is gas chromatography coupled to flame ionisation detector (GC-FID). The GC is an instrument able to separate chemicals compounds in a complex mixture sample. It uses a capillary column through which different chemical constituents of a sample pass in a gas stream,

called carrier gas (mobile phase) at different velocities depending on their chemical and physical properties and their interaction with the column coating (stationary phase). The stationary phase separates the components, causing each one a different retention time. Beyond the stationary phase, other components are determinant in the retention time, such as the carrier gas flow rate, type of carrier gas, column length, diameter and coating material, and temperature ramp in the oven. When the chemical compounds exit at the end of the column, they are detected by FID (Branco, 2005). A schematic representation of a GC-FID is shown in the **Figure 1.9**.

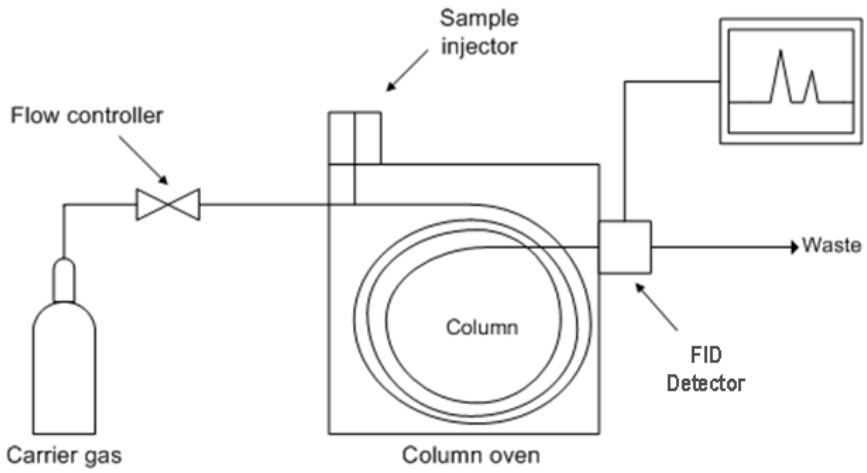

Figure 1.9. Schematic representation of a GC-FID.

FID is a non-selective detector used in conjunction with a GC. It works by directing the gas phase output from the column into the hydrogen flame. The high temperature is needed to make sure that as soon as the carrier gas (eluent) exits the column, it does not come out of the gaseous phase and deposit on the interface between the column and the FID. This deposition would result in loss of eluent and errors in detection. As the eluent travels up the FID, it is mixed with the hydrogen fuel and then with the oxidant. The

eluent, fuel and oxidant mixture continues to travel up to the nozzle head where a positive bias voltage exists. A voltage is applied between the flame and an electrode located away from the flame. This positive bias helps to repel the reduced carbon ions created by the flame pyrolysing the eluent. The ions are repelled up toward the collector plates that are connected to a very sensitive ammeter, which detects the ions hitting the plates, then feeds that signal to an amplifier, integrator and display system. Although the signal current is very small, the noise level is also very small. Except for a very few organic compounds (e.g. carbon monoxide) the FID detects all carbon containing compounds (Scott, 2003). A schematic representation of a FID is depicted in **Figure 1.10**.

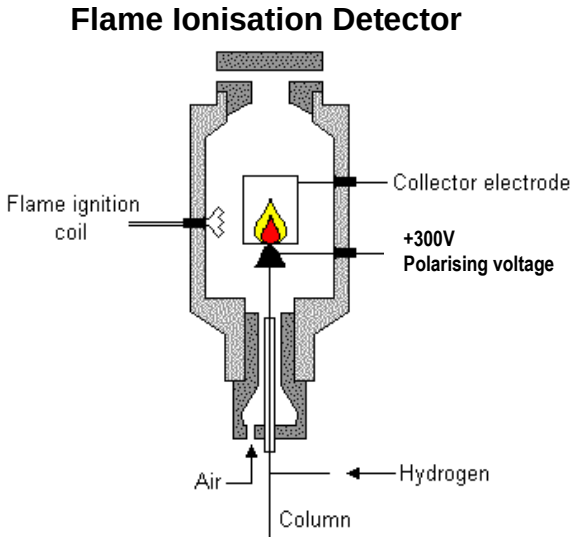

Figure 1.10. Schematic representation of a FID.

VOCs adsorved in activated charcoal Radiello® cartridges (RAD 130, Sigma-Aldrich) were recovered by 2 ml of carbon disulfide (CS_2 from Aldrich) with the internal standard 2-fluorotoluene with 7.2 ng μl^{-1} (Sigma-Aldrich)**,** during 30 min. Depending on the sampling campaign, analyses were performed by gas chromatography in a Chrompack CP 9001 or a Thermo Scientific Trace GC Ultra, coupled to flame ionisation detectors (GC-FID), using nitrogen or helium as carrier gas at constant pressure of 20 psi. Injections

of 4 µl of each standard solution or sample were made, with a split ratio of 25:1. A 100% dimethylpolysiloxane column (0.2 mm, 50 m, film thickness 0.5 µm) was used under the following temperature programme: 50°C for 5 min, 5°C min^{-1} up to 80°C, 15°C min^{-1} up to 135°C, 20°C min^{-1} up to 220°C, final isotherm for 20 min. The injector and detector temperatures were 240 and 300°C, respectively. The equipments were calibrated before and during the analyses of samples by injecting standard solutions of all compounds identified in CS_2, specifically: butanol, ethanol, acetone, pentane, *n*-hexane, cyclohexane, *n*-heptane, *n*-butyl acetate, styrene, eucalyptol, nonane, α-pinene, sabinene, β-pinene, *n*-decane, (+)-3-carene, limonene (all from Fluka), methyl acetate, ethyl acetate, isooctane, *m*,*p*-xylene, *o*-xylene (all from Merck), benzene (AnalytiCals), toluene (Lab-Scan), ethylbenzene, methyl cyclohexane, *n*-undecane, naphthalene, tridecane, 4-metil-2-pentanone, 2-etoxietanol, *n*-heptane, propyl acetate, isopropanol, γ-terpinene (all from Aldrich), and dichloromethane (Fischer Scientific). Standard solutions containing these compounds in CS_2 and internal standard have been prepared. The analytes in these standard solutions were present in concentrations of 40, 20, 10 and 5 ng μl^{-1}. From the calibration, it was possible to obtain the relative response factor (RRF) for each compound or chemical group. The RRF is calculated through the following equation:

$$RRF = \frac{m_{IS} \times A_c}{m_c \times A_{IS}} \qquad (1.1)$$

where m_{IS} is the injected mass of internal standard (ng), A_c is the area in the chromatogram of the compound injected, m_c is the injected mass of the compound, and A_{IS} is the area of internal standard. After calculation of RRF values, by inverting equation (1.1), it is possible to determine the amounts of analytes in the samples (m_C).

All the chromatograms were analysed and integrated by Xcalibur Software for Thermo Scientific.

Average concentration (in µg m^{-3}) over the whole exposure time is calculated according to the following expression:

$$C = \frac{m}{Q \times t} \times 1000000 \qquad (1.2)$$

where C is the concentration of a specific VOC in the air (μg m^{-3}), m is the mass of analyte in μg, Q is the sampling rate at the temperature K, and t is the exposure time in minutes. Sampling rates were calculated as follows:

$$Q_K = Q_{298}\left(\frac{K}{298}\right)^{1.5} \qquad (1.3)$$

where Q_K is the sampling rate at the temperature K and Q_{298} is the reference value at 298 K. This produces a variation of ±5% for 10 °C variation (upwards or downwards) from 25 °C. The sampling rate is invariant with humidity in the range 15-90% and with wind speed between 0.1 and 10 m s^{-1}. The average concentration over the exposure time interval is therefore calculated from the mass of analyte found onto the cartridge and exposure time without introducing any corrective factor, apart from corrections due to average temperatures different from 25 °C.

Figure 1.11 illustrates the procedure, from sampling to analysis, for the determination of VOCs.

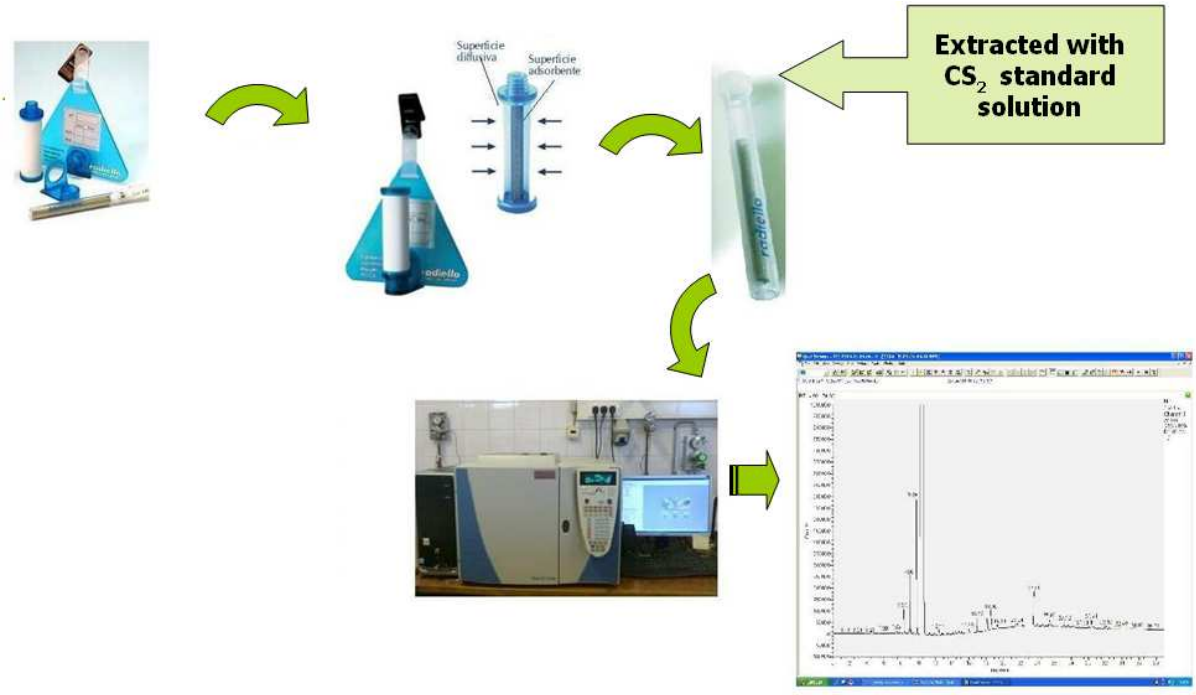

Figure 1.11. Cartridge RAD130 with the white diffusive tube and triangular support for sampling, cartridge after sampling in the glass tube for extraction, GC-FID, and example of chromatogram.

1.7.5 Carbonyls

Carbonyls collected in Radiello® cartridges filled with 2,4-dinitrophenylhydrazine (RAD165, Sigma-Aldrich) react and are converted into the corresponding 2,4-dinitrophenylhydrazones. These were extracted with 2 ml of acetonitrile (from Fisher Scientific). The glass vials were shaken for approximately 30 minutes and the extract filtered through 0.45 μm disc membrane filters (filtration kit RAD 174) and injected into the high-performance liquid chromatography (HPLC) system. The analytical system consisted of a Jasco PU- 980 pump, a Rheodyne manual injection valve (sample loop of 20 μl), a Supelcosil LC-18 column (250×4.6 mm; 5 μm; Supelco) and a Jasco MD-1510 diode array detector, all connected in series. Isocratic elution at room temperature was performed using an acetonitrile/ultrapure water solution (60/40, v/v) as the mobile phase at a flow rate

of 1.5 ml min^{-1}. Ultrapure water (Milli-Q system, Millipore) was used for the preparation of eluent for HPLC. The carbonyl concentrations were quantified with external calibrations curves. A standard solution containing 15 DNPH derivatives (TO11/IP6A carbonyl – DNPH Mix from Supelco) was used for the identification and quantification of the carbonyl compounds in the samples. The compounds present in the original calibration mix were: formaldehyde, acetaldehyde, acetone, acrolein, propionaldehyde, crotonaldehyde, butiraldehyde, benzaldehyde, isovaleraldehyde, valeraldehyde, *o*-tolualdehyde, *m*-tolualdehyde, *p*-tolualdehyde, hexaldehyde, and 2,5-dimethylbenzaldehyde, all of them in a concentration of 15 µg ml^{-1}. The original standard was diluted in acetonitrile to obtain solutions with 3.0, 1.0, 0.5, 0.25, and 0.0 µg ml^{-1}. The calibration line constructed from the standard solutions was confirmed every day before the analysis (U.S. EPA, 1999). The limit of detection (LOD) ranged from 1.29 to 2.09 µg ml^{-1}.

The average concentration of carbonyls in passive samples over the whole sampling period is derived from the following equation:

$$C = \frac{m}{Q \times t} \times 1000000 \qquad (1.4)$$

where C is the concentration of carbonyl compound in the air (µg m^{-3}), m is the mass of aldehydes or ketones (µg), Q is the sampling rate at the temperature K, and t is the exposure time in minutes. The sampling rate varies with the effect of the temperature and can be calculated by the following equation:

$$Q_K = Q_{298}\left(\frac{K}{298}\right)^{0.35} \qquad (1.5)$$

where Q_K is the sampling rate at the temperature K and Q_{298} is the reference value at 298 K. As mentioned for VOCs, there is not variation in the sampling rate with humidity in the range 15-90% and with wind speed between 0.1 and 10 m s^{-1}.

Figure 1.12 illustrates the steps for the determination of carbonyl compounds.

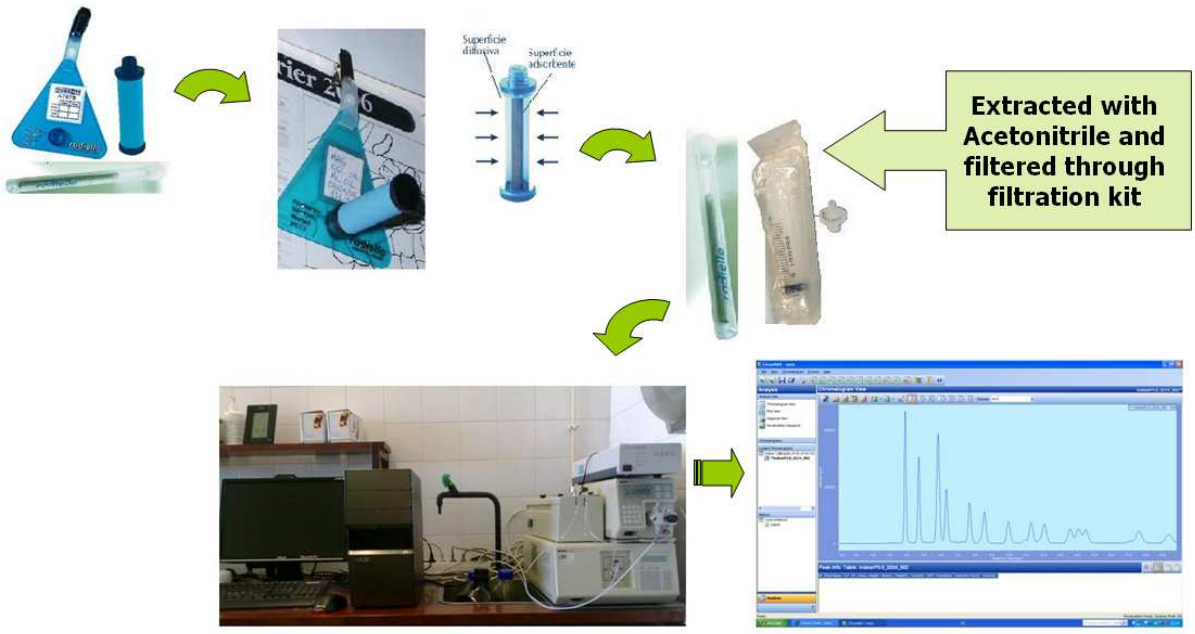

Figure 1.12. Cartridge RAD165 with the blue diffusive tube and triangular support for sampling, cartridge after sampling in the glass tube for extraction, filtration kit RAD174 to filter the extracts, HPLC, and example of chromatogram.

Active sampling of carbonyls was carried out by pulling air through Sep-Pak® DNPH-silica cartridges. The sampling train consisted of a Thomas pump to draw in air at a flow rate of 2 l min^{-1} for a sampling time of one or two hours in agreement with the classroom cycles, through the silica gel cartridges impregnated with 2,4-dinitrophenylhydrazine reagent, a dry gas meter to register the volume of air and ozone scrubbers to minimise ozone interferences. The analytes were extracted with 5 ml of acetonitrile using sonication extraction. The extracts were filtrated through gravity feed elution with the filtration kit RAD174, collected in 3 ml vials, and afterwards analysed in the same HPLC system as passive samples (ASTM, 1997). The calibration was made with the same standard solutions as previously described. **Figure 1.13** shows some details of the carbonyl active sampling and analysis.

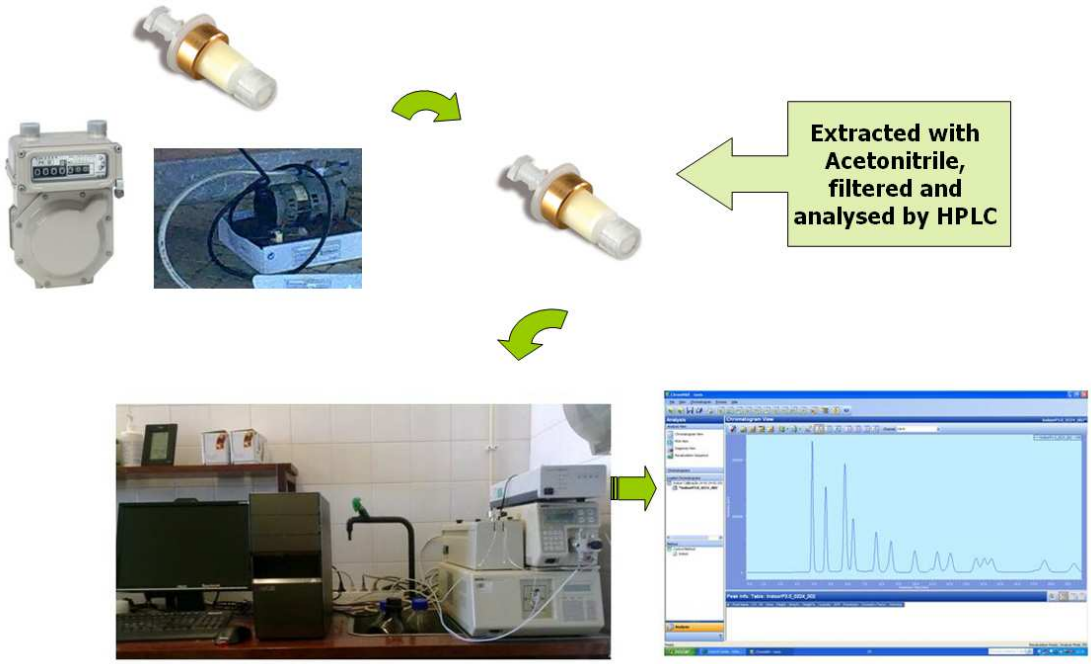

Figure 1.13. Sampling components (cartridge Sep-Pak®, Thomas pump and dry gas meter), cartridge after sampling for extraction of carbonyls with acetonitrile, HPLC, and example of chromatogram.

1.7.6 Particulate matter

Quartz fibre filters with a 47 mm diameter have been used as particle collection substrates. All filters used in this work were wrapped in aluminium foil and pre-baked at 550ºC for 6 hours to eliminate organic contaminants. The filters were placed in a desiccator overnight. Before and after sampling the gravimetric determination was performed with a microbalance Mettler Toledo AG245 (readability- 0.1 mg/0.01 mg) (**Figure. 1.14**). The filter weights were obtained from the average of about 5-6 weights with similar values. Typically it was necessary to weigh each filter approximately 10 times to have 5-6 equal measures. The gravimetric determinations were done at 45-50% relative humidity.

Figure 1.14. Filter loaded with PM_{10} being weighted in the microbalance**.**

To carry out the PM_{10} collection two pairs of samplers were simultaneously used one in the classroom and other at the playground (**Figures 1.15** and **1.16**). One of the sampling systems was a Tecora with PM_{10} European inlet. The flow was controlled automatically and set at 38 l min^{-1}, in accordance with the EN 12341 standard. The other sampling systems were composed of Gent heads with 10 μm cut-off containing a filter holder, a dry gas meter, and a vacuum pump. These assemblies were operated at a flow rate of about 12 l min^{-1}.

Outdoors, sampling was performed at a height of about 3 m. The Gent inlet was protected against bad weather conditions by covering with an inverted bucket.

Figure 1.15. Indoor PM_{10} sampling.

Figure 1.16. Outdoor PM_{10} sampling.

To perform the calibration of the PM_{10} Gent samplers, the sampling pump, the dry gas meter and a calibrated mass flow meter were connected in series. The volume registered over a period of time by the dry gas meter was compared with the value obtained by the mass flow meter, and a conversion factor was calculated.

Since two different sampling systems (Gent and Tecora) have been used, it was necessary to determine if the samplers led to comparable concentrations of PM_{10}. From parallel samplings, it was concluded that measurements by both systems correlate well (**Figure. 1.17**).

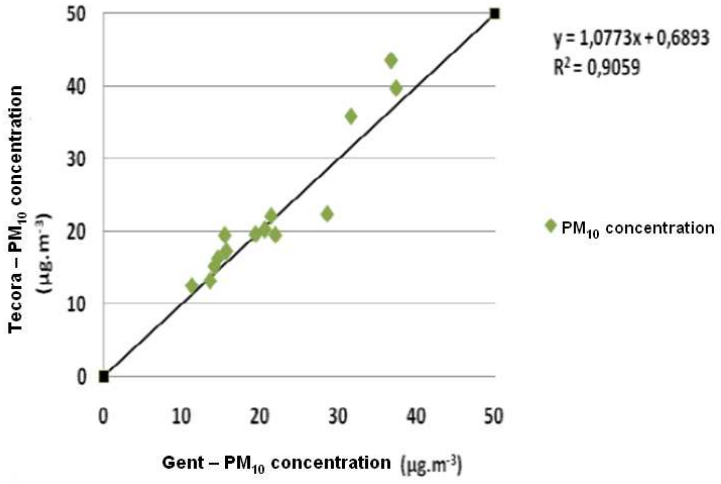

Figure 1.17. Relationship between PM_{10} concentrations determined by Gent and Tecora samplers.

1.7.7 Carbonaceous content of PM_{10}

The carbonaceous material (organic carbon, elemental carbon and carbonate) of PM_{10} was analysed by a home-made thermal-optical transmission system. The principle of operation is related to the volatilisation and oxidation of all the carbonaceous material to CO_2 (Pio et al., 1994). The temperature programme allows the separation of two different organic carbon fractions.

The samples were previously acidified to minimise interference of carbonates in the quantification of EC and OC. Punches of the filters were exposed to vapours of hydrochloric acid (HCl – 6 M) for approximately 4 hours. After this period, the samples were transferred to a desiccator containing hydroxide sodium (NaOH), where they were kept overnight. The purpose of this process is to neutralise any excess of acid in the sample to protect de CO_2 analyser from corrosive HCl fumes.

The thermo-optical system comprises a quartz oven with two distinct heating zones with a thermocouple each one to monitor the evolution of the temperature. It also contains a helium-neon laser (632.8 nm) and a detector connected to a transducer. Associated with the laser, there is a chopper whose function is to eliminate interferences that may occur due to the existence of other light sources. To detect the amount of carbon in various stages of heating, the system has a calibrated infrared non-dispersive CO_2 analyser. The temperature programme is imposed by a controller. To control the flow of gases (N_2 and O_2) passing through the analysis system, a mass flow meter is used. A computer terminal makes the data acquisition every second, recording various parameters, such as temperature, flow rate, and CO_2 concentrations. **Figure 1.18** depicts a schematic representation of the thermo-optical system.

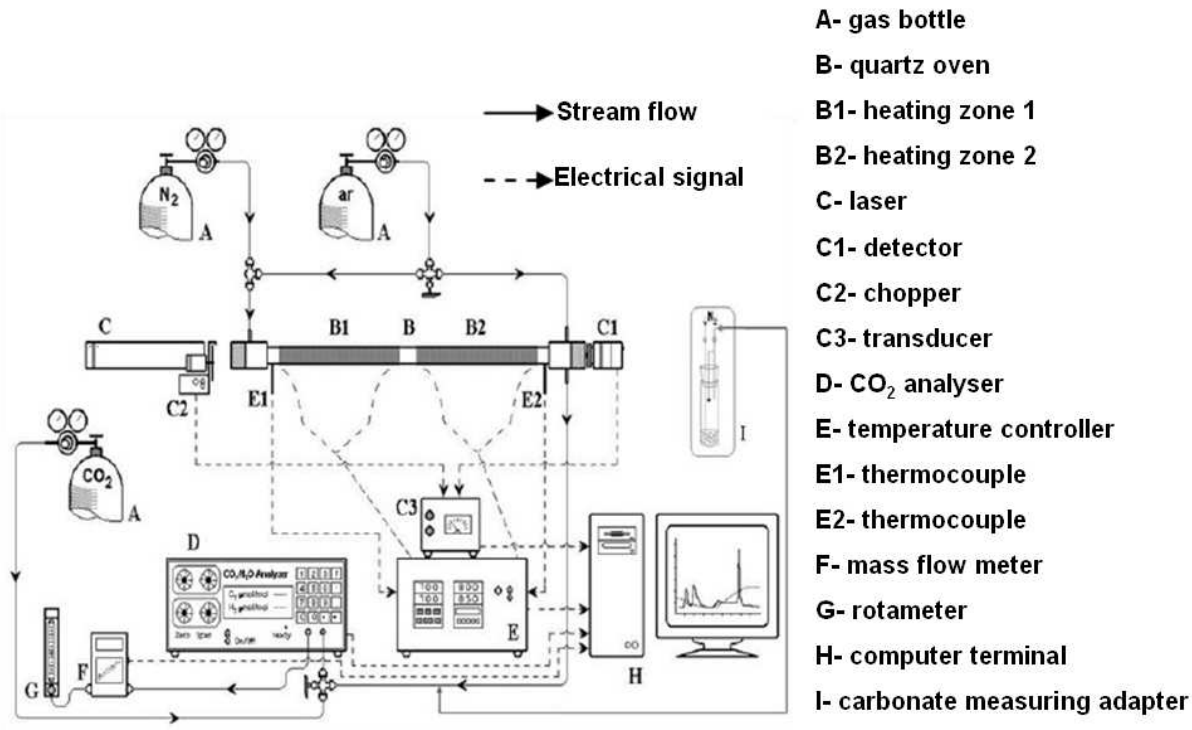

Figure 1.18. Scheme of the thermo-optical analyser to determine OC, EC and carbonate (Cerqueira et al., 2004).

For each filter, two 9 mm diameter punches were used in each analytical run. To start the analysis, a purge to remove all traces of CO_2 is carried out until zero is read by the analyser. The data acquisition can be started as soon as the purge is completed. Due to the existence of two distinct zones of heating, the analysis is done in two stages. In the first phase, the sample is subjected to an anoxic environment where there is only nitrogen. Controlled heating in anoxic conditions is performed to separate OC into two fractions of increasing volatility. The first fraction corresponds to the volatilisation at T<200°C of lower molecular weight organics (OC1). The second fraction is related to the decomposition and oxidation of higher molecular weight species at temperatures ranging from 150 to 600°C (OC2). The last fraction of OC is identified by transmittance and corresponds to pyrolysed organic carbon (PC) produced in the previous heating steps (Alves et al., 2011).

The second stage starts by opening a valve that introduces air into the oven. Oxygen will join the existing stream of nitrogen and will transform the atmosphere of the

first heating zone in a oxidising atmosphere. This factor, coupled with a further increase in temperature, promotes oxidation and volatilisation of EC. The remaining fraction is sequentially evaporated/burnt under a gas flow containing O_2. This last carbon fraction contains initial EC plus OC that has pyrolysed during heating under an inert atmosphere. The interference between PC and EC can be controlled by continuous evaluation of the blackening of the filter using a laser beam and a photodetector measuring the filter light transmittance. At the point where the laser reaches the value of signal value is equal to the initial point of separation of EC and pyrolitic carbon (Castro, 1997). It is considered that whole pyrolitic carbon is the carbon mass recorded since it introduces oxygen into the system until the value of the transmittance of the laser to reach its initial value. From this point, it is considered the carbonaceous mass being present as EC. The second heating zone has a constant temperature of 650ºC and the atmosphere inside comprises air and nitrogen. The walls of this area are coated with a catalyst (CuO), which certifies the conversion of any carbonaceous material to CO_2 and can thus be ensured that there was complete oxidation of carbon volatilised in the previous zone. This procedure was originally developed by Pio et al. (1994) and Carvalho et al. (2006) and was adapted by Alves et al. (2011).

Since it was analysed only a portion of the filter, it is needed to estimate the mass of carbon in the whole filter area.

To determine the carbonate (CO_3^{2-}) concentration in indoor and outdoor PM_{10} samples, the same CO_2 analyser of the thermal-optical system was used. The carbonate measurement setup comprises basically four components: a mass flow meter, a reaction cell, the CO_2 analyser, and a computer terminal for data acquisition. A portion of each filter with diameter 9 mm was punched. This fraction was subsequently dipped in an acid medium to covert the carbon carbonate to CO_2, which is then detected by the infra-red analyser. The acidifying agent used was phosphoric acid (H_3PO_4) 20%, which, as a solution wispy volatile, represents less danger for the entire system. The setup used for analysis of the carbonate is shown in **Figure 1.19**.

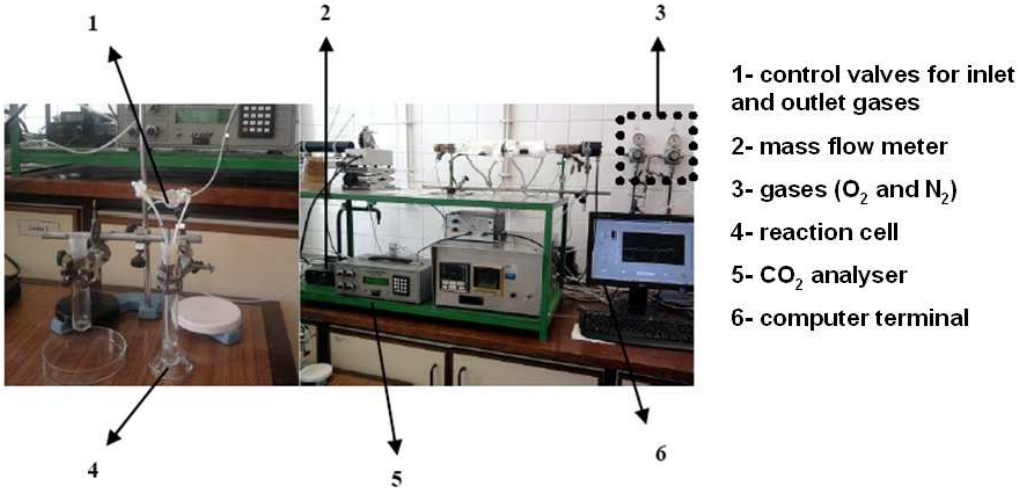

Figure 1.19. Carbonate system analyser.

The method includes placing of approximately 15 ml of acid in a clean flask. The flask is sealed with a stopper, which has a sample holder. The stopper is pierced by two tubes, one of them allowing the nitrogen inlet (carrier gas) and the other one providing the output to the gas analyser. These tubes are controlled by two valves, which promote the transfer between the cell reaction and a short circuit, avoiding cell reaction. Once the filter is placed on the holder, a purge to eliminate CO_2 inside the impinge flask is done (long circuit). The purge is maintained until the moment when the CO_2 analyser registers a concentration of zero. Then, carrier gas is passed through the short circuit and the filter is dropped in the acid solution. After 3 minutes (reaction time), the gas carrier is transferred to the long circuit and all the CO_2 evolved is detected by the analyser (Almeida, 2009). The carrier gas flow rate used was approximately 200 ml min^{-1}. This flow is defined according to two factors. The first factor is the rate at which the gas reaches the analyser to determine the type of peak obtained. The second factor is the intensity of the flow rate. If it is used a flow rate very high, it is possible that some droplets of acid solution contact with the filter in the sample holder before starting the reaction after the purge. The system was calibrated with solutions with known concentrations of carbonate. Three filters impregnated with three different standards were used to check the reliability of the CO_2 analyser readings.

1.7.8 Water soluble inorganic ions

The water soluble inorganic ions in PM_{10} were analysed by ion chromatography. The separation taking place in this method is based on different tendencies of the ionic or ionised compounds from the sample to carry out an exchange with ions present in the stationary matrix. The separation is due to competition between the ions in the sample and counter-ions from the stationary matrix. Basically, the analyser consist of an integrated system that includes an adjustable flow rate pump, an injection valve, an exchange column, a differential detector and a data acquisition terminal. The sample is introduced into the upstream zone of the separation column (stationary phase) and then dragged by the solvent (mobile phase) until the separation of components in different areas. The signal differential detector measures the instantaneous concentrations. It represents the total amount of each component present in the analysed samples. The set of signals (peaks) is sent by the detector to the differential data acquisition terminal constructing a chromatogram.

In this work, Dionex AS14 and CS12 chromatographic columns with Dionex AG14 and CG12 guard columns coupled to Dionex AMMS II and Dionex CMMS III suppressors, respectively for anions and cations, have been used (**Figure 1.20**).

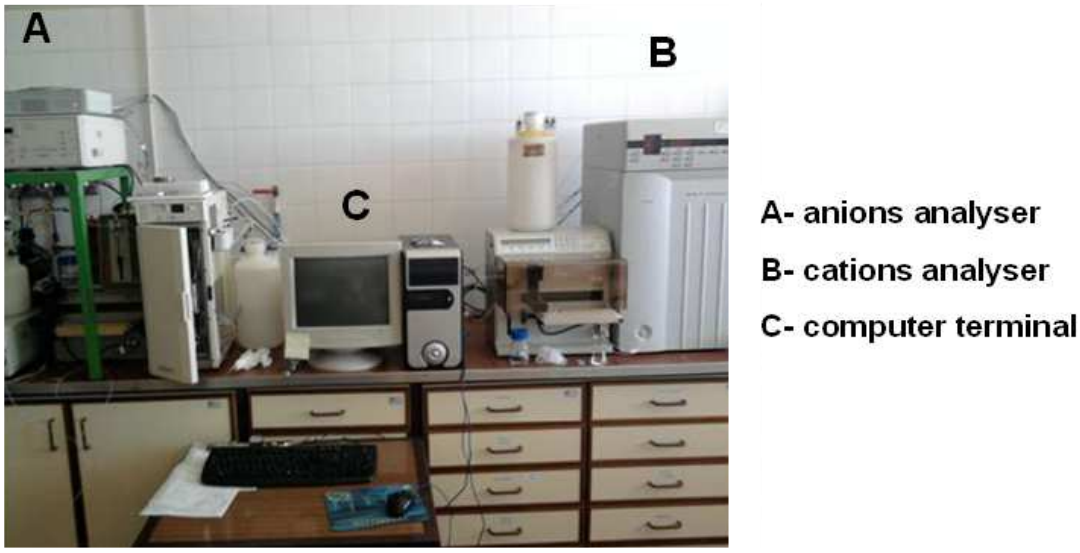

Figure 1.20. Ion exchange chromatographic system.

To make the extraction of the water soluble inorganic material, a known portion of each filter was cut and introduced into small plastic containers previously cleaned. The containers were washed, dipped in ultra-pure water and sonicated during 15 min. This procedure was repeated three times. The samples were extracted in 2.5 or 2 ml of ultra-pure water (varying with the campaign) by sonication for 15 minutes. After this, the samples were transferred to the vials, previously cleaned as described for the containers, using Acrodisc® syringe filters (0.45 µm pore). The amount of solution to be analysed was split in two portions: one part for anion analysis, and other part for cation analysis. The same procedure was done for some blank filters. Sets of multi-cation and anion standards were prepared from a stock solution with 1000 mg l^{-1} for each ion. This method made possible to identify and quantify three anions (chlorides (Cl^-), nitrates (NO_3^-), and sulphates (SO_4^{-2})), and five cations (sodium (Na^+), potassium (K^+), magnesium (Mg^{2+}) and

calcium (Ca^{2+}). The concentration of each ion in each sample was obtained through the individual calibration curves

1.7.9 Organic speciation

To identify and quantify the organic compounds present in the PM_{10}, it was necessary to separate the constituents with analytical interest from a mixture by dissolving in a solvent where only those constituents are soluble. This process is called extraction. The organic constituents of PM_{10} were extracted from filters by refluxing 300 ml of dichloromethane (DCM from Fischer Scientific) for 24 hours. Some filters were combined to meet the limits of detection from speciated organic compounds. During this process, the filters were placed with the solvent in a round-bottom flask connected to a condenser. Under heating, the solvent boils and a water cooled condenser prevents vapours from escaping, enabling the recovery of the solvent (**Figure 1.21**). The liquid extraction of a solid matrix results in dilution of the sample in a large volume of solvent.

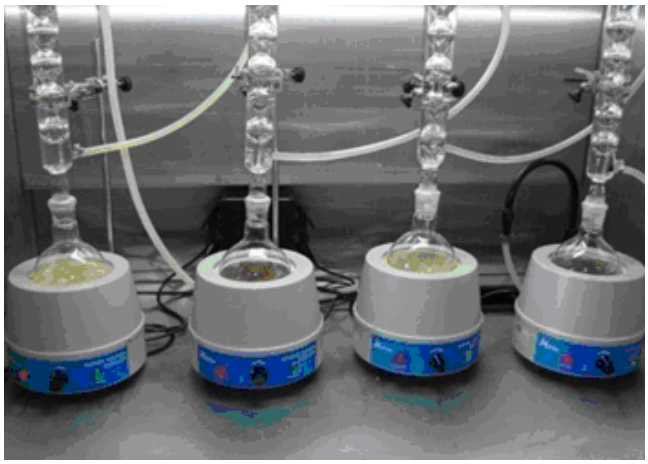

Figure 1.21. Heating blankets, glass flasks with samples and DCM, and condensers.

After extraction, the DCM was first subjected to filtration to remove pieces of filters (**Figure 1.22**). Filter pieces were then extracted 3 times with 75 ml of methanol for 10 min, each extraction, in an ultrasonic bath. Then the solvent was concentrated to a volume of about 4 ml using a rotary evaporator (IKA HB10 basic and Laborota 4002 – Digital) at a constant temperature bath of 33°C (**Figure 1.23**). The second extraction step with methanol aims at increasing the efficiency of removal of polar compounds. The efficiency increased from approximately 70%, when a simple extraction with DCM is done, to more than 90%, when subsequent extractions with methanol combined with DCM are performed. The total organic extract was transferred to vials and then subjected to a stream of nitrogen at low flow, to dry it up.

Figure 1.22. Filtration of the organic extracts and concentration of the solvent in a rotary evaporator (IKA HB 10 basic and Laborota 4002 – Digital, respectively).

The dry total organic extracts were subjected to a fractionation procedure by flash chromatography in a silica gel column. This technique uses eluents of increasing polarity in order to separate different families of organic compounds present in the sample. The laboratorial setup includes glass pear-shapedround flasks to collect the eluents and a nitrogen-pressurised glass column (30×0.7 cm) with adsorbent material (1.5 g of silica gel 3-6 mm (from Panreac), previously activated at 150°C during 3 hours). A needle valve is used to regulate the nitrogen flow through the column (**Figure 1.23**). The vial, containing

the total organic extract, was washed three times with different mixtures of eluents for each fraction of interest, subjected to mechanical agitation by vortex (Heildolph Vortex Mixer) and the mixture was transferred to the top of the silica column. The following solvents were used to elute the different compound classes: (1) 15 ml *n*-hexane (from Fisher Scientific) [fraction 1, aliphatics]; (2) 15 ml toluene–*n*-hexane (9.6 + 5.4 ml, from Lab Scan and Fisher Scientific) [fraction 2, polycyclic aromatic hydrocarbons (PAHs)]; (3) 15 ml *n*-hexane–dichloromethane (7.5 + 7.5 ml, from Fisher Scientific) [fraction 3, carbonyl compounds]; (4) 20 ml ethyl acetate–*n*-hexane (8 + 12 ml, from Merck and Fisher Scientific) [fraction 4, *n*-alkanols, sterols and other hydroxyl compounds]; and (5) 30 ml solution of pure formic acid in methanol (4%, v/v, from Merck and Sigma Aldrich) [fraction 5, acids and sugars]. The different fractions were passed successively through the silica column with the help of a nitrogen stream. For each fraction collected in pear-shaped flasks, the solvent was concentrated on the same rotary evaporator used after extraction, approximately up to 2 ml, maintaining the bath temperature at about 33°C. Then, the resulting extracts were transferred to 1.8 ml vials and dried under a nitrogen stream. Recovery efficiency tests for several compounds can be found in Alves (2001), Carvalho (2003), and Oliveira et al. (2007).

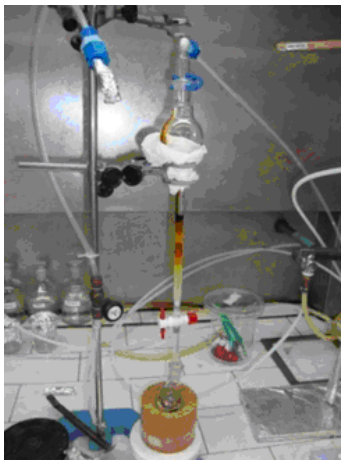

Figure 1.23. Flash chromatography in a silica gel column to separate compounds based on differences in polarity.

Fractions 4 and 5 followed a derivatisation process before the chromatographic analysis. Thus, both fractions were subjected to a silylation procedure. Silylation is one of the most used modes of derivatisation, due to the fact that there are a wide variety of chemical agents available. The *N*,*O*-bis(trimethylsilyl)-trifluoroacetamide (BSTFA) has been widely used as a reagent for silylation, because its products are enough volatile, rarely interfering with the analyte peaks in the chromatograms. For GC-MS analysis, the addition of trimethylchlorosilane groups (TMCS) to polar compounds gives thermal and chemical stability, as well as an increase in volatility (Evershed, 1993). The silylation of fractions 4 and 5 was carried out by adding BSTFA:TMCS (99:1) (Supelco 33149-U) at a ratio of 1:1 (one part of internal standard in pyridine to one part of BSTFA:TMCS solution in each vial) with subsequent heating to 70 °C for 3 hours in an oven.

GC-MS is the union between a gas chromatographer and a mass spectrometer. GC can separate volatile and semi-volatile compounds with great resolution but can not identify them. MS can provide detailed structural information on most compounds such that they can be exactly identified, but it can not separate those (Hites, 1997). **Figure 1.24** shows a schematic representation of a GC-MS.

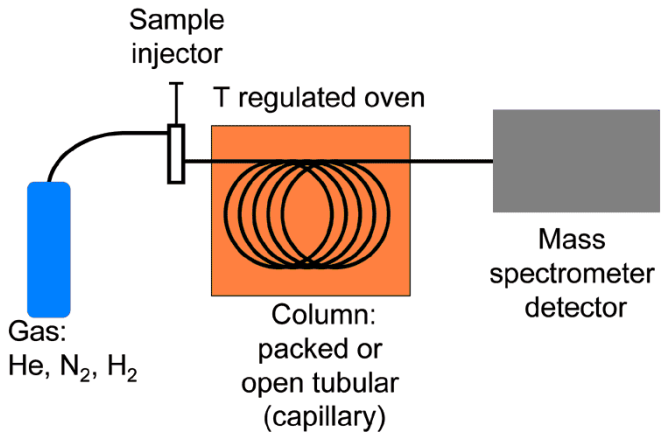

Figure 1.24. Scheme representing a GC-MS.

The fractionated extracts were analysed with a GC model 6890, quadrupole MSD 5973 from Hewlett Packard (fractions 4 and 5), and a GC Trace Ultra, quadrupole DSQ II from Thermo Scientific (fractions 1 and 2), both equipped with TRB-5MS 60 m×0.25 mm×0.25 μm columns. Fraction 3 was not analysed because in previous works it was found that carbonyl compounds in the particulate phase are not relevant since most carbonyls are semi-volatile (Báez et al., 2001; Grosjean et al., 2002; Ho et al., 2002; Pang et al., 2006; Pang and Lewis, 2011). Data were acquired in the electron impact (EI) mode (70 eV). The oven temperature programme was as follows: 60 °C (1 min); 60–150°C (10°C min^{-1}), 150–290°C (5°C min^{-1}), 290°C (30 min) and using helium as carrier gas at 1.2 ml min^{-1}. The injection was made in the splitless mode. The GC-MS system was accurately calibrated using about 150 high purity compounds in different concentration levels with RRF determined individually for the majority of compounds. The RRF were determined in a similar way, as described for VOCs. All samples and authentic standards were injected with two internal standards: tetracosane-D_{50} (Sigma-Aldrich) and 1-chlocohexadecane (Merck). Additionally, the EPA 8270 semi-volatile internal standard mix (Supelco), containing six deuterated compounds (1,4-dichlorobenzene-d_4, naphthalene-d_8, acenaphthene-d_{10}, phenanthreme-d_{10}, chrysene-d_{12}, and perylene-d_{12}), has been used for PAH analysis. A detailed description of the analytical methodology, including recovery efficiency tests for several compounds, can be found in Alves and Pio (2005) and Oliveira et al. (2007). This methodology was previously tested in our laboratory (Alves, 2001; Carvalho et al., 2003). Compound identification was based on comparison of resulting spectra with mass spectra libraries (Wiley 275 and NIST MS Search 2.0), co-injection with authentic standards and analysis of fragmentation patterns. HP ChemStation (Hewlett Packard) and Xcalibur (Thermo Scientific) softwares were used for integration.

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Chapter 2

2. RISK FACTORS AND PREVALENCE OF ASTHMA AND RHINITIS AMONG PRIMARY SCHOOL CHILDREN IN LISBON

Published

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Abstract

Aims: A cross-sectional study was carried out with the objective of identifying nutrition habits and housing conditions as risk factors for respiratory problems in schoolchildren in Lisbon.

Material and Methods: Between October and December 2008, parents of 900 students of the basic schools of Lisbon were invited to answer a questionnaire of the International Study of Asthma and Allergies in Childhood Program (ISAAC). The response rate was 40%. Logistic regression was used in the analysis of results.

Results: The prevalence of asthma, allergic rhinitis and wheeze was 5.6%, 43.0% and 43.3%, respectively. Risk factors independently associated with asthma were wheezing attacks, and dry cough at night not related to common cold in the last 12 months. Wheezing crises were found to affect children daily activities. Risk factors for wheeze were hay fever and the presence of a pet at home. A risk factor for rhinitis was cough at night. The frequent consumption of egg was also associated with increased risk of rhinitis.

Conclusion: Contrarily to asthma, the prevalence of allergic rhinitis and wheeze increased in comparison with previous ISAAC studies. Wheezing attacks were associated with asthma and hay fever was identified as a risk factor of manifesting wheezing symptoms. Having pets at home was pointed out as a significant risk factor for rhinitis, but not smoking exposure, mould, plush toys, diet (except egg consumption), breastfeeding or other conditions.

Key-words: asthma, rhinitis, wheeze, questionnaire, children.

2.1 Introduction

Asthma and allergic diseases are the leading cause of chronic illness in children and, for unknown reasons, are progressively increasing (Baena-Cagnani, 2001; Bateman and Jithoo, 2007; Beasley et al., 2000; Galassi et al, 2006; Pearce et al., 2007; Plácido, 2004). Although recent studies have shown that the genetic factors predispose people to allergic diseases (Mapp, 2003; Sandford et al., 1996; Steinke et al., 2008), the environmental factors have a significant influence on their occurrence and progression. Such factors include air pollution and several domestic triggers (Bjorksten, 2004; Dong et al., 2008; Salo et al., 2004; Zhang et al., 2004). The lifestyle, including the type of diet in early childhood, also plays an utmost role (Kim et al., 2009; Pawlinska-Chmara et al., 2008; Vellinga et al., 2002). As a consequence of diverse interactions between genetic and environmental risk factors, the prevalence rates show inconsistent results around the world (Bazzazi et al., 2007; Barraza-Villarreal et al., 2001; Devenny et al., 2004; Grize et al., 2006; Hasnain et al., 2009; ISAAC, 1998a, b; Leung et al., 1997; Owayed et al., 2008; Romano-Zelekha et al., 2007; Sánchez-Lerma et al., 2009; Vries et al., 2009; Waked et al., 2009; Wilson et al., 2006). Written respiratory symptom questionnaires intended to determine the prevalence of asthma and allergies in children have been extensively used in epidemiological studies (Fernández et al., 2005; Hong et al., 2003; Maçãira et al., 2005; Redline et al., 2004; Richardson et al., 2006). The International Study of Asthma and Allergies in Childhood (ISAAC) was the first investigation carried out worldwide using standardised questionnaires in order to generate a consistent global map of childhood allergy (Asher et al., 1995; ISAAC, 1998 a, b). Portugal joined the ISAAC in 1993 with 5 local study centres (Lisbon, Oporto, Coimbra, Portimão and Funchal) questioning 13-14 year old children. In 3 of these centres (Lisbon, Portimão and Funchal), 6-7 year old children were also studied (Pinto et al., 2006; Trindade et al., 1999). Besides the current trends in the prevalence of childhood asthma and asthma-like symptoms, the ISAAC program concluded that further population studies are urgently needed to discover more about the underlying mechanisms and the burden of these conditions.

With the objective of determining prevalence and risk factors of asthma and allergic diseases in Lisbon schoolchildren, as well of comparing the results with previous data obtained through the same protocol, a questionnaire-based study was conducted in elementary schools of the Portuguese capital city. Research on potential risk factors of asthma and allergic diseases can enhance our understanding of geographic differences and inform decisions on preventive strategies.

2.2 Material and Methods

Elementary school children were selected as the target population. Twenty two schools with a wide geographical coverage representing the Lisbon urban area were invited for participation in the study (Khan et al., 2007). Fourteen schools accepted to take part in the investigation. After obtaining consent from the school authorities, two classrooms from each school were selected for an indoor air quality monitoring program (Pegas et al., 2010a, b). A questionnaire, accompanied by an explanatory letter, was distributed to 900 children in every selected classroom. The questionnaire used in this study is the Portuguese version of the ISAAC program and had to be filled out by the parents. The questionnaire was adapted to facilitate the parents' responses, taking out some questions about medicine consumption, which did not constitute the objective of this study. The survey took place between October and December 2008 comprising children aged 5-12 years. A total of 342 questionnaires were returned. They included questions on the frequency of respiratory symptoms and allergy occurrence in the child, physical activity, socio-demographic characteristics, housing conditions, and other possible sources of indoor air pollution (**Table 2.1**). Among the factors related to lifestyle, particular attention was paid to the child's exposure to tobacco smoke, the way of feeding the child during the first months of its life (breast-feeding, artificial milk feeding), and the current type of diet. The manually written answers were transferred to a computer, codified, and confirmed by two independent persons. Multivariate logistic

regression models controlling for possible confounders were used to evaluate variables associated with asthma and allergic symptoms, and adjusted odds ratios (ORs and 95% confidence intervals, CI) were calculated.

Table 2.1 *- Questions in the questionnaire used in this study*

Wheezing	Has your child ever had wheezing or whistling in the chest at any time in the past?
	Has your children had wheezing or whistling in the chest in the last 12 months?
	How many attacks of wheezing has your child had in the last 12 months?
	How often, on average, has your child's sleep been disturbed due to wheezing in the last 12 months?
	Has your child's chest sounded wheezy during or after exercise in the last 12 months?
Asthma	Has your child ever had asthma?
Nocturnal dry cough	Has your child's chest sounded wheezy during or after exercise in the last 12 months?
Rhinitis	Has your child ever had sneezing or a runny/blocked nose when he/she did not have a cold or flu?
	Has your child had sneezing or a runny/blocked nose when he/she did not have a cold or flu in the last 12 months?
	Have nasal symptoms interfered with your child's daily activities in the last 12 months?
Hay fever	Has your child ever had hay fever?
Alimentary habits	What were the eating habits for meat, fish, fruit, vegetables, cereals, pasta, bread, rice, butter, margarine, dry fruits, potatoes, milk, eggs and fast-food in the last 12 months?
Breastfeeding	Has your child had been breastfeeding?
Sports	Does your child practise some sport activities?
	How many times for week does your child do exercise until to be puffy
House	Fuel type used for cooking; use of indoor clothes airer dryers;

characterisation and habits	household coal use for cooking or space heating; intensity of heavy vehicle traffic in the street; use of heating devices; signs of flooding, water damage or mould growth (any surfaces other than floor); contact with household pets or farm animals; presence of plush toys (e.g. teddy bears) in the bedroom; type of bedroom flooring and finishing.
Parents' smoking habits	Smokers in regular contact with the child (mother, for example, grandparents or baby-sitters); number of daily smokers of cigarettes in the child's home; paternal or maternal smoking while living in the home with their children.

2.3 Results

The sample population comprised 342 schoolchildren between 5 and 12 years, although 92% of the total was included in the age group of 6-8 years. No dimorphic differences were found concerning the frequency of allergies, therefore no division by gender was applied in further analysis. The percentage of children with wheezing or whistling in the chest was 43.3%. Asthma prevalence was 5.6%. Symptoms of allergic rhinitis were reported for 42.9% of children.

Almost 9.5% of children were born abroad. The proportion of parents with elementary education degree was 20%, 56% reported having a secondary degree and 20% were university graduates. Housing characteristics of respondents were evaluated (**Table 2.2**): about 33% of the families lived near streets with heavy traffic, 23% used drying clothes airers and indoor drying racks for the drying of washing and laundry, and only 3% of children's bedrooms had carpeting. Gas use as a cooking fuel was asserted by 84% of respondents. Almost 23% of the families stated having a furry pet at home, whereas 62% reported plush toys in the child's bedroom. The appearance or detection of moulds and water damage within the past 12 months occurred in 19% of the homes, and 23% of children had been exposed to environmental tobacco smoke during the first year of life. More than half of all children lived with one or more smokers in their homes.

Table 2.2 *- Housing characteristics and environmental factor exposure in children living in Lisbon.*

Housing characteristics	**Definition**	**%**
Cooking equipments	cooking fuel type:	
	- electricity	5.6
	- gas	83.9
	- other	0.0
Indoor laundry drying	The use of indoor clothes airer dryers	22.8
Indoor coal use	The use of coal in a household for cooking or space heating	0.0
Pollution source near the house	heavy vehicle traffic in the street:	
	- all day long	9.6
	- frequently	23.7
	- rarely	47.9
	- never	17.5
Use of home heating devices	the use of any of the following heating devices:	
	- electricity	43.3
	- gas	12.6
	- wood	9.4
	- other	1.7
Mould in the past 12 months	signs of flooding, water damage or mould growth (any surfaces other than food)	19.0
Pet keeping	refers to the feeding in a household dogs, cats or farm animals:	
	- cats in the past 12 months	10.8
	- cats in the first year of life	8.5

	- dogs in the past 12 months	22.8
	- dogs in the first year of life	9.3
	- contact during the first year of life with farm animals	12.9
Plush toys	presence of plush toys (e.g. teddy bears) in the bedrooms	62.3
Bedroom flooring	types of bedroom flooring:	
	- carpet	2.6
	- wooden	70.5
	- tiled	14.3
	- other	8.2
Bedroom walls	types of bedroom finishes:	
	- painting	95.0
	- wallpaper	0.6
Early-life exposure to tobacco smoke in the 1st year	smokers in regular contact with the child (mother, for example, grandparents or baby-sitters)	23.0
Current smokers in the household	number of daily smokers of cigarettes in the child's home:	
	- none	43.9
	- one	35.1
	- two	15.8
	- three	2.6
	- four or more	2.0
Parents smoking	paternal or maternal smoking while living in the home with their children:	
	- mother	30.4
	- father	36.5

The results of the logistic regression analysis reveal that the questions “How many wheezing attacks did your child had during the past year?” and “Has your child had ever dry cough at night not associated with common cold in the last 12 months?” are statistically significant predictors of asthma. Concerning the first question, the estimate of the probability of occurrence of childhood asthma is 10 times superior for the answer category “1 to 3” (one to three wheezing attacks in the past year) than for those responding “none” (ODs=10.07; CI=2.98, 33.96). Children in the category “4 to 12” have approximately a 20 times higher chance of developing the disease compared with those in the category “none” (ODs=19.88; CI=4.22, 93.54). Occurrence of dry cough at night increases by almost 6 times the probability of asthma manifestation (ODs=5.77; CI=1.20, 27.70).

For the variable represented by the question “During the last 12 months, have the wheezing problems affected your child’s daily activities?”, the odds ratio between the category “did not affect daily activity” and the category “daily activity affected a little” is 2.55 (CI=1.28, 5.08). This means that the point estimate of the probability of occurrence of wheezing is 2.55 higher for those responding “did not affect” than for those answering “affected a little”. The odds ratio between the categories “did not affect daily activity” and “daily activity affected moderately” is approximately 27 (CI=6.17, 126.36). The point estimate of the probability of occurrence of wheezing is 13 times higher for positive answers to “Has your child ever had hay fever?” (ODs=13.02; CI=1.52, 109.5). (CI=1.27, 10.57). Children who had a pet in their home during the last 12 months appear to have a higher risk of developing wheezing symptoms (ODs= 3.66; CI=1.27, 10.57).

The occurrence of dry cough at night not associated with common cold in the last 12 months was also positively associated with rhinitis (ODs= 2.77; CI=1.19, 6.44). The point estimate of the probability for allergic rhinitis is approximately 145 times higher among children with sneezing crisis, runny nose or nasal congestion not associated with common cold in relation to those without these symptoms (ODs= 145.47; CI=53.53, 395.28). Among diet variables, the only statistical significant relationship found was for egg consumption, with frequent egg eaters having a 90% higher risk for allergic rhinitis than those that were not (OR = 0.10, CI =0.01, 0.54).

2.4 Discussion

The male to female ratio for the diagnosis of asthma has narrowed considerably in the past 35 years, with almost complete disappearance of the previous male predominance (Devenny et al., 2004). In comparison with previous studies in Portugal, schoolchildren living in Lisbon show a trend to reduction in the current prevalence of asthma (**Table 2.3**). This might be explained by a better control of the disease through educational measures and improved preventive treatment to better control of the disease, taking into account that more children are now using inhaled corticosteroids. These findings are sustained by other studies that used the ISAAC questionnaire (Romano-Zelekha et al., 2007). The ISAAC found the greatest prevalence of asthma in Australia and New Zealand (29.7%), followed by North America (24.4%) and Latin America (17.0%) (Baena-Cagnani et al., 2001). In contrast to our study, a trend towards an increase in asthma has been observed in other regions: Taiwan (Lee et al., 2007), United Kingdom (Devenny et al., 2004), Hong Kong (Leung et al., 1997), US (Eggleston, 2007), Australia (Wilson et al., 2006), Brasil (Fiore et al., 2001), Austria (Schernhamme et al., 2008), and Spain (García-Marcos et al., 2004). However, signs indicative of a halt in the rising trend in asthma prevalence have been found in other recent investigations (Fleming et al., 2000; Owayed et al., 2008; Romano-Zelekha et al., 2007; Ronchetti et al., 2001; Toelle et al., 2004; Zollner et al., 2005). According to Bazzazi et al. (2007) it is unresolved why the disparities in the prevalence of asthma and allergic disorders are so large. Two overlapping though competing theories have related changes in environmental factors to observed trend profiles in asthma and allergy epidemiology. The oldest theory, the “hygiene hypothesis”, claims that modifications in the infectious environment and in the pattern of microbial exposure of children associated with westernisation are decisive factors contributing to the increasing severity and prevalence of atopic disorders. According to this theory, environmental exposures that promote a generalised suppression of Th2 cytokines and trigger strong Th1 responses are becoming progressively less common (Strachan, 1989). The most recent theory, the “immunotolerance hypothesis”, claims that early high levels of exposure to allergens

reduce risk by potentiating the regulatory capacity of the immune system (Platts-Mills et al., 2001).

Table 2.3 - *Prevalence of allergy symptoms worldwide (values are given in %).*

	Asthma	**Allergic rhinitis**	**Wheeze**	**References**
European countries				
Lisbon, Portugal	5.6	43.0	43.3	This study
Oporto, Portugal	11.9	12.9	18.3	Falcão et al. (2008)
Lisbon, Portugal	9.2	26.9	26.7	Khan et al. (2007)
Portugal 2002	9.4	29.1	28.1	Plácido (2004), Pinto et al. (2006)
Portugal 1993/94	10.8	23.6	27.9	Trindade (1999)
Aberdeen, Scotland	24		28	Devenny et al. (2004)
Sanliurfa, Turkey	1.9	2.9		Zeyrek et al. (2006)
Italy	9.1	6.3	7.8	Galassi et al. (2006)
Other countries				
Gorgan, Iran	7	35.3	28.8	Bazzazi et al. (2007)

Ciudad Juárez, México	6.8	5.0	20	Barraza-Villarreal et al. (2001)
Israel	6.4	10.5	13.8	Romano-Zelekha et al. (2007)
Canary Islands	18.4	40.3	46.8	Sánchez-Lerma et al. (2009)
Pakistan	15.8	28.58	11.7	Hasnain et al. (2009)
Oman	20.7	10.5		Al-Riyami et al. (2003)
India	15	20-30		Singh et al. (2004)
Saudi Arabia	23	25		Al Frayh et al. (2001)
Australia	46			Wilson et al. (2006)
Hong Kong	11	52	20	Leung et al. (1997)
Tibet	1.1	5.2	1.4	Droma et al. (2007)
Lebanon	19.5	24.5		Waked and Salameh (2009)
Taiwan	7.4			Lee et al. (2007)
Tonga	12.5	16.1	26.6	Foliaki et al. (2007)
French Polynesia	16	12.3	12.2	Foliaki et al. (2007)
Kuwait	15.6	41.4	13.4	Owayed et al. (2007)
Brazil	16.5-31.2	19.3-35.9		Solé et al. (2006)

Children with sneezing crisis, runny nose or nasal congestion not associated with common cold were 43.0%. Regarding the last year rhinitis prevalence in this age group, it was estimated to be 39.5%. The prevalence of this allergic disease in Lisbon is greater than the mean estimated national prevalence. Since Portugal is a country with diverse

geographic areas, the divergent prevalence ratios obtained in different cities can be explained by the type of weather, the level of air pollution and the diverse levels of contact to allergens. Lee et al. (2007) surveyed an increased prevalence of allergic rhinitis among children in Hong Kong from 1995 to 2001. The same rising trend was observed among Israeli adolescents (Romano-Zelekha et al., 2007). In Brazil, last year rhinitis prevalence in schoolchildren and adolescents was found to fall in wide ranges: 1.5-41.8% and 3.2-66.6%, respectively (Solé et al., 2006). In Italy, the prevalence of rhinitis symptoms in the past 12 months increased from 13.8 to 18.9% and from 31.6 to 35.1% among children (6-7 years old) and adolescents (13-14 years old), respectively, between 1994 and 2002 (Galassi et al., 2006).

The proportion of children with respiratory symptoms reporting wheeze experienced a significant increase between 1993/94 and 2008 (**Table 2.3**). However, the prevalence of wheezing symptoms in the last 12 months was only 15%. The worldwide prevalence of current wheeze studied in 155 centres ranged from 2.1 to 32.2% (ISAAC, 1998b). In Australia, a 26% decrease in wheezing in the past 12 months was found in younger children between 1993 and 2002 (Robertson et al., 2004). In Spain, the prevalence of current wheeze in 13-14 year old children did not change from 1994-1995 to 2002-2003 (García-Marcos et al., 2004). In Belgium, there was no clear change in asthma, but wheeze decreased from 1996 to 2002 (Vellinga et al., 2002). Several other studies from Great Britain, Germany, Italy and Denmark conducted in the last decade reported dissimilar findings of an increase in the prevalence of asthma and of wheeze in the past 12 months (Devenny et al., 2004; Galassi et al., 2006; Maziak et al., 2003; Thomsen et al., 2004).

Frequent consumption of egg was also associated with increased risk of respiratory symptoms among schoolchildren in Taipei (Tsai and Tsa, 2007). Allergic reactions to food are either immunoglobulin (IgE) mediated or non-IgE-mediated. Persons who are hereditarily predisposed to atopy produce specific IgE antibodies to certain proteins to which they are exposed. These antibodies bind to mast cells and other cells in body tissues and to basophiles circulating in the blood stream. When a food protein is ingested, the IgE recognises it on the surface of these cells; mediators (e.g., histamine) are released, and symptoms arise. Besides the skin and gastrointestinal

tract, the symptoms of IgE-mediated reactions usually involve the respiratory system (Sicherer, 1999). Eggs are among the food most commonly causing these allergic reactions in children.

No associations with any of the other dietary factors were found. A significant protective effect of breastfeeding against current respiratory allergies in children was not observed in this study. Besides pets, no statistically significant relationship was found with other housing conditions.

Our study had some limitations; namely recalling bias in cross-sectional questionnaires and the lack of objective laboratory measures. However, most estimates of asthma, wheeze and rhinitis have been based on data from questionnaires with questions concerning symptoms or preceding physician diagnosis.

2.5 Conclusions

Contrarily to asthma, a statistically significant increase in the prevalence of rhinitis and wheeze was observed among primary schoolchildren in Lisbon. Differences in prevalence obtained in several studies may point out exposure to different risk factors, as well as variable racial, environmental, and socioeconomic conditions, heterogeneous diagnostic criteria, or a true increase in the prevalence of allergic diseases. In this study, wheezing attacks were associated with asthma and hay fever was identified as a risk factor of manifesting wheezing symptoms. Children with dry cough at night should be evaluated for both rhinitis and asthma, and a combined strategy should be ideally used to treat the upper and lower airway diseases in terms of efficacy and safety. Having pets at home was pointed out as a significant risk factor for rhinitis, but not smoking exposure, mould, plush toys, diet (except egg consumption), breastfeeding or other conditions. The results support the observation that deep changes in the epidemiologic dynamics of asthma and allergic diseases are occurring worldwide, demanding ample, continuous, epidemiologic monitoring. Future studies, such as birth cohorts, are warranted to evaluate risk and protective factors and to continue surveying the features of the prevalence of asthma and allergic diseases in Portugal. Research on

potential risk factors of asthma and respiratory allergies can enhance our understanding of geographic differences and support decisions on preventive strategies.

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Chapter 3

3. OUTDOOR/INDOOR AIR QUALITY IN PRIMARY SCHOOLS IN LISBON: A PRELIMINARY STUDY

Published

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Abstract

Simultaneous measurements of outdoor and indoor pollution were performed at three schools in Lisbon. Volatile organic compounds (VOCs), formaldehyde and NO_2 were passively monitored over a two-week period. Bacterial and fungal colony-forming units and comfort parameters were also monitored at classrooms and playgrounds. The highest indoor levels of CO_2 (2666 µg m^{-3}), NO_2 (40.3 µg m^{-3}), VOCs (10.3 µg m^{-3}), formaldehyde (1.03 µg m^{-3}) and bioaerosols (1634 CFU m^{-3}), and some indoor/outdoor ratios greater than unity, suggest that indoor sources and building conditions might have negative effects on air indoors. Increasing ventilation rates and use of low-emission materials would contribute towards improving indoor air quality.

Keywords: indoor air quality, VOCs, formaldehyde.

3.1 Introduction

Outdoor air quality has become of growing concern during the past 50 years, because of increasing traffic and industrial emissions. However, evidence has been found that citizen spend most of their time in buildings and are far more exposed to pollution indoors than outdoors (Blondeau et al., 2005).

In Lisbon, the number of children with asthma and rhinitis represents, respectively, about 15% and 40% of the school-age population (Khan et al., 2007a) and almost nothing is known about indoor air quality (IAQ) in schools. Mendell et al. (2002) observed that health problems from poor indoor environments may reduce the performance of occupants in buildings. According to Mendell and Heath (2005), indoor environments in schools need to be studied with the aim of finding connections between IAQ and performance or attendance, due to two primary reasons:

- Schools are seen as particularly likely to have environmental deficiencies because chronic shortages of funding contribute to inadequate operation and maintenance of facilities.
- Children have greater susceptibility to some environmental pollutants than adults, because they breathe higher volumes of air relative to their body weights and their tissues and organs are actively growing. In addition, a child's immune system is not fully developed. Currently, children also spend more time in school than in any indoor environment other than their home.

Persuasive evidence links higher indoor NO_2 concentrations to reduced school attendance and low ventilation rates to reduce performance. Concerning indirect associations, some studies link indoor dampness and microbiologic pollutants to asthma exacerbations and

respiratory infections, which in turn have been related to reduced performance and attendance (Kim et al., 2007; Mendell and Heath, 2005).

The first aim of this preliminary study was to measure comfort parameters, CO_2, bacterial and fungal contamination and gaseous inorganic and organic pollutants in indoor and outdoor air of three schools in winter. The second aim was to study associations between these factors and possible sources inside or outside the schools. As far as we know, this is the first IAQ monitoring study in schools of Lisbon.

3.2 Experimental

3.2.1 Schools Description

Indoor and outdoor air samples were collected at three schools (183, SJB and SJ) in Lisbon (Portugal), in December 2008. These schools were located in the city centre and were previously considered representative of all the elementary-level educational institutions (Khan et al., 2007a, b). Two classrooms from each of the three schools were selected for this study. One of the classrooms of both 183 and SJB schools always had the electric heating connected and closed windows. This classroom of the 183 School presented activities of arts with paints and glue in one day during the sampling; the other classrooms had windows and doors opened frequently. In the SJ School, both classrooms were always shut. All the classrooms depend only on the natural ventilation through the doors and windows existent. Details of each sampling site are listed in **Table 3.1**.

Table 3.1 *- Characteristics of each school*

	183	**SJB**	**SJ**
Environment	Urban	Urban	Urban
Heating	Yes	Yes	No
Ventilation	Windows/Doors		
Type of board	Blackboard and chalk	White board with pen	Blackboard and chalk
Floor	Ceramic tile		
Material of desks and chairs	Wood, plywood, plastic and metal		
Plants	Outdoor	Outdoor	Indoor/Outdoor
Animals	No	Yes	No

3.2.2 Sampling and Analysis

Pollutants and parameters of interest were carbon dioxide (CO_2), temperature, relative humidity (RH), total VOCs, bacterial and fungal colony-forming units per cubic metre, NO_2, speciated VOCs and formaldehyde. Continuous measurements of temperature, relative humidity (RH), CO_2 and total VOCs were performed with an automatic portable Indoor Air IQ-610 Quality Probe (GrayWolf® monitor) in one classroom of each school. This IAQ monitor includes a Pt100 probe for measuring temperature, a capacitance probe to sense RH and a CO_2 non-dispersive infrared sensor, all of them with an extremely fast response. The monitor also includes a photo-ionisation detector to track total VOCs over time. It displays measurements in real time allowing logged data to be downloaded to WolfSense® PC software for analysis. The equipment was supplied with a factory calibration certificate, but it

is checked prior to next use with appropriate calibration kits. Based on their results, it was expected to evaluate the contribution of ventilation, combustion processes, tobacco smoke and traffic for the IAQ. Bacterial and fungal colony-forming units per cubic metre of air were monitored by liquid impinger sampling in the two classrooms and playgrounds during one day in each school selected (May and Harper, 1957). Passive samplers for VOCs, formaldehyde and NO_2 were used for the simultaneous measurements of indoor (in one classroom of each school) and outdoor levels. At each point, samples were collected in duplicate. NO_2 concentrations were passively monitored for a two-week period. The diffusive tubes (with steel grids impregnated with triethanolamine) chemiadsorb NO_2, as nitrite, which was quantified by visible spectrophotometry (Bhugwant and Hoareau, 2003). Passive samplers for VOCs and formaldehyde from Radiello® (www.radiello.com) were used to obtain a screening of heavy and light molecular weight compounds over a two-week period. Indoor passive samples were collected at a height of about 1.5 m above the floor. They were positioned at a distance that should exceed 1 m from a window or a door. Outdoor passive samples were collected at heights of about 2 m above the ground. VOCs adsorved in activated charcoal cartridges were recovered by 2 ml of carbon disulfide (CS_2) with the internal standard, during 30 minutes. Analyses were performed by gas chromatography (Chrompack CP 9001) coupled to a flame ionisation detection (GC/FID), using nitrogen carrier gas at constant pressure of 20 psi.[9] A 100% dimethylpolysiloxane column (0.2 mm, 50 m, film thickness 0.5 μm) was used under the following temperature program: 50°C for 5 minutes, 5°C min^{-1} up to 80°C, 15°C min^{-1} up to 135°C, 20°C min^{-1} up to 220°C, final isotherm for 20 minutes. Injector and detector temperatures were 240°C and 300°C, respectively. The equipment was calibrated before and during the analyses of samples by injecting standard solutions of all compounds identified in CS_2, specifically: pentane, *n*-hexane, ciclohexane, *n*-heptane, *n*-butyl acetate, styrene, *α*-pinene, sabinene, *β*-pinene, *n*-decane, (+)-3-carene,

limonene (all from Fluka), methyl acetate, ethyl acetate, isooctane, *m,p*-xylene, *o*-xylene (all from Merck), benzene (AnalytiCals), toluene (Lab-Scan), and γ-terpinene (Aldrich). Four standard solutions, each one containing five compounds in CS_2, have been prepared. The analytes in these four standard solutions were present in concentrations of 40 ng μl^{-1}, 20 ng μl^{-1}, 10 ng μl^{-1} and 5 ng μl^{-1}.

Formaldehyde collected in the 2,4-dinitrophenylhydrazine in sampling cartridges reacted to give the corresponding 2,4-dinitrophenylhydrazones. The analytes were extracted with 2 ml of acetronitrile and analysed by high-performance liquid chromatography (HPLC). The analytical system consisted of a Jasco PU- 980 pump, a Rheodyne manual injection valve (sample loop of 20 µl), a Supelcosil LC-18 column (250×4.6mm; 5µm; Supelco) and a Jasco MD-1510 diode array detector, all connected in series. Isocratic elution at room temperature was performed using an acetonitrile/water solution (60/40, v/v) as the mobile phase at a flow rate of 1.5 ml min^{-1}. The carbonyl concentrations were quantified with external calibrations curves constructed from standard solutions of formaldehyde-DNPH derivative in acetonitrile (www.radiello.com; U.S.EPA, 1997). After compilation of data, the different environments were compared with the aim of finding a relation between indoor and outdoor pollutants and the possible compound sources.

3.2.3 Evaluation of the Chromatographic Analysis

Parameters, such as selectivity, linearity, reproducibility and limit of detection, were evaluated by twelve injections of three standard solutions of ten compounds with three concentrations each one, between 5 ng μl^{-1} and 40 ng μl^{-1}. The selectivity of an instrumental separation method refers to the ability to discriminate between the analyte and interfering

components (Ribani et al., 2004). As condition for the method selectivity, the absence of peaks in the region of the retention time for the investigated compounds was observed. Linearity is the ability to elicit test results that are directly proportional to the concentration of analytes in samples within a given range (Ribani et al., 2004). The repeatability measures are the success rate in successive experiments conducted by the same experimenters. It was evaluated from the calculation of the standard deviation of the chromatographic peak areas corresponding to 10 - 12 injections, each day, in 5 successive days. The limit of quantification (LOQ) represents the lesser concentration of the substance in examination that can be quantitatively analysed with reasonable reliability. Limit of detection (LOD) represents the lesser concentration of the substance in examination that can be detected, but it is not necessarily quantified by a method. The LOQ and LOD have been calculated as described in Ribani et al. (2004).

3.3 Results and Discussion

3.3.1 Results of the Evaluation of the Chromatographic Analysis

The chromatographic analyses of samples exhibited good selectivity and separation capability of analytes. After multiple injections of different concentration standard solutions, it was observed that the plots of peak areas, as a function of analyte mass, produced regression lines that had an intercept not significantly different from 0 and Pearson correlation coefficients ranging from 0.958 to 0.999 (**Table 3.2**). Consecutive injections of the same sample under variable conditions showed repeatability among measurements. The maximum

standard deviation did not exceed 0.04 (**Table 3.2**). Depending on the analyte, LOQ and LOD were in the ranges 1.04-7.64 ng μl^{-1} and 0.34-2.52 ng μl^{-1}, respectively (**Table 3.2**).

Table 3.2. *- Average relative response factor, standard deviation (STDEV), linearity, limit of detection and limit of quantification for each compound.*

Compounds	Average RRF*	STDEV	Pearson correlation coefficients	LOD** (ng μl^{-1})	LOQ*** (ng μl^{-1})
Ethyl acetate	0.27	0.01	0.999	2.52	7.64
Ciclohexane	0.82	0.02	0.999	1.35	4.10
Isooctane	0.89	0.02	0.996	1.06	3.22
***n*-Heptane**	0.97	0.02	0.958	1.03	3.11
Toluene	1.15	0.02	0.999	0.74	2.25
Internal standard	1.00	0.00	0.999	1.06	3.21
***o*-Xylene**	1.28	0.04	0.999	0.43	1.31
***β*-Pinene**	1.23	0.04	0.999	0.38	1.15
***n*-Decane**	1.20	0.04	0.999	0.34	1.04
Limonene	1.15	0.04	0.999	0.38	1.14

* RRF (relative response factor) = (area of compound/mass of compound)*(area of internal standard/mass of internal standard);

**LOD (limit of detection) = 3.3(s/S), where s is the STDEV of areas and S is the slope;

***LOQ (limit of quantification) = 10(s/S), where s is the STDEV of areas and S is the slope.

3.3.2 Air Quality Monitoring Data

The average room temperature for the three schools was 20ºC±1.4ºC, and the relative humidity presented values between 52 and 61%. These high indoor relative humidity values

are not surprising since, according to the Environment Portuguese Agency, the Lisbon region usually records values between 75 and 85%. It should be stated that higher relative humidity values contribute to the survival and the dispersion of airborne allergens such as mould spores and bacteria, worsening the symptoms of allergy suffers.

Carbon dioxide concentrations are often used as a surrogate of the rate of outside supply air per occupant. Indoor CO_2 concentrations above approximately 1000 µg l^{-1} are generally regarded as indicative of ventilation rates that are unacceptable with respect to body odours (ASHRAE, 1999). The National System for Energy and Indoor Air Quality Certification of Buildings (*Regulamento dos Sistemas Energéticos de Climatização de Edifícios* –RSECE) (RSECE, 2006) establishes an acceptable maximum value (AMV) of CO_2 of 1800 µg l^{-1} for buildings in Portugal. The indoor concentrations of CO_2 showed inadequate classroom air exchange rates. **Figure 3.1** depicts the variation of indoor CO_2 concentrations in a typical working day at the three schools. A strong correlation of the CO_2 level with occupancy has been observed. CO_2 spikes were even more pronounced when students started physical activities inside the classrooms, as for example, art classes or entrance and exits to the playgrounds. Room 12 of the 183 School presented the greatest CO_2 concentration (2666 µg l^{-1}). This room was the only one that had the electric wall heating constantly connected and windows and doors always closed. Lower outdoor air ventilation rates at homes have been associated with increased prevalence of asthma and allergic symptoms in children (Bornehag et al., 2005).

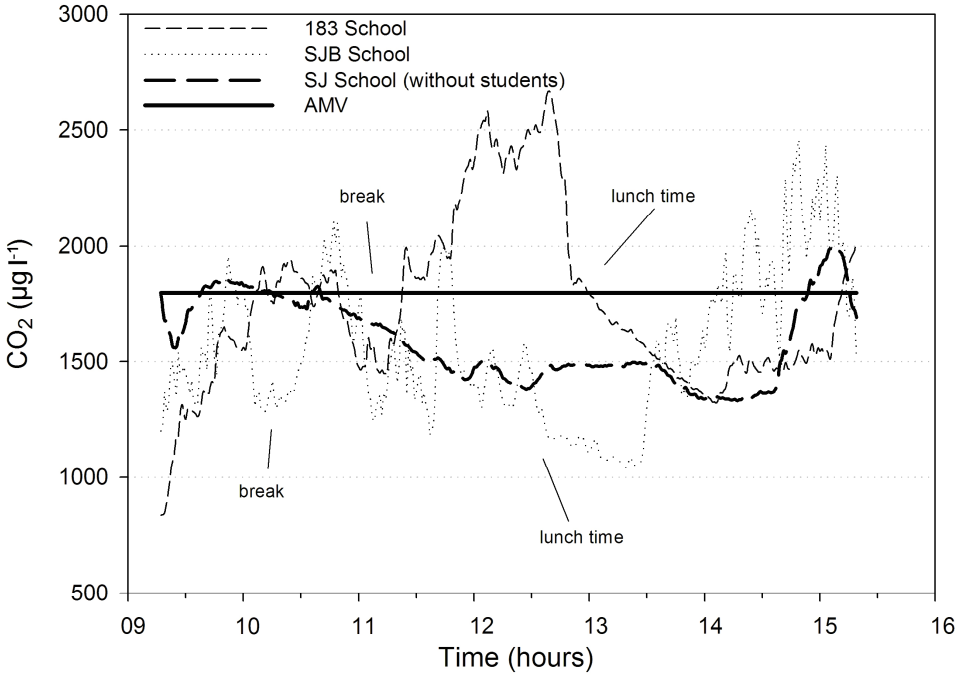

Figure 3.1 – Indoor carbon dioxide levels in the three schools.

No standards have been agreed upon for nitrogen oxides in indoor air in Portugal. ASHRAE (ASHRAE, 1999) and the U.S. EPA National Ambient Air Quality Standards list 0.053 ppm as the average 24-hour limit for NO_2 in outdoor air. NO_2 concentrations were higher outdoors than indoors (**Table 3.3**), probably as a result of vehicular exhaust emissions from nearby traffic. The I/O NO_2 ratio ranged between 0.63 and 0.84. SJ School, which is located near an avenue with intense traffic, presented the smallest level of indoor NO_2, possibly because the windows and the doors were always closed.

***Table 3.3* - .** *Indoor and outdoor NO_2 concentrations ($\mu g\ m^{-3}$) in the three schools.*

	Indoor	**Outdoor**	**Indoor/Outdoor**
SJB School	40.3	48.0	0.84
SJ School	36.4	56.9	0.64
183 School	37.1	44.4	0.83

In the SJ and SJB Schools, the total fungal colony-forming units in both indoor and outdoor air (**Figure 3.2**) were below the acceptable maximum value (AMV) of 500 CFU m^{-3} defined by the Portuguese Legislation, Decree-Law 79/2006. In the 183 School, fungal colony-forming units higher than this standard were observed in both indoor and outdoor air. Fungal species exceeding 500 CFU m^{-3} may be indicative of building-related sources, poor ventilation rates or overcrowding, highlighting the need for remedial action (Godish, 1995).

Excepting for the outdoor measurements of SJ School, the total bacteria colony-forming units presented values above 500 CFU m^{-3} for all the environments. The main factors affecting atmospheric dispersion and survival of microorganisms are the relative humidity, temperature, oxygen, wind and air turbulence, air pollutants and water and nutrient availability. The high amounts of bacteria in both indoor and outdoor may derive from several factors, including high seasonal level of bioaerosols in outdoor air, from the human self-activities, such as breathing, sweating and movement causing particle resuspension. Cold weather favours children's respiratory infections, which are usually caused by bacteria or virus. Thus, respiratory morbidity among children may also contribute to the airborne spread of bioaerosols.

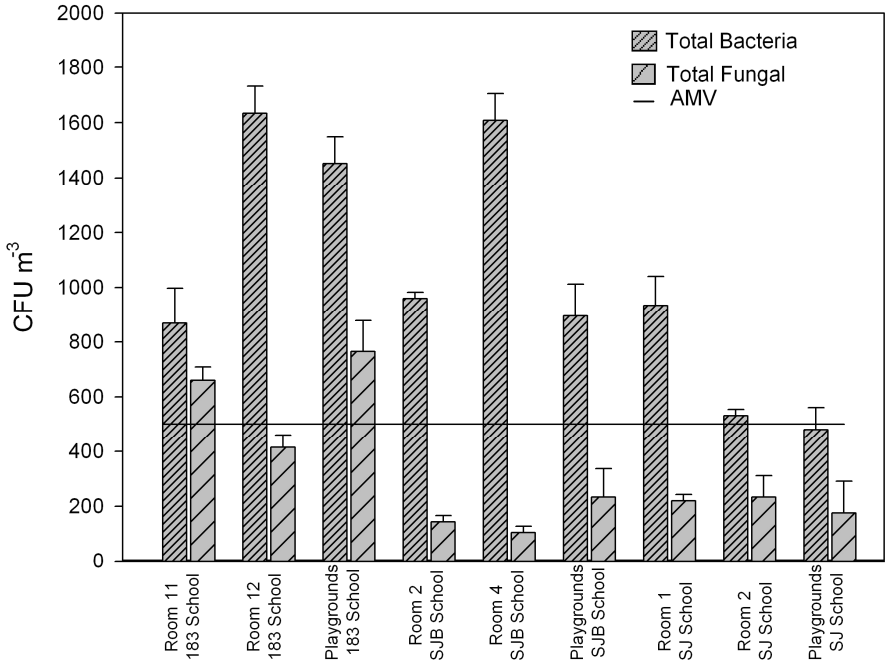

Figure 3.2 – Average of total bacteria and fungal colony-forming units per cubic metre of air and standard deviation.

Two institutions presented indoor/outdoor (I/O) fungal ratios in the range 0.45-0.86, while values higher than 1 have been registered for the SJ School. Depending on classroom, variable I/O bacterial ratios, ranging from 0.62 and 1.95, have been found. Scheff et al.(2000) reported that, in a middle school of Springfield, the indoor fungal and bacterial counts were significantly higher than the outdoor concentrations. Conversely, Godwin and Batterman (2006) found that the outdoor bioaerosol levels exceeded indoor levels in 64 school classrooms in Michigan.

Total VOC concentrations could give information about the influence of aerosol sprays, solvents, cleaning agents, pesticides, paints and repellents. **Figure 3.3** shows a daily profile for the total VOC concentrations. SJ and SJB Schools exhibit very constant levels and

similar daily patterns. In the 183 School, there was a huge increase in the VOC concentrations around 13 pm, when pupil's art class was occurring with the use of glue and paints. This makes evident that collage and painting materials increase the VOC levels in indoor air. Zhang et al.(2006) also identified a visual art classroom with a relatively high level of VOCs. Standards have been agreed upon for total VOCs by Decree 79/2006 of the Portuguese Legislation that establishes the thermal regulations for buildings (RSECE, 2006). The results obtained in schools were above the proposed target guideline value of 600 μg m^{-3}.

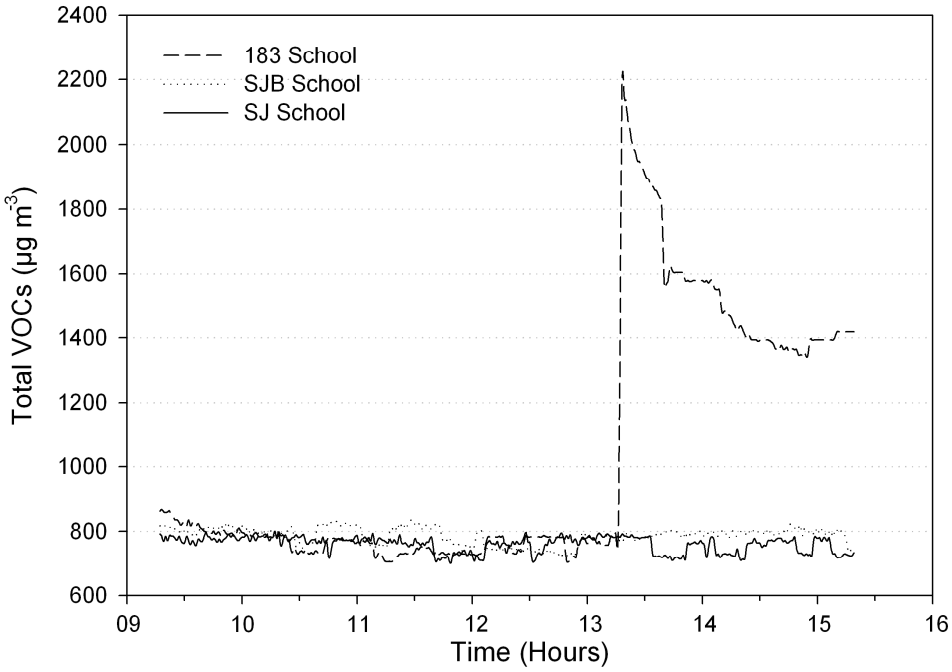

Figure 3.3 – Diurnal variation of total VOCs (non-methane hydrocarbons) in the three schools.

Table 3.4 present the results for the VOC concentrations and speciation. In general, concentrations of VOCs were higher indoors than outdoors for all schools. Those compounds that have only been detected in indoor air have a probable indoor source. Ethyl acetate,

methyl acetate, styrene, ethanol and limonene were only found in the indoor air. Pollutants identified in both indoor and outdoor samples, but with higher concentrations in the indoor environments, may indicate additional indoor sources or inadequate ventilation ratios. I/O ratios higher than 1 were observed for *n*-hexane, *n*-heptane, *n*-butyl-acetate and *o*-xylene at all the schools. I/O ratios exceeding the unity were also determined for pentane, toluene α-pinene, *n*-decane and terpinene, but not in all institutions. The measured benzene concentrations were below the annual ambient EU limit value of 5 μg m^{-3}. Toluene concentrations were higher than those reported by Stranger et al. (2008) in primary schools of Antwerp, Belgium. The high benzene and toluene concentrations observed in Lisbon are in the same range of those measured in schools of Oporto, Portugal (Madureira et al., 2009). In this preliminary study, the toluene levels were very similar to those found in schools of Curitiba, Brazil (Godoi et al., 2009).

Table 3.4 *- VOC concentrations (μg m^{-3}) in the three schools.*

COMPOUNDS	**SJB School**		**183 School**		**SJ School**	
	Indoor	**Outdoor**	**Indoor**	**Outdoor**	**Indoor**	**Outdoor**
Pentane	3.61	0.71	0.97	1.08	1.40	1.13
Methyl acetate	52.0	ni	34.0	ni	83.0	Ni
Ethyl acetate	2.08	ni	1.30	ni	3.55	Ni
***n*-Hexane**	2.98	0.53	1.15	0.62	1.06	0.84
Benzene	2.88	<ld	3.01	3.13	2.54	2.46
Ciclohexane	0.87	0.22	0.17	0.13	1.60	0.16
Isooctane	1.19	0.15	0.16	0.19	0.44	0.21
***n*-Heptane**	3.22	0.37	3.35	0.50	0.95	0.52
Toluene	10.3	2.00	2.51	2.58	4.59	2.93
***n*-Butyl acetate**	4.18	0.62	1.41	0.87	6.74	1.42

***m,p*-Xylene**	8.8	1.22	1.42	1.26	2.82	1.78
Styrene	ni	ni	ni	ni	0.28	Ni
***o*-Xylene**	3.09	0.39	1.05	0.46	5.45	0.57
***α*-Pinene**	0.50	ni	0.15	ni	4.27	0.16
Sabinene	0.77	ni	ni	0.14	12.2	0.17
***β*-Pinene**	ni	ni	ni	ni	29	Ni
***n*-Decane**	1.00	0.40	0.46	0.30	1.71	0.65
(+)-3-Carene	ni	ni	ni	ni	0.24	Ni
γ-Terpinene	0.65	ni	ni	0.18	0.78	0.23
Limonene	3.17	ni	0.39	ni	86	Ni

ld – below limit of detection; ni – not identified.

SJ School, which has the oldest building among all institutions, registered both the highest concentrations and diversity of VOC compounds. Perhaps the inadequate ventilation observed favours accumulation of pollutants with additional indoor sources. The highest levels of limonene, *β*-pinene, sabinene, *n*-butyl acetate, methyl acetate and formaldehyde (1.03 µg m^{-3}) were achieved in this school. *n*-Hexane, *n*-heptane and *n*-decane could have indoor sources in some architectural finishes, floor adhesives, PVC flooring, consumer products (e.g. floor waxes and aerosol air fresheners). Limonene could be derived from cleaning products, air fresheners and many other consumer products. Benzene, toluene, xylenes and styrene could be originated from engine vehicle exhaust, gasoline/fuel, tobacco smoke, solvent-based paints, floor adhesives, PVC flooring, carpeting, printed material and solvent-based consumer products (Mendell, 2007). The 183 School registered the lowest concentrations of VOCs, probably because this institution had better ventilation than the other schools, higher classroom volumes and lesser number of pupils.

3.4 Conclusions

Indoor and outdoor concentrations of NO_2, VOCs, formaldehyde and microbiological components were measured for the first time in three elementary schools in Lisbon during December 2008. The results suggest that schools with closed windows could have smaller I/O ratios of NO_2 (0.64), but higher indoor levels of VOCs (10.3 µg m^{-3}) and formaldehyde (1.03 µg m^{-3}) with an origin in building materials and consumer products. Total VOC concentrations increase during art classes, reaching about 2200 µg m^{-3}. Low ventilation ratios and the children's physical activities have also an impact upon the CO_2 levels. Fungal and bacterial counts exceeding 500 CFU m^{-3} for one school (765 CFU m^{-3}) and for all of them (934-1634 CFU m^{-3}), respectively, may be indicative of building-related sources, poor air exchange rates or overcrowding, highlighting the need for remedial action. Most of the assessed gaseous pollutants can be credited to the traffic emissions and indoor sources (some architectural finishes, floor adhesives, PVC flooring, consumer products and cleaning products). More studies are needed (currently underway), to find additional possible sources of indoor contamination; to calculate air exchange rates on a seasonal basis, to evaluate if there is a causal relationship between pollutant exposure and health symptoms in schools, and to assess if school IAQ can adversely affect academic performance or attendance.

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Chapter 4

4. INDOOR AIR QUALITY IN ELEMENTARY SCHOOLS OF LISBON IN SPRING

Published

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Abstract

Indoor air quality (IAQ) in schools usually presents higher levels of pollutants than outdoor environments. The aims of this study were to measure indoor and outdoor concentrations of NO_2, speciated volatile organic compounds (VOCs) and carbonyls at fourteen primary schools in Lisbon (Portugal). The investigation was carried out in May-June 2009. Three of the schools were selected to also measure comfort parameters, such as temperature and relative humidity, carbon dioxide (CO_2), carbon monoxide (CO), total VOCs, and bacterial and fungal colony-forming units per cubic metre. The indoor concentrations of CO_2 in the three main schools indicate inadequate classroom air exchange rates. The indoor/outdoor (I/O) NO_2 ratio ranged between 0.36 and 0.95. At the three main schools, the total bacterial and fungal colony-forming units (CFU) in both indoor and outdoor air were above the advised maximum value of 500 CFU m^{-3} defined by the Portuguese legislation. The aromatic compounds benzene, toluene, ethylbenzene and xylenes, followed by ethers, alcohols and terpenes, were usually the most abundant classes of VOCs. In general, the indoor total VOC concentrations were markedly higher than those observed outdoors. In all places, the indoor aldehyde levels were higher than those observed outdoors. This is particularly valid for formaldehyde. The inadequate ventilation observed likely favours accumulation of pollutants with additional indoor sources.

Key words: carbon dioxide, carbon monoxide, carbonyls, indoor air quality, nitrogen dioxide, schools, volatile organic compounds.

4.1 Introduction

Human exposure is the event when a person comes into contact with a pollutant of a certain concentration during a certain period of time (Ott et al., 2007). This means that exposure requires both the pollutant and the person to be present. 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 micro-environment is uniquely characterised, which is determined by the local outdoor air, specific building characteristics and indoor activities. Consequently, each individual's personal exposure will be determined by the different indoor micro-environments to which the person is exposed to, and the permanence time in each (Stranger et al., 2007).

Many studies are being conducted on indoor air pollution because most people spend a lot of their time indoors living, working, and studying (Lee et al., 2001a, 2002a, b; Li et al., 2001). Reports about buildings with air related problems have received increasing attention since the seventies (Hodgson, 1992; Spangler and Sexton, 1983). Sick building syndrome (SBS) is a commonly used term for symptoms resulting from problems with indoor air quality (IAQ). Complaints common to SBS include allergic rhinitis, headaches, flu-like symptoms, watering of eyes, and difficulty in breathing (Mishra et al., 1992). The first official study about SBS that examined more than one structure was published in 1984 (Finnigan et al., 1984).

IAQ 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. Therefore, odour and comfort complains have been related to IAQ problems in schools, as well as increased incidence of allergic, asthma and infectious diseases. Poor IAQ can also affect scholarly performances and attendance, since children are more vulnerable than adults to health risk from exposure to environmental hazards (Daisey et al., 2003; Godoi et al., 2009). The significance of IAQ in schools is underscored by the large number of worldwide studies: Blondeau et al. (2005), Chew et al. (2005), Godoi et al (2009), Godwin and Batterman (2007), Griffiths and Eftekhari (2008), Hodgson et al. (2004), Kim et al. (2007), Klinmalee

et al. (2009), Lee and Chang (2000), Meklin et al (2002), Mukerjee et al. (2009), Shendell et al. (2004), Sohn et al. (2007), Stranger et al. (2008), Zhang et al (2006). However, most of these studies concentrate on a specific group of pollutants or on thermal conditions. Multidisciplinary indoor field campaigns, measuring a wide range of health relevant chemical and physical properties, are still missing. Lisbon, the number of children with asthma and rhinitis is about 15% and 40%, respectively (Plácido, 2004), and the school work environment has not received much attention. Therefore, IAQ in Portuguese schools is almost unknown.

The main aims of this work were: (a) to measure indoor comfort parameters (temperature, relative humidity, CO, CO_2 and total VOCs) and bacterial and fungal contamination in three representative schools; (b) to evaluate VOCs, carbonyls and NO_2 gaseous pollutants, by passive sampling, in indoor and outdoor air at 14 schools, and (c) to identify possible sources, activities or other conditions contributing to the measured levels.

4.2 Materials and Methods

4.2.1 Description of Schools

Indoor and outdoor air samples were collected at fourteen schools with a wide geographical coverage representing the Lisbon urban area, in May and June 2009. Two classrooms from each of the fourteen schools were selected for this study. All the classrooms depend only on the natural ventilation through the doors and windows existent. Details of each sampling site are listed in **Table 4.1**.

Table 4.1 – Characteristics of each school**.**

Schools Characteristics	A	B	C	D	E	F	G	H	I	J	K	L	M	N
Urban environment	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Heating	X		X		X	X	X	X	X	X	X	X	X	X
Ventilation	Windows/Doors													
Blackboard and chalk	X		X		X	X	X	X	X	X	X	X	X	X
White board with pen		X		X										
Ceramic tile floor	X	X	X	X		X	X		X					X
Vinyl floor					X						X	X		
Wood floor								X		X			X	
Animals inside		X					X	X	X					
Plants inside		X			X			X						X
Area (m^2)	64.51	46.82	50.14	51.2	46.95	62.68	63.7	50.08	36.5	50.34	48.36	51.2	49.77	46.68
Height (m)	3.7	3.5	3.5	3.2	3.15	3.4	3	3.2	2.23	3.2	3.8	3.2	3.7	2.64

4.2.2 Comfort parameters and airborne microorganisms

For comfort parameters and airborne microorganisms three of the fourteen schools were selected: schools A, B and C. These schools were previously considered representative of all the elementary-level educational institutions (Khan et al., 2007a, b). Continuous measurements of temperature, relative humidity (RH), CO_2 and total VOCs were performed with an automatic portable Indoor Air IQ-610 Quality Probe (GrayWolf® monitor) in one classroom of each school during the 8 hour occupancy periods. This IAQ monitor includes a Pt100 probe for measuring temperature, a capacitance probe to sense RH and a CO_2 non-dispersive infrared sensor, all of them with an extremely fast response. The monitor also includes a photo-ionisation detector to track total VOCs over time. It displays measurements in real time allowing logged data to be downloaded to WolfSense® PC software for analysis. The equipment was supplied with a factory calibration certificate, but it is checked prior to next use with appropriate calibration kits. Indoor CO_2 levels are an indicator of the adequacy of outdoor air ventilation relative to indoor occupant density.

Bacterial and fungal colony-forming units per cubic metre of air (CFU m^{-3}) were monitored by liquid impinger sampling (May and Harper, 1957) in the two classrooms and playgrounds during one day in each one of the 3 main schools. The flow rate was set at 2.5 L min^{-1}. In each sampling place (classrooms and playgrounds), one-hour samples were taken. To obtain representative results, five replicates were obtained per site.

4.2.3 Sampling and analysis of VOCs, carbonyls and NO_2

VOCs and carbonyls were sampled in parallel using Radiello® (Fondazione Salvatore Maugeri, Padova, Italy) diffusive passive tubes (cartridges codes 130 and 165, respectively) for 14 consecutive days. In each sampling place, for each one of these two groups of compounds, two replicate samples were collected. Indoor samples were collected at a height of about 1.5 m above the floor. The diffusive samplers were positioned at a distance that should exceed 1 m from a window or a door. Outdoor passive samples were collected at heights of about 2 m above the ground. The VOC adsorbing cartridges consist of 60 mm length stainless steel net cylinders, with 100 mesh grid opening and 5.8 mm diameter, packed with 530±30 mg of activated charcoal with a particle size of 35-50 mesh (Cocheo et al., 1996).

VOCs were extracted from the exposed samplers with 2 ml carbon disulfide (CS_2 from Aldrich) containing 2-fluorotoluene (from Aldrich) as an internal standard. The glass vials were shaken for approximately 30 min. The analyses of the extracts were performed by gas chromatography (Chrompack CP 9001) coupled to a flame ionisation detector (GC/FID), using nitrogen carrier gas at constant pressure of 20 psi. A 100% dimethylpolysiloxane column (0.2 mm, 50 m, film thickness 0.5 μm) was used. The temperature program was as follows: 50°C for 5 minutes, 5°C min^{-1} up to 80°C, 15°C min^{-1} up to 135°C, 20°C min^{-1} up to 220°C, final isotherm for 20 minutes. Injector and detector temperatures were 240°C and 300°C, respectively. The equipment was calibrated before and during the analyses of samples by injecting standard solutions of all compounds identified in CS_2, specifically: pentane, *n*-hexane, ciclohexane, *n*-heptane, *n*-butyl acetate, styrene, *α*-pinene, sabinene, *β*-pinene, *n*-decane, (+)-3-carene, limonene (all from Fluka), methyl acetate, ethyl acetate, isooctane, *m,p*-xylene, *o*-xylene (all from Merck), benzene

(AnalytiCals), toluene (Lab-Scan), and γ-terpinene (Aldrich). Four standard solutions, each one containing five compounds in CS_2, have been prepared. The analytes in these four standard solutions were present in concentrations of 40 ng μl^{-1}, 20 ng μl^{-1}, 10 ng μl^{-1} and 5 ng μl^{-1}. The limit of detection was calculated for ethyl acetate, ciclohexane, isooctane, *n*-heptane, toluene, *n*-decane and limonene. Depending on the analyte, the limit of detection (LOD= 3.3(s/S), where s is the STDEV of areas and S is the slope), ranged from 0.34 to 2.52 ng μl^{-1} (Pegas et al., 2010). This corresponds to environmental concentrations between 0.27 and 2.97 $\mu g\ m^{-3}$.

Carbonyls collected in cartridges filled with 2,4-dinitrophenylhydrazine reacted to give the corresponding 2,4-dinitrophenylhydrazones. These were extracted with 2 ml of acetonitrile (from Fisher Scientific). The glass vials were shaken for approximately 30 min and the extract filtered through 0.45 μm disc membrane filters (filtration kit RAD 174) and injected into the high-performance liquid chromatography (HPLC) system. The analytical system consisted of a Jasco PU- 980 pump, a Rheodyne manual injection valve (sample loop of 20 μl), a Supelcosil LC-18 column (250×4.6mm; 5μm; Supelco) and a Jasco MD-1510 diode array detector, all connected in series. Isocratic elution at room temperature was performed using an acetonitrile/water solution (60/40, v/v) as the mobile phase at a flow rate of 1.5 ml min^{-1}. The carbonyl concentrations were quantified with external calibrations curves constructed from standard solutions of TO11/IP6A carbonyl – DNPH Mix (from Supelco). The limit of detection (LOD) ranged from 1.29 to 2.09 $\mu g\ ml^{-1}$, depending on the analyte.

NO_2 concentrations were also passively monitored for fourteen days. The diffusive tubes (with steel grids impregnated with triethanolamine) chemiadsorb NO_2, as nitrite, which was quantified by visible spectrophotometry (Bhugwant and Hoareau, 2003).

4.3 Results and Discussion

4.3.1 Comfort parameters and airborne microorganisms

The daily variation of comfort parameters throughout the two-week monitoring period was performed. To illustrate contrasting conditions, two specific days were chosen to exemplify the daily profiles. The mean daily temperature and RH values during the monitoring period, taken at the three main schools, ranged from 21.9 ± 1.09^{o}C to 25.9 ± 1.56^{o}C and from 34.6 ± 3.49% to 56.2 ± 3.28%, respectively (**Figure 4.1**). In general, the temperature varied between 18.6^{o}C and 28.2^{o}C, whereas RH was in the 25.1-66.8% interval. Thermal comfort requirements differ for each individual due to factors such as clothing, activity level, age, and physiology. ANSI/ASHRAE Standard 55-2004 describes the temperature and humidity ranges that are comfortable for 80% of people engaged in chiefly sedentary activities. These values were conceived for adults in office environments and presume “normal indoor clothing". The effects of moderate heat stress on the performance of office work in subjects aged 18-29 years were evaluated through questionnaires by Witterseh et al. (2004). Raised temperature increased eye, nose and throat irritation ($P < 0.05$), headache intensity ($P < 0.05$), difficulty in thinking clearly ($P < 0.01$) and concentrating ($P < 0.01$), and decreased self-estimated performance. Usually, the recommended indoor temperature ranges for comfort are from 20 to 23ºC in the winter and from 23 to 26ºC in the summer. The suggested indoor RH values for comfort are in the range 30-60%. Control of RH also helps limit the growth of microorganisms. Maintaining RH below 50% inhibits mould growth, dust mite infestations, and bacteria. If RH levels fall below 25%, building occupants can experience respiratory irritation and possibly dry, itchy eyes and skin. Generally, in every school studied, the temperature and RH values were within the recommended ranges.

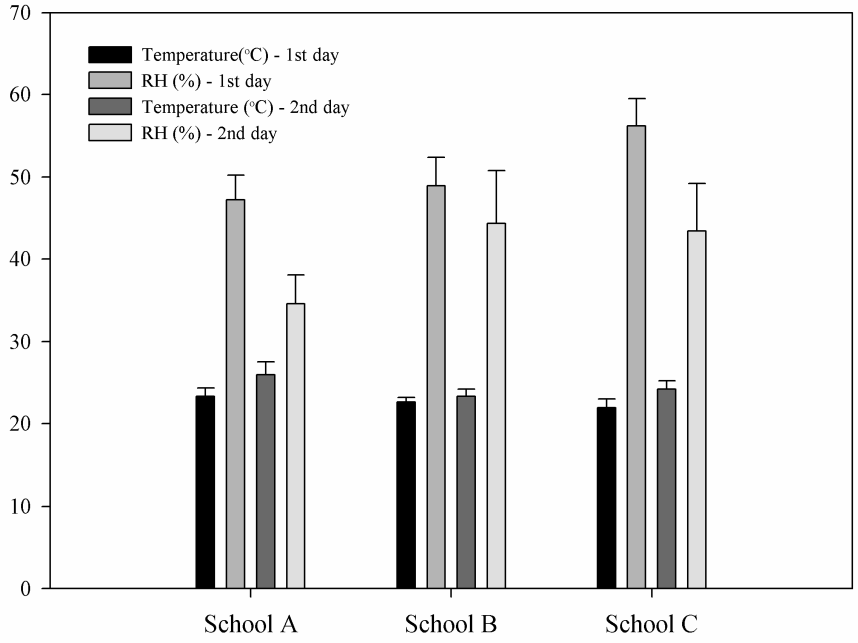

Figure 4.1 - Indoor daily mean temperature (^{o}C) and relative humidity (RH) (%). Bars indicate the standard deviations (STDEV).

The National System for Energy and Indoor Air Quality Certification of Buildings (*Regulamento dos Sistemas Energéticos de Climatização de Edifícios* - RSECE) establishes an acceptable maximum value (AMV) of CO_2 of 1800 mg m^{-3} for buildings in Portugal (RSECE 2006). CO_2 levels ranged widely (705 to 6821 mg m^{-3}) and exceeded 1800 mg m^{-3} in all the three main schools. Carbon dioxide concentrations are often used as a surrogate of the rate of outside supply air per occupant. Indoor CO_2 levels above about 1000 ppm are normally considered as indicative of ventilation rates that are unacceptable with respect to body odours. Concentrations of CO_2 below 1000 ppm do not always guarantee that the ventilation rate is adequate for removal of air pollutants from indoor sources (Daisey et al., 2003). The indoor concentrations of CO_2 showed inadequate classroom air exchange rates. **Figure 4.2** depicts the variation of indoor CO_2 concentrations in a typical working day in the three main schools. A strong correlation of the CO_2 levels with occupancy has been observed. CO_2 spikes were even more pronounced when students started physical activities inside the classrooms, such as art classes or entrance and exits to the playgrounds. Seppanen

et al. (1999) reviewed available literature for the association between both ventilation rates and CO_2 concentrations and health. The authors were not able to determine a clear threshold value for CO_2 below which further reductions in concentration were not associated with further decreases in SBS symptoms. However, 7 of the 16 reviewed studies suggested that the risk of SBS symptoms continued to decrease with decreasing CO_2 concentrations below 800 ppm. Mostly, CO_2 measurements in schools indicate that the most classrooms probably do not meet the ASHRAE Standard 62-1999 for minimum ventilation rate of 2.5 l s^{-1} per person. Concentrations of a variety of pollutants emitted by occupants and building materials and furnishings will be higher under these conditions than if the ASHRAE ventilation standard was met. The potential for increased risks of contracting certain communicable respiratory illnesses, such as influenza and common colds, in classrooms with low ventilation rates is higher than in adequatly ventilated places (Fisk, 2001).

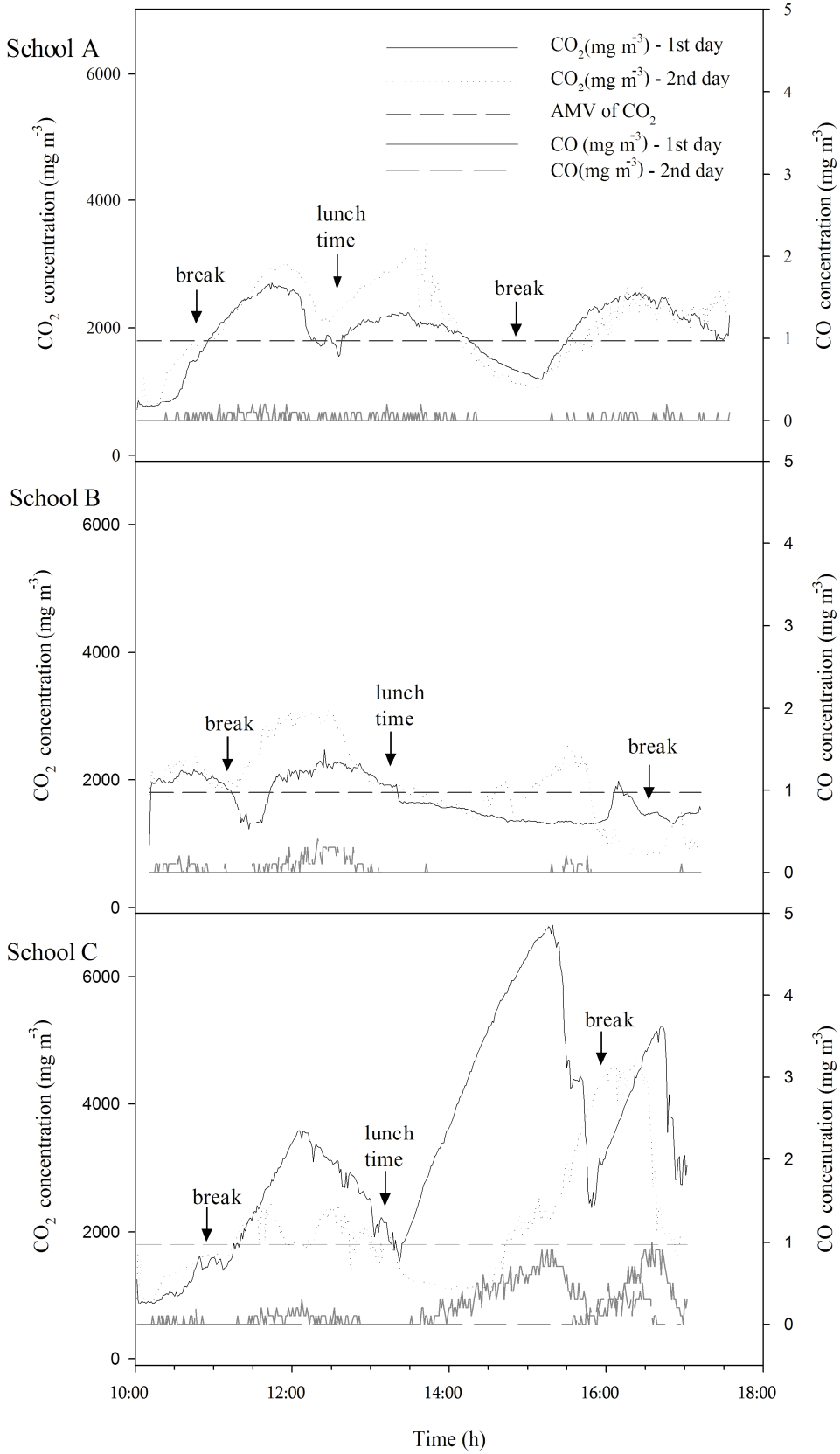

Figure 4.2 - Indoor carbon dioxide and carbon monoxide levels in the three main schools.

CO levels ranged from 0.0 to 1.0 mg m^{-3} (**Figure 4.2**) and did not exceed 12.5 mg m^{-3}, the recommended exposure limit (RSECE 2006). To prevent carboxy-hemoglobin levels in the blood from exceeding 2.5%, the World Health Organisation (WHO) has set specific air quality guidelines for distinct averaging periods: 100 mg m^{-3} (15 min), 60 mg m^{-3} (30 min), 30 mg m^{-3} (1 h) and 10 mg m^{-3} (8 h) (Chaloulakou et al., 2003). CO is one of the most characteristic traffic pollutants usually observed in urban areas. However, in this study, concomitant increases of CO_2 and CO concentrations were observed. This suggests a linear correlation between both CO and CO_2 (r=0.787), and a direct relationship between increasing concentrations and classroom occupancies. CO is produced as a by product of incomplete combustion of organic materials. In the human body, CO is produced endogenously by the class of enzymes known collectively as heme oxygenase (Mines, 1997). CO is detectable in small quantities in the exhaled air of health people (Zayasu et al., 1997). Exhaled CO is increased in patients with inflammatory pulmonary diseases such as bronchial asthma, bronchiectasis, upper respiratory tract infections, and seasonal allergic rhinitis (Zayasu et al., 1997). This is supported by the fact that inhaled corticosteroids inhibit the increase in exhaled CO in asthmatic patients (Zayasu et al., 1997). According to Jones and Lam (2006), human exposure to microenvironments with high CO levels can increase exhaled CO concentrations. Thus, exhaled CO levels can potentially act as a functional indicator of air pollutant levels. In the city of Lisbon the most common sources of the total CO emissions are vehicle exhausts (Borrego et al., 2000). Taking into account the CO levels recorded by the 3 monitoring stations close to the 3 main schools, mean I/O ratios close to zero were obtained. The highest CO levels were registered in the school located near one of the busiest streets of Lisbon (Avenida da Liberdade). The average daily concentrations measured on the air quality monitoring station in this street were in the range 0.36-0.52 mg m^{-3}. Based on a comprehensive literature review, the INDEX project (Kotzias et al., 2005), concluded that current CO sources in EU residences contribute essentially to short-term, rather than long-term, exposures.

Very few measurements of total VOCs in a typical school-day are reported in the scientific literature (e.g. Pegas et al., 2009, 2010). Total VOC concentrations could give information about the influence of aerosol sprays, solvents, cleaning agents, pesticides, paints and repellents. The measurements ranged from L.O.D. (< 0.005 mg m^{-3}) to 2.1 mg m^{-3}

^{3} and did not surpass the recommended value of 0.6 mg m^{-3} (RSECE 2006) (**Figure 4.3**). Peak concentrations of VOCs were observed around 10 A.M. at school A, on the first day, decreasing progressively thereafter. This may be explained by the fact that, on this particular day, classrooms were cleaned with VOC-release products in the morning, before classes start. Normally, the cleaning staff tidy up the rooms at the end of the day. An increase in concentrations was also observed at School B during a period coincident with an art class where glue and paints were in use. This makes evident that collage and painting materials can significantly enhance the VOC levels in indoor air. Zhang et al. (2006) also identified a visual art classroom with a relatively high level of VOCs.

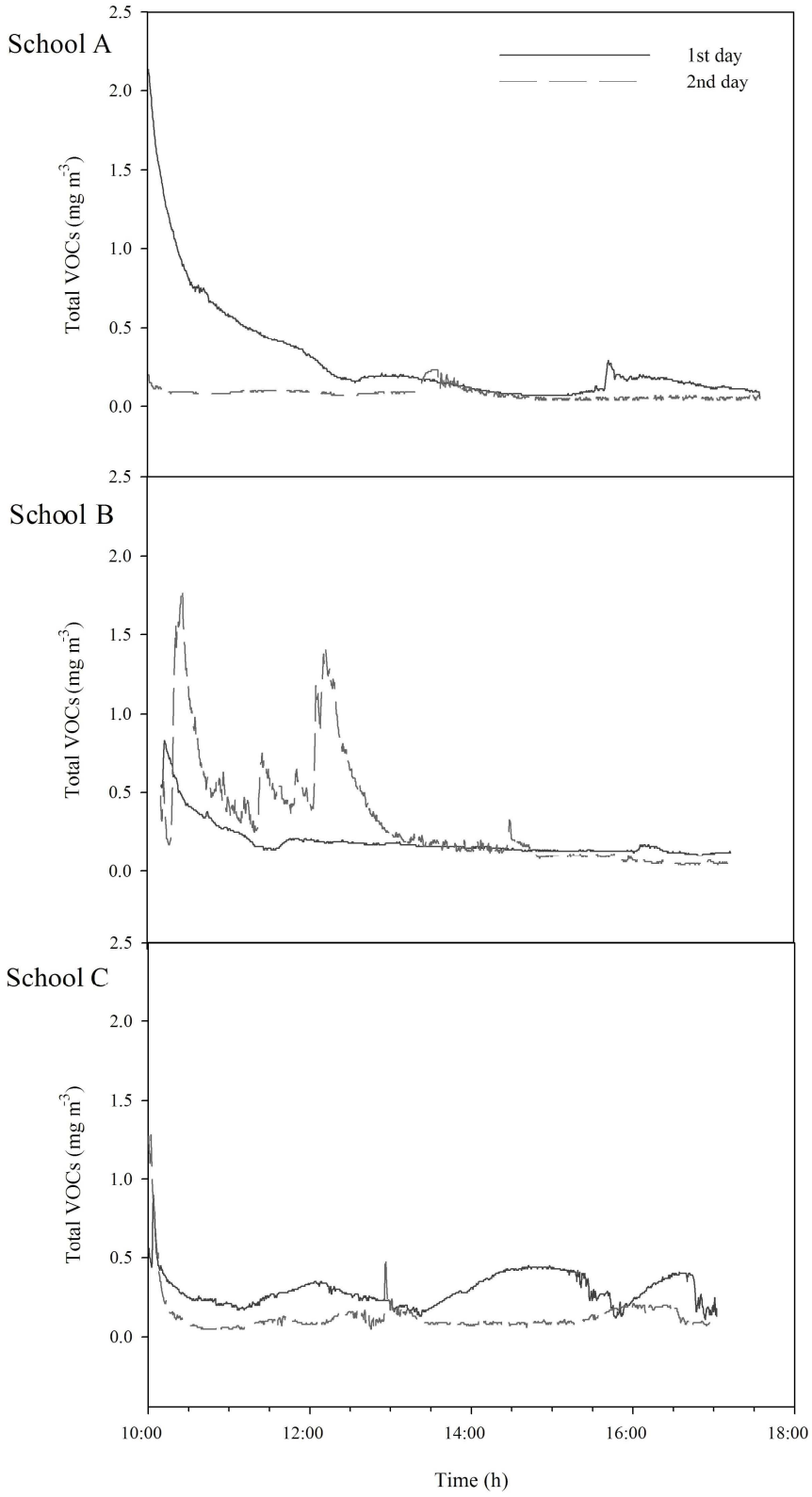

Figure 4.3 - Diurnal variation of total VOCs (non-methane hydrocarbons) in the three main schools.

Table 4.2 shows indoor and outdoor average levels of total bacterial and total fungal CFU m^{-3}. In all schools, the total fungal and total bacterial colony-forming units in both indoor and outdoor air were above the AMV of 500 CFU m^{-3} defined by the Portuguese Legislation, Decree-Law 79/2006 (RSECE 2006). The main factors affecting atmospheric dispersion and survival of microorganisms are the relative humidity, temperature, oxygen, wind and air turbulence, air pollutants and water and nutrient availability. Very high levels of microorganisms were obtained in all five replicates performed for every sampling site. The repetition of the whole experience one week apart (again with five replicates) was carried out to confirm the huge microbial counts. It was necessary to count some quadrants of the Micropore filters (0.45 µm) to extrapolate for all quadrants of each filter and estimate the minimum CFU number per sample. The high amounts of bacteria in both indoor and outdoor environments may derive from several factors, including high seasonal level of bioaerosols in outdoor air (spring), and human self-activities, such as breathing, sweating and movement causing particle resuspension.

High bacteria counts were probably due to high occupancy loading, poor hygienic condition of occupants, inadequate ventilation rates, movement of textiles, food products, etc. (Lee et al., 2002; Mentese et al., 2009). Scheff et al. (2000) reported that, in a middle school of Springfield, the indoor fungal and bacterial counts were significantly higher than the outdoor concentrations. Similarly, Jo and Seo (2005) reported, for both the total bacteria and the total fungi, higher indoor concentrations compared to the outdoor environment at 11 elementary schools in Korea. Mentese et al. (2009) studied different indoor and outdoor environments in terms of bioaerosol contamination. The highest total bacteria counts were measured in kindergartens, primary schools, restaurants, high schools, and homes, while the highest mould levels were observed in kitchens, bathrooms, and offices. Gonçalves et al. (2010) studied indoor and outdoor atmospheric fungal spores in the Sao Paulo metropolitan area (Brazil), and obtained levels above 36000 CFU.

Table 4.2. Measurement results for microorganisms.

School A		
	Bacterial (CFU m^{-3})	**Fungal (CFU m^{-3})**
Indoor I	≥ 27051	≥ 2023
Outdoor	≥ 25651	≥ 2697
Indoor II	≥ 29009	≥ 1802
School B		
	Bacterial (CFU m^{-3})	**Fungal (CFU m^{-3})**
Indoor I	≥ 30423	≥ 2023
Outdoor	≥ 14096	≥ 2930
Indoor II	≥ 22123	≥ 1945
School C		
	Bacterial (CFU m^{-3})	**Fungal (CFU m^{-3})**
Indoor I	≥ 39838	≥ 1335
Outdoor	≥ 39838	≥ 1698
Indoor II	≥ 39838	≥ 1958

4.3.2 VOCs, carbonyls and NO_2

The aromatic compounds benzene, toluene, ethylbenzene and the xylenes, followed by ethers, alcohols and terpenes, were usually the most abundant classes of VOCs. Indoor total VOC concentrations were generally markedly higher than those observed outdoors

(**Figure 4.4** and **Table 4.3**). The sum of the individual VOC concentrations in indoor air varied from 37 to 317 μg m^{-3}. Outdoor concentrations ranged between 6 and 80 μg m^{-3}. In general, all the different classes of VOCs presented higher concentrations indoors than outdoors. Ethanol, dichloromethane, 1,2-dichloropropane, propyl acetate methylcyclohexanol, 2,2-dimethylbutane and 4-methyl-2-pentanone were only found in the indoor air. Those compounds that have only been detected in indoor air have a probable indoor source. Pollutants identified in both indoor and outdoor samples, but with higher concentrations in the indoor environments, may indicate additional indoor sources or inadequate ventilation ratios. For example, terpenes are well-known as emitted substances from cleaning products and room fresheners (Singer et al., 2006). Additionally, α-pinene is an intrinsic component in wood and furniture (Yrieix et al., 2010). Other VOC sources in indoor air include cooking fuels, aerosols propellants, refrigerants, paints, varnishes, cosmetics, adhesives, biocides, disinfectants, printed paper, etc. (Srivastava et al., 2004). The observed indoor levels in school C may be the reflex of inefficient ventilation conditions (windows and doors were always closed), and cooking activities in the same building of the classrooms. The school E presented both the highest aliphatic hydrocarbon and ester levels in comparison with other schools, probably due to the fact that the building was recently painted. The highest aromatic hydrocarbon concentrations were observed at school K, more likely due to its location in a street canyon with intense traffic.

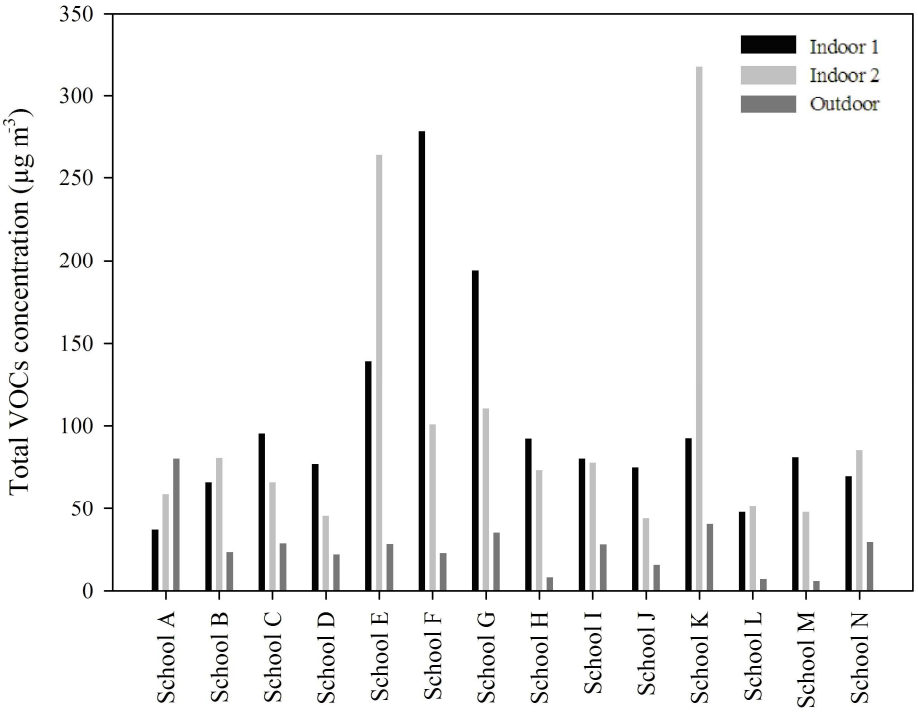

Figure 4.4 - Indoor (2 classrooms) and outdoor VOC concentrations (sum of all compounds identified).

Table 4.3 – Indoor and outdoor VOC and carbonyl concentration (μg m^{-3}) in all schools**.**

			Aliphatic Hydrocarbons	Aldehydes and Ketones	Ethers and Alcohols	Aromatic Hydrocarbons	Terpenes	Esters	Halogenated Hydrocarbons	Others
School A	Indoor	I	3.8	8.0	18.2	5.0	0.24	9.4	-	0.55
		II	5.5	15.0	25.7	6.4	0.75	11.1	-	9.16
	Outdoor		3.8	4.5	52.0	17.6	2.9	3.2	-	0.75
School B	Indoor	I	4.1	12.8	28.3	5.9	3.1	20.9	-	2.98
		II	5.6	31.2	31.2	9.0	4.6	29.1	-	0.94
	Outdoor		2.1	3.7	17.9	3.4	-	-	-	-
School C	Indoor	I	8.4	29.7	36.9	12.6	7.5	27.0	-	0.86
		II	8.0	17.2	27.8	10.2	5.2	13.2	-	1.14
	Outdoor		3.7	4.2	20.0	4.6	0.31	-	-	-
School D	Indoor	I	6.5	18.1	29.4	6.7	7.51	25.3	-	1.2
		II	6.0	10.0	23.9	4.0	2.8	3.5	-	4.6
	Outdoor		2.1	3.3	16.0	2.9	0.55	-	-	0.36
School E	Indoor	I	18.5	32.3	47.7	17.5	7.9	38.7	-	7.1
		II	43.6	29.5	79.7	27.6	13.3	79.1	0.12	19.0
	Outdoor		3.0	17.6	18.3	4.7	0.22	1.9	-	0.26
School F	Indoor	I	3.9	22.5	245.4	4.0	4.6	8.8	-	10.8
		II	3.1	26.2	29.8	3.7	4.4	59.3	-	0.35
	Outdoor		2.3	3.2	16.8	3.4	0.16	-	-	-
School G	Indoor	I	16.4	53.6	48.3	46.5	10.2	12.9	0.41	57.9
		II	7.0	24.8	60.3	14.4	6.5	18.5	-	3.2
	Outdoor		2.9	3.2	26.5	4.2	0.56	0.71	-	0.23
School H	Indoor	I	5.6	33.1	25.5	6.4	40.3	13.8	-	0.61
		II	3.3	29.2	17.6	5.1	28.3	18.6	-	0.33
	Outdoor		2.5	5.2	-	3.2	0.29	-	-	0.12
School I	Indoor	I	5.6	33.7	8.7	19.0	4.69	37.9	-	4.5
		II	4.6	25.8	15.6	10.8	4.19	38.7	-	3.0
	Outdoor		2.5	4.1	20.4	4.0	0.49	0.37	-	0.20
School J	Indoor	I	2.7	15.2	44.4	5.6	9.87	8.5	-	3.9
		II	3.7	20.0	19.3	4.3	7.87	7.3	-	1.4
	Outdoor		1.5	3.0	11.7	2.2	0.12	-	-	-
School K	Indoor	I	4.4	21.2	40.2	8.1	9.3	27.7	-	1.1
		II	20.7	19.3	127.3	69.9	4.2	17.8	-	77.5
	Outdoor		3.6	3.4	30.1	5.1	0.57	0.58	-	0.29
School L	Indoor	I	3.8	11.8	18.8	10.8	1.5	10.6	-	2.4
		II	5.4	11.1	21.3	9.8	2.6	10.8	-	1.0
	Outdoor		3.2	3.4	-	3.7	0.14	-	-	0.21
School M	Indoor	I	4.4	10.1	26.6	9.0	6.2	29.8	-	1.8
		II	2.4	17.5	32.6	3.6	4.5	4.5	-	0.11
	Outdoor		2.5	3.9	-	3.1	0.16	-	-	-
School N	Indoor	I	3.1	22.4	33.0	9.0	2.4	21.1	-	0.45
		II	10.6	19.3	21.4	19.8	10.6	19.1	-	3.8
	Outdoor		2.4	2.9	23.4	3.7	-	-	-	-

Notes: - : not identified

Aliphatic Hydrocarbons: Pentane, 2,2-Dimethylbutane, *n* -Hexane, Isooctane, *n* -Heptane, Octane, Nonane, *n* -Decane;

Aldehydes and Ketones: Formaldehyde, Acetone, 4-Methyl-2-Pentanone, Acetaldehyde, Propynaldehyde, Benzaldehyde;

Ethers and Alcohols: Methanol, Ethanol, Isopropanol, Butanol, 2-Ethoxyethanol, Methylcyclohexanol;

Aromatic Hydrocarbons: Benzene, Ethylbenzene, *m+p* -Xylene, Styrene, *o* -Xylene, Naphfthalene;

Terpenes: α -Pinene, (+)-Sabinene, β -Pinene, (+)-3-Carene, γ -Terpinene, Isoprene, Limonene, Eucalyptol;

Esters: Methyl acetate, Ethyl acetate, Propyl acetate, *n* -Butyl acetate;

Halogenated Hydrocarbons: Dichloromethane, 1,2-Dichloropropane;

Others: Cyclohexane, Methylcyclohexane.

Among all monitored VOCs, benzene, toluene, ethylbenzene and xylenes (BTEX) are of particular interest due to their known carcinogenic effects (Kotzias et al., 2009). Indoor and outdoor BTEX concentrations are summarised in **Table 4.4**. Benzene concentrations were higher for all indoor environments, ranging from 0.2 to a maximum of 0.9 μg m^{-3}. All measurements were below the EU limit value of 5 μg m^{-3} for mean annual exposure to benzene. However, as it is a carcinogenic compound, the WHO has not yet established a guide or safe value (WHO 2000). Toluene is a ubiquitous indoor pollutant (Bruno et al., 2008). Its indoor concentrations were higher than the corresponding outdoor levels, ranging from 0.9 to 7.3 μg m^{-3}. Concentrations of ethylbenzene comprise values from 0.3 to 14.2 μg m^{-3}, whereas the xylene isomers, *m*+*p*-xylene and *o*-xylene, were in the ranges 0.6 – 40 μg m^{-3} and 0.2 – 13.5 μg m^{-3}, respectively. Results for BTEX in this study correlate well with those of Stranger et al. (2007), except for toluene. The high benzene and toluene concentrations observed in Lisbon are in the same range of those measured in schools of Oporto, Portugal (Madureira et al., 2009). Toluene levels were very similar to those found in schools of Curitiba, Brazil (Godoi et al., 2009). The BTEX levels in schools of Lisbon are far below the weekly average concentrations in non-residential indoor environments, such as libraries, pharmacies, offices, gymnasiums, newspaper stands, copy centres, coffee shops, etc., in Bari, Italy (Bruno et al., 2008). BTEX values were much lower than the WHO guidelines from 2000 (260 μg m^{-3} over one week for toluene and 4.8 mg m^{-3} over 24 h for xylenes). However, some studies have correlated exposure to low concentrations of benzene and toluene with increased risks of cancer or eye and airway irritations (Guieysse et al., 2008).

The highest indoor VOC concentrations were found in schools E, F, G and K. A possible indoor source in schools E and K was the vinyl flooring and floor adhesives, which are described as emitter materials, especially of benzene, toluene, xylenes, styrene, and ethylbenzene, among others (Mendell, 2007). In addition to these indoor sources, the inadequate ventilation (closed windows) likely favours accumulation of pollutants. New furniture and/or the fact of being a new building could also explain the high levels in school E. The VOC loads in school G are possibly related to the proximity to congested motorways surrounding the city. School F is located close to an old cigarette factory, near motorways, in an area without green spaces and with urban planning deficit. These housing conditions may have contributed to the high concentrations of ethers and alcohols. Better ventilation

conditions, lower occupancy density and larger classrooms in school A in relation to other institutions, may explain the low indoor levels observed at that school.

Table 4.4 – Overview of indoor and outdoor BTEX concentration in fourteen schools in Lisbon.

			BTEX (µg m^{-3})				
			Benzene	**Toluene**	**Ethylbenzene**	**m+p-Xylene**	**o-Xylene**
School A	**Indoor**	**I**	0.3	1.98	0.73	0.95	0.99
		II	0.29	2.2	0.84	1.78	1.25
	Outdoor		0.38	5.31	2.67	6.68	2.53
School B	**Indoor**	**I**	0.31	2.12	0.54	1.04	1.89
		II	0.34	6.45	0.73	0.7	0.82
	Outdoor		0.31	1.56	0.39	0.86	0.24
School C	**Indoor**	**I**	0.34	2.14	1.66	3.54	4.96
		II	0.33	1.96	1.39	3.04	3.45
	Outdoor		0.37	1.74	0.57	1.4	0.47
School D	**Indoor**	**I**	0.36	2.83	1.11	1.86	0.55
		II	0.28	1.99	0.33	0.87	0.34
	Outdoor		0.29	1.24	0.34	0.77	0.23
School E	**Indoor**	**I**	0.37	5.34	2.58	6.18	2.99
		II	0.29	7.31	4.37	9.38	5.42
	Outdoor		0.35	1.91	0.62	1.32	0.46
School F	**Indoor**	**I**	0.3	1.63	0.59	1.01	0.52
		II	0.22	1.45	0.5	0.92	0.56
	Outdoor		0.29	1.41	0.44	0.89	-
School G	**Indoor**	**I**	0.27	4.47	14.18	19.71	7.9
		II	0.28	2.91	1.58	3.28	6.38
	Outdoor		0.36	1.84	0.48	1.16	0.38
School H	**Indoor**	**I**	0.26	1.98	0.97	2.2	0.93
		II	0.23	1.81	0.73	1.7	0.63
	Outdoor		0.27	1.28	0.33	0.99	0.34
School I	**Indoor**	**I**	0.41	5.55	2.6	5.35	5.06
		II	0.41	3.21	1.17	2.39	3.6
	Outdoor		0.26	1.79	0.48	1.14	0.35
School J	**Indoor**	**I**	0.29	1.72	0.6	0.94	2
		II	0.32	1.59	0.29	0.92	0.56
	Outdoor		0.26	0.87	0.9	0.62	0.2
School K	**Indoor**	**I**	0.32	3.13	1.18	2.65	0.79
		II	0.49	2.61	13.97	40.01	9.71
	Outdoor		0.45	5.74	0.43	1.17	0.37
School L	**Indoor**	**I**	0.28	1.42	0.58	1.33	7.18
		II	0.31	5.5	0.48	1.15	2.4
	Outdoor		0.33	1.42	0.64	1	0.27
School M	**Indoor**	**I**	0.94	4.34	1	1.81	0.95
		II	0.28	1.47	0.47	0.96	0.36
	Outdoor		0.22	1.35	0.31	0.97	0.27
School N	**Indoor**	**I**	0.31	1.52	0.74	1.6	4.87
		II	0.28	2.01	1.22	2.8	13.46
	Outdoor		0.4	1.6	0.44	0.98	0.27

Note: - not identified

In all places, the indoor concentrations of atmospheric aldehydes (formaldehyde, acetaldehyde, propionaldehyde and benzaldehyde) were higher than those outdoors. This is particularly valid for formaldehyde (**Figure 4.5**), classified as a human carcinogenic by the International Agency for Cancer Research. Formaldehyde concentrations ranged from 1.48 to 42.3 μg m^{-3}. Higher levels in classrooms than outdoors suggest that indoor sources are more important contributors to the indoor levels than outdoor sources, such as infiltration of vehicle exhaust (Ongwandee et al., 2009). Formaldehyde could be originated from composite wood and other products with urea-formaldehyde resin, some architectural finishes, tobacco smoke and other combustion processes (Mendel, 2007). Concentrations of formaldehyde are significantly affected by season and age of the buildings (Dingle and Franklin, 2002). It was observed that levels are higher in the presence of furniture bought new or restored less than one year before measurements (Lovreglio et al., 2009). In spring and summer, outdoor formaldehyde levels increase due to the acceleration of the photochemical activity (Lee et al., 2001b), while the opposite trend is observed indoors, since the interchange rate between indoor–outdoor air is higher due to open windows or the use of air conditioning (Pilidis et al., 2009). The highest level of formaldehyde was observed at school G. The high levels may be related to the fact that this institution is located in the vicinity of major motorways with very intense traffic. It should be also noted that the ceilings were painted during the Shrovetide period and new furniture was purchased just one month before the sampling campaign. In addition, the school corridors are wood coated. Pressed wood products use adhesive containing urea formaldehyde that can break down, releasing formaldehyde into the air. Formaldehyde is also found as a preservative in paint. Acute symptoms from formaldehyde exposures have sometimes been found including eye, nose and throat irritation, as well as lower airway and pulmonary effects (Kotzias et al., 2009). Among the identified aldehydes, formaldehyde was the most abundant. However, other carbonyl compounds were also present at appreciable amounts: acetaldehyde (0.88-7.02 μg m^{-3}), propynaldehyde (0.48-2.28 μg m^{-3}), and benzaldehyde (0.03-0.96 μg m^{-3}).

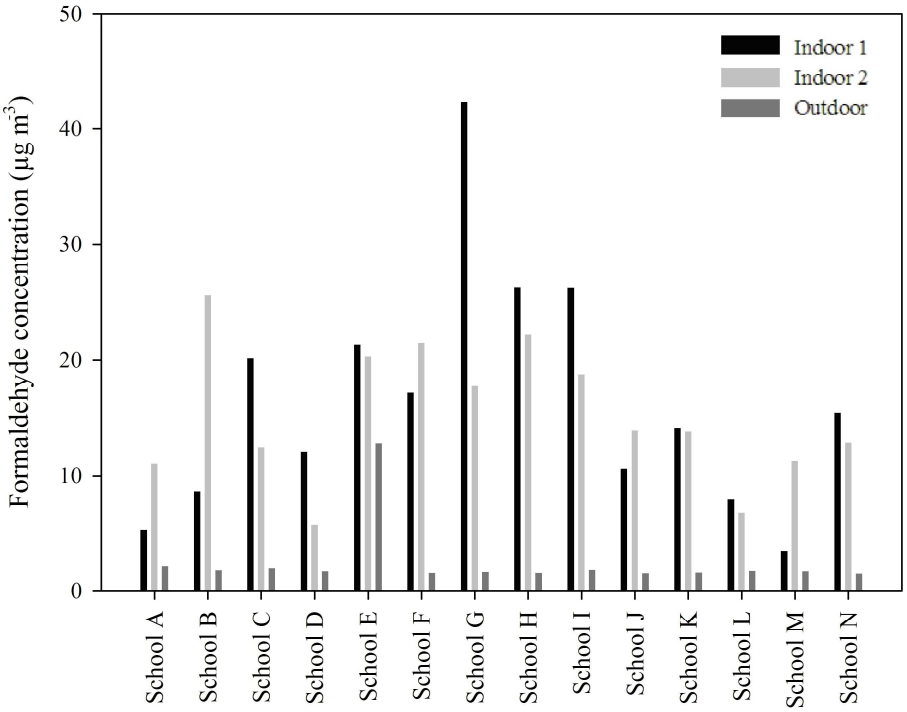

Figure 4.5 - Formaldehyde concentration in all schools.

Animal and human experimental studies indicate that NO_2 at short-term concentrations exceeding 200 μg m^{-3} is a pollutant with significant health effects (Kraft et al., 2005). Exposure to NO_2 at hourly peak levels of the order of ≥ 80 ppb, compared with background levels of 20 ppb, was associated with a significant increase of sore throat, colds and absences from school (Pilotto et al., 1997). The average NO_2 concentrations were higher outdoors than indoors (**Table 4.5**), probably as a result of vehicular exhaust emissions from nearby traffic. The I/O NO_2 ratios ranged between 0.36 and 0.95. Indoor NO_2 levels were within the interval 15 – 37 μg m^{-3}, not exceeding the current WHO guideline value of 40 μg m^{-3} (annual mean) to protect the public health. School E, which presented an outdoor concentration of 42 μg m^{-3}, registered the lowest level of indoor NO_2 (15 μg m^{-3}), possibly because the windows and the doors were always closed. An average NO_2 concentration of 39 μg m^{-3} was registered in classrooms in Taiyuann, China (Zhao et al., 2008). Levels varying from 9.5 to 23 μg m^{-3} and from 11 to 19 μg m^{-3} were obtained, respectively, in the indoor air and outside of elementary schools in Curitiba, Brazil (Godoi

et al., 2009). Lee and Chang (2000) found indoor and outdoor NO_2 levels ranging from 12 to 176 μg m^{-3} and 19 to 244 μg m^{-3}, respectively, for five classrooms at different schools in Hong Kong.

Table 4.5 – Indoor and outdoor NO_2 concentrations in fourteen schools in Lisbon.

	NO_2 atm concentration (μg m^{-3})				
	Indoor	**STDEV**	**Outdoor**	**STDEV**	**I/O NO_2**
School A	31.0	2.97	36.5	1.90	0.85
School B	35.2	11.2	37.2	2.85	0.95
School C	32.6	4.38	45.9	5.23	0.71
School D	33.3	3.26	39.4	2.87	0.85
School E	14.9	2.26	41.6	3.10	0.36
School F	33.5	1.95	35.7	16.9	0.94
School G	21.7	1.03	42.4	3.42	0.51
School H	34.0	3.67	37.5	4.63	0.91
School I	37.4	0.31	41.5	9.32	0.90
School J	20.2	8.22	25.1	9.22	0.81
School K	29.6	3.96	45.7	3.83	0.65
School L	32.2	2.22	39.1	4.76	0.82
School M	35.5	6.30	39.1	0.80	0.91
School N	30.7	5.35	35.9	1.82	0.85

4.4 Conclusions

Indoor and outdoor concentrations of NO_2, VOCs, carbonyls, microbiological components and comfort parameters (temperature, relative humidity, carbon dioxide (CO_2), carbon monoxide (CO) and total VOCs) were measured in fourteen basic schools in Lisbon. The concentration of CO_2 and bioaerosols greatly exceeded the AMV of 1800 mg m^{-3} and 500 CFU m^{-3}, respectively, perhaps due to overcrowded classrooms and inefficient ventilation. Schools located near traffic busy streets presented the highest outdoor (45.7 μg m^{-3}) and the lowest indoor (29.6 μg m^{-3}) NO_2 levels, possibly because the windows and the doors were always closed. Generally, the assessed VOCs occurred at I/O ratios above unity,

showing the important influence of indoor sources and building conditions in IAQ. Most of the gaseous pollutants can be credited to the traffic emissions and indoor sources (some architectural finishes, floor adhesives, PVC flooring, consumer products and cleaning products). Better ventilation should be provided for these public buildings and air cleaners should be used in order to improve children's health, and their performance. More studies are needed (currently underway) to find additional possible sources of indoor contamination, to calculate air exchange rates on a seasonal basis, to evaluate if there is a causal relationship between pollutant exposure and health symptoms in schools, and to assess if school IAQ can adversely affect academic performance or attendance.

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Chapter 5

5. SEASONAL EVALUATION OF OUTDOOR/INDOOR AIR QUALITY IN PRIMARY SCHOOLS IN LISBON

Published

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Abstract

The aim of this study was to evaluate the indoor (I) and outdoor (O) levels of NO_2, speciated volatile organic compounds (VOCs) and carbonyls at fourteen primary schools in Lisbon (Portugal) during spring, autumn and winter. Three of these schools were also selected to be measured for comfort parameters, such as temperature and relative humidity, carbon dioxide (CO_2), carbon monoxide (CO), total VOCs, and both bacterial and fungal colony-forming units per cubic metre. The concentration of CO_2 and bioaerosols greatly exceeded the acceptable maximum values of 1800 mg m^{-3} and 500 CFU m^{-3}, respectively, in all seasons. Most of the assessed VOCs and carbonyls occurred at I/O ratios above unity in all seasons, thus showing the importance of indoor sources and building conditions in indoor air quality. However, it has been observed that higher indoor VOC concentrations occurred more often in the colder months, while carbonyl concentrations were higher in the warm months. In general, the I/O NO_2 ratios ranged between 0.35 and 1, never exceeding the unity. Some actions are suggested to improve indoor air quality in Lisbon primary schools.

Key words: carbon dioxide, carbon monoxide, carbonyls, indoor air quality, nitrogen dioxide, schools, volatile organic compounds.

5.1 Introduction

Indoor air quality (IAQ) is often much worse than that of outdoor air (Pegas et al., 2010; Kotzias et al., 2009). The Environmental Protection Agency (EPA) in USA estimates that indoor air pollutant levels could be two to five times higher than pollution levels outdoors. Evidence shows that citizens spend most of their time inside buildings, so it is easy to understand that they are, by far, more exposed to pollution indoors than outdoors (Blondeau et al., 2005; Sundell, 2004). Most chemical compounds to which people are exposed everyday constitute an additional risk factor in the development of several pathologies (Sundell, 2004). In particular, exposure to indoor air pollution can potentially be a greater threat than exposure to outdoor air. Changes in construction designs and the increasing application of synthetic products could enhance the number of complaints about IAQ at several environments (home, workplaces, schools, transportation and others) (Yang et al., 2004).

Daisey et al. (2003) performed a survey and a critical review of the existing published reports on IAQ, ventilation, and building-related health symptoms in schools. The type of health problems observed in schools was very similar to those defined as the sick building syndrome (SBS). Therefore, the IAQ and ventilation in school buildings may affect the children's health and indirectly influence learning performance and attendance.

There are several reasons to consider IAQ at school a public concern. One is that children breathe higher volumes of air, relatively to their body weights. Children's physiological vulnerability to air pollution arises from their narrower airways and the fact that their lungs are still developing. Also, many children breathe through their mouths, bypassing the nasal passages' natural defences. Thus, children are more likely to suffer the consequences of indoor pollution. Another reason for environmental deficiencies in schools is due to chronic shortages of funding, which contribute to inadequate operation and maintenance of facilities (Mendell and Heath, 2005).

In Lisbon, the number of children with asthma and rhinitis represents, respectively, about 15% and 40% of the school-age population (Khan et al., 2007a). However, almost

nothing is known about IAQ in Portuguese schools. The main objectives of this work were: (a) to evaluate the contribution of ventilation, combustion processes, tobacco smoke and traffic, to the bacterial and fungal levels and to the IAQ; (b) to assess their air quality by determining the concentrations of different indoor and outdoor pollutants (c) to compare the measured concentrations with relevant standards (d) and to analyse the seasonal variation of indoor and outdoor pollutant concentrations.

5.2 Material and Methods

5.2.1 Description of schools

Indoor and outdoor air samples were collected at fourteen schools with a wide geographical coverage representing the Lisbon urban area (Khan et al., 2007 a, b) (**Figure 5.1**), in May and June 2009 (spring period), in November 2009 (autumn period), and in February 2010 (winter period). Two classrooms from each of the fourteen schools were selected for this study. All classrooms depended only on the natural ventilation through the existing doors and windows. Details of each sampling site are listed in **Table 5.1**.

Figure 5.1 - Distribution of the fourteen target schools in Lisbon.

Table 5.1 – Characteristics of classrooms in each school.

School	Urban environment	Electric Heating	Blackboard and chalk or whiteboard with pen	Number of students per room	Floor	Animals inside	Plants inside	Area (m^2)	Height (m)
A	suburban	X	blackboard	23	ceramic tile			64.51	3.70
B	city centre		whiteboard	24	ceramic tile	X	X	46.82	3.50
C	city centre	X	blackboard	22	ceramic tile			50.14	3.50
D	suburban		whiteboard	21	ceramic tile			51.20	3.20
E	suburban	X	blackboard	20	vinyl		X	46.95	3.15
F	suburban	X	blackboard	19	ceramic tile			62.68	3.40
G	suburban	X	blackboard	22	ceramic tile	X		63.70	3.00
H	city centre	X	blackboard	21	wood	X	X	50.08	3.2
I	suburban	X	blackboard	23	ceramic tile	X		36.50	2.23
J	suburban	X	blackboard	22	wood			50.34	3.20
K	city centre	X	blackboard	21	vinyl			48.36	3.80
L	city centre	X	blackboard	21	vinyl			51.20	3.20
M	city centre	X	blackboard	21	wood			49.77	3.70
N	city centre	X	blackboard	21	ceramic tile		X	46.68	2.64

Note: All classrooms were natural ventilated (windows and doors).

5.2.2 Comfort parameters and airborne microorganisms

Three schools were previously considered representative of all the elementary-level educational institutions: the A, B and C schools (Khan et al., 2007a, b). At these three main schools, continuous measurements of temperature, relative humidity (RH), CO_2, CO and total VOCs were performed with an automatic portable Indoor Air IQ-610 Quality Probe (Gray Wolf® monitor) in one classroom of each school, throughout a whole occupancy day, during the spring period. During the autumn and winter campaigns, these parameters were monitored in parallel with sampling of microorganisms, in classrooms and playgrounds. This IAQ monitor includes a Pt100 probe for measuring temperature, a capacitance probe to sense RH, a CO_2 non-dispersive infrared sensor and a CO electrochemical sensor, all of them with an extremely fast response. The monitor also includes a photo-ionisation detector to track total VOCs over time. It displays measurements in real time allowing logged data to be downloaded to Wolf Sense® PC software for analysis. The equipment was supplied with a factory calibration certificate, but it was further checked prior to its use, with appropriate calibration kits.

Taking into account that the National System for Energy and Indoor Air Quality Certification of Buildings (*Regulamento dos Sistemas Energéticos de Climatização de Edifícios* – RSECE) (RSECE, 2006) restricts the bioaerosol measurements to bacterial and fungal colony-forming units per cubic metre of air (CFU m^{-3}), only viable and culturable fungi and bacteria were quantified. Viable microorganism levels were monitored by liquid impinger sampling (May and Harper, 1957) in the two classrooms and playgrounds, during one day, in each one of the 3 main schools. The flow rate was set at 2.5 l min^{-1}. Sampling took one hour at each sampling place. Five replicates of 150 l of air from each classroom and playground were collected and analysed to confirm the validity of results. The Petri dishes were incubated for 5 and 7 days for bacterial and fungal, respectively, in dark boxes with constant ambient temperature (25^{o}C).

5.2.3 Sampling and analysis of VOCs, carbonyls and NO_2

VOCs and carbonyls were sampled in parallel using Radiello® (Fondazione Salvatore Maugeri, Padova, Italy) diffusive passive tubes (cartridges codes 130 and 165, respectively) for 14 consecutive days in two replicates. Indoor samples were collected at a height of about 1.5 m above the floor. The diffusive samplers were positioned at a distance that exceeded 1 m from a window or a door. Outdoor passive samples were collected at heights of about 2 m above the ground. The VOC adsorbing cartridges consisted of 60 mm length stainless steel net cylinders, with 100 mesh grid opening and 5.8 mm diametre, packed with 530±30 mg of activated charcoal with a particle size of 35-50 mesh (Cocheo et al., 1996).

VOCs were extracted from the exposed samplers with 2 ml carbon disulfide (CS_2 from Aldrich) containing 2-fluorotoluene (from Aldrich) as an internal standard. The glass vials were shaken for approximately 30 min. The analyses of the extracts were performed by gas chromatography (Thermo Scientific Trace GC Ultra) coupled to a flame ionisation detector (GC/FID), using nitrogen carrier gas at a constant pressure of 20 psi. A 100% dimethylpolysiloxane column (0.2 mm, 50 m, film thickness 0.5 μm) was used. The temperature program was as follows: 50^{o}C for 5 minutes, 5^{o}C min^{-1} up to 80^{o}C, 15^{o}C min^{-1} up to 135^{o}C, 20^{o}C min^{-1} up to 220^{o}C, final isotherm for 20 minutes. Injector and detector temperatures were 240^{o}C and 300^{o}C, respectively. The equipment was calibrated before and during the sample analyses by injecting four standard solutions of all compounds identified in CS_2 (Pegas et al., 2010). The analytes in these four standard solutions were present in concentrations of 40 ng μl^{-1}, 20 ng μl^{-1}, 10 ng μl^{-1} and 5 ng μl^{-1}. Depending on the analyte, the limit of detection (LOD= 3.3(s/S) where s is the STDEV of areas and S is the slope) ranged from 0.34 to 2.52 ng μl^{-1} (Pegas et al., 2010).

Carbonyls collected in cartridges filled with 2,4-dinitrophenylhydrazine reacted to result in the corresponding 2,4-dinitrophenylhydrazones. These were extracted with 2 ml of acetonitrile (from Fisher Scientific). The glass vials were shaken for approximately 30 minutes and the extract filtered through 0.45 μm disc membrane filters (filtration kit RAD 174) and injected into the high-performance liquid chromatography (HPLC) system. The analytical system consisted of a Jasco PU- 980 pump, a Rheodyne manual injection valve (sample loop of 20 μL), a Supelcosil LC-18 column (250×4.6mm; 5μm; Supelco) and a Jasco MD-1510 diode array detector, all connected in series. Isocratic elution at room

temperature was performed using an acetonitrile/water solution (60/40, v/v) as the mobile phase at a flow rate of 1.5 ml min^{-1}. The carbonyl concentrations were quantified with external calibrations curves constructed from standard solutions of TO11/IP6A carbonyl – DNPH Mix (from Supelco) (U.S. EPA, 1999). The limit of detection (LOD) ranged from 1.29 to 2.09 μg ml^{-1}.

NO_2 concentrations were also passively monitored for fourteen days. The diffusive samplers (70 mm length and 12 mm diameter polycarbonate tube) with steel grids impregnated with triethanolamine chemiadsorb NO_2, as nitrite, which was quantified by visible spectrophotometry (Bhugwant and Hoareau, 2003).

Although ozone is an important pollutant with health effects, its monitoring was not done, because preliminary studies in several Portuguese indoor environments, including schools, showed that its levels were always below or close to the detection limit (Borrego et al., 2007), except near photocopiers (Nunes et al., 2007). All the schools involved in this study, do not have photocopiers inside or near the classrooms.

5.3 Results and Discussion

The mean daily indoor temperature and RH values during the spring monitoring period, taken at the three main schools, ranged from 23.3 ± 0.85°C to 25.9 ± 1.56°C and from 34.6 ± 3.5% to 44.3 ± 6.5%, respectively (**Table 5.2**). During the autumn period, the mean daily indoor temperature and RH values ranged from 19.0 ± 0.7°C to 23.4 ± 0.7°C and from 48.9 ± 1.8% to 69.1 ± 4.5%, respectively. Finally, during the winter period, the mean daily indoor temperature and RH values ranged from 14.4 ± 0.75°C to 21.3 ± 0.39°C and from 56.0 ± 1.77% to 84.0 ± 5.18%, respectively.

Table 5.2 - Average microorganism counts (CFU m^{-3}), and daily (spring)* and hourly (autumn/winter) ** averages for comfort parameters in a seasonal basis.

Spring

		Bacterial (CFU m^{-3})	STDEV	**Fungal (CFU m^{-3})**	STDEV	**TVOCs (mg m^{-3})**	STDEV	**CO_2 (mg m^{-3})**	STDEV	**CO (mg m^{-3})**	STDEV	**Temperature (°C)**	STDEV	**Humidity (%)**	STDEV
	Indoor I	**≥ 27,051**	-	**≥ 2,023**	-	0.10	0.03	**2,085**	601.8	<L.D.	0.01	25.9	1.56	34.6	3.5
School A	Indoor II	**≥ 29,009**	-	**≥ 1,802**	-	-	-	-	-	-	-	-	-	-	-
	Outdoor	**≥ 25,651**	-	**≥ 2,697**	-	-	-	-	-	-	-	-	-	-	-
	Indoor I	**≥ 30,423**	-	**≥ 2,023**	-	0.30	0.33	**1,826**	636.9	0.04	0.08	23.3	0.85	44.3	6.5
School B	Indoor II	**≥ 22,123**	-	**≥ 1,945**	-	-	-	-	-	-	-	-	-	-	-
	Outdoor	**≥ 14,096**	-	**≥ 2,930**	-	-	-	-	-	-	-	-	-	-	-
	Indoor I	**≥ 39,838**	-	**≥ 1,335**	-	0.10	0.10	**2,102**	996.7	<L.D.	0.09	24.2	0.97	43.4	5.9
School C	Indoor II	**≥ 39,838**	-	**≥ 1,958**	-	-	-	-	-	-	-	-	-	-	-
	Outdoor	**≥ 39,838**	-	**≥ 1,698**	-	-	-	-	-	-	-	-	-	-	-

Autumn

		Bacterial (CFU m^{-3})	STDEV	**Fungal (CFU m^{-3})**	STDEV	**TVOCs (mg m^{-3})**	STDEV	**CO_2 (mg m^{-3})**	STDEV	**CO (mg m^{-3})**	STDEV	**Temperature (°C)**	STDEV	**Humidity (%)**	STDEV
	Indoor I	**1,320**	367	**1,440**	305	1.00	0.20	1,673	304.3	<L.D.	0.00	21.9	0.30	56.9	1.4
School A	Indoor II	**10,303**	1,250	**1,400**	224	0.70	0.90	1,094	174.3	0.10	0.10	19.0	0.70	66.4	4.1
	Outdoor	**660**	222	**560**	230	3.20	0.30	610.0	23.80	<L.D.	0.00	15.9	0.10	83.1	1.9
	Indoor I	**8,380**	353	**10,499**	332	0.90	0.20	1,407	238.3	0.20	0.20	20.8	0.60	50.6	3.9
School B	Indoor II	**2,320**	410	**1,560**	391	0.90	0.10	**1,930**	411.9	0.10	0.10	22.0	0.30	48.9	1.8
	Outdoor	**1,160**	450	**1,460**	422	0.70	0.00	689.0	36.10	<L.D.	0.10	17.3	0.20	54.5	1.8
	Indoor I	**2,480**	446	**1,840**	261	1.50	0.10	**2,039**	351.7	<L.D.	0.00	23.4	0.70	60.2	3.2
School C	Indoor II	**2,001**	618	**800**	409	0.50	0.30	1,099	229.2	0.80	0.50	20.6	0.80	69.1	4.5
	Outdoor	500	220	**700**	240	0.80	0.20	643.0	38.60	0.30	0.40	18.5	0.40	81.9	3.9

Winter

		Bacterial (CFU m^{-3})	STDEV	**Fungal (CFU m^{-3})**	STDEV	**TVOCs (mg m^{-3})**	STDEV	**CO_2 (mg m^{-3})**	STDEV	**CO (mg m^{-3})**	STDEV	**Temperature (°C)**	STDEV	**Humidity (%)**	STDEV
	Indoor I	**710**	370	468	199	-	-	1,572	96.90	0.05	0.08	21.3	0.39	56.0	1.8
School A	Indoor II	**2,218**	380	**1,750**	392	-	-	1,453	171.1	0.08	0.19	18.8	0.57	66.6	3.0
	Outdoor	**1,854**	388	**711**	269	-	-	782.0	49.20	<L.D.	0.01	15.7	0.60	70.3	5.7
	Indoor I	**3,396**	894	225	145	-	-	**3,850**	196.1	0.68	0.15	18.6	0.35	81.0	2.3
School B	Indoor II	**1,456**	651	329	125	-	-	**2,511**	93.10	0.37	0.13	14.4	0.75	83.9	5.2
	Outdoor	**849**	465	225	98	-	-	694.0	21.90	0.52	0.19	10.4	0.47	103	0.1
	Indoor I	**1,196**	262	295	133	-	-	**2,829**	191.4	0.49	0.11	18.7	0.92	74.9	5.5
School C	Indoor II	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	Outdoor	**589**	72	399	131	-	-	741.0	43.00	0.01	0.04	14.6	0.54	80.5	4.1

Notes: - not identified; <L.D. bellow the detection limit; * monitoring during a full day of occupancy; ** monitoring concomitant one hour period of microorganisms sampling.

Comfort standards specify exact physical criteria for producing acceptable thermal environments, which include temperature, and humidity limits (Kwok et al., 2003). The ANSI/ASHRAE Standard 55-2004 (ASHRAE, 2004) recommends indoor temperature ranges from 20 to 23ºC in the autumn/winter seasons and from 23 to 26ºC in the spring/summer seasons. The suggested indoor RH values are in the 30-60% range. Thermal comfort is affected by heat, convection, human occupancy, radiation and evaporative heat loss. It is maintained when the heat generated by human metabolism is allowed to dissipate, thus maintaining thermal equilibrium with the surroundings. Any heat gain or loss beyond this generates a sensation of discomfort (Hussein and Rahman, 2009). School children are susceptible to heat stress. At high temperatures, children are less able to concentrate and can exhibit irritable or aggressive behaviours. Adults can be similarly affected. A decrease in temperature may also make people restless and less attentive. During the spring monitoring campaigns of this study, the thermal conditions in classrooms were within the recommended ranges. However, during the winter period, classrooms did not have conditions within the comfort zone. Thus, heating systems should be implemented in these schools, namely by convection through panel heating or a combination of radiation and convection. The recommended systems in schools are the Hybrid Radiant Heating Systems or the Thermo Active Building Systems (Mumma, 2001). High relative humidity above 65% can lead to mould, mildew, and other biological growth. Mould growth is linked to allergic reactions, asthma attacks, and hypersensitivity pneumonitis (inflamed airways). The primary cause of high relative humidity levels is moisture-laden outdoor air entering the buildings, especially during rainy winters, such as the one registered in Lisbon. Desiccant based dedicated outdoor air systems are suggested as an effective way to operate school facilities in accordance with the ASHRAE Standards (Mumma, 2001). Considering that school-day peaks in humidity could still be problematic and provide sufficient moisture to condense on surfaces and provide wetting of surfaces, which could ultimately still support microbial growth, possible solutions could range from controlling the humidity with an energy efficient noiseless dehumidifier to overcoming building pathologies (wall cracks, infiltrations, etc.).

During the spring period, CO_2 levels ranged widely (705 to 6821 mg m^{-3}) (**Figure 5.2**). The National System for Energy and Indoor Air Quality Certification of Buildings (*Regulamento dos Sistemas Energéticos de Climatização de Edifícios* - RSECE) establishes

an acceptable maximum value (AMV) of 1800 mg m^{-3} for buildings in Portugal (RSECE, 2006). Therefore, the CO_2 average levels surpassed the acceptable threshold in the B and C schools for almost all the monitoring surveys, whereas the exceedances in the A school only occurred in spring (**Table 5.2**). It is not easy to adequately characterise indoor CO_2 concentrations because they are a function of occupancy and ventilation rate, both varying as a function of time. Short-term measurements could be inadequate to provide information on the long-term ventilation conditions in schools, but it may be very important to have measurements of different sampling places and to understand the influence of outdoor in indoor environment. High indoor CO_2 levels are normally considered as indicative of ventilation rates that are unacceptable with respect to body odours. Low concentrations of CO_2 do not always guarantee that the ventilation rate is adequate for the removal of air pollutants from indoor sources (Daisey et al., 2003). Normally, CO_2 measurements in schools suggest that a significant number of classrooms do not meet the ANSI/ASHRAE Standard 62-2010 (ASHRAE, 2010) for minimum ventilation rates of 5 l s^{-1} per person. **Figure 5.2** shows a strong correlation of the CO_2 levels with occupancy: CO_2 spikes were even more pronounced when students started physical activities inside the classrooms. CO_2 concentrations varied seasonally. In accordance with another study of British school classrooms (Coley and Beisteiner, 2002), in Lisbon schools, higher CO_2 levels in winter than in spring were observed (**Table 5.2**). This indicates that during the spring period the windows were more open, which explains the drop in CO_2 levels. A broad literature review for indoor environments generally suggests a consistent relationship between ventilations rates, high CO_2 concentrations and health symptoms (Seppänen et al., 1999).

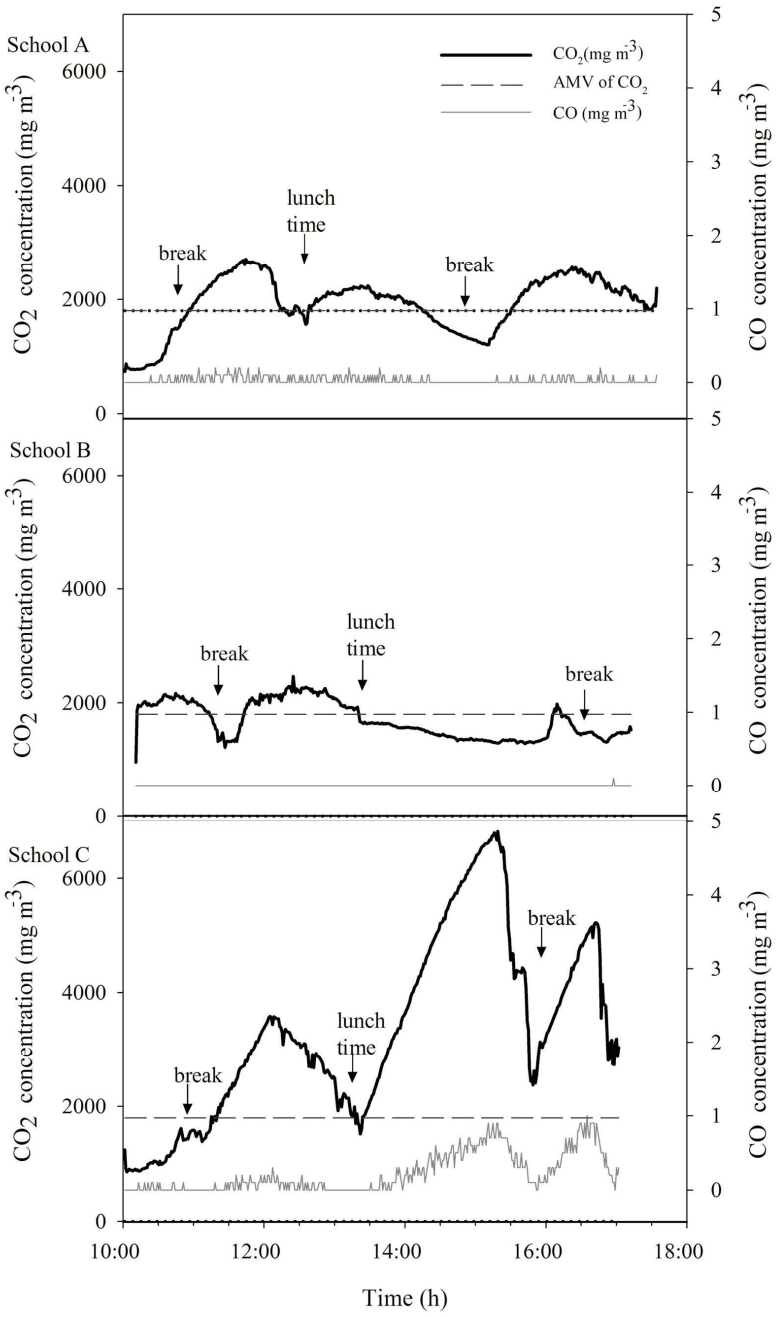

Figure 5.2 - Indoor carbon dioxide and carbon monoxide levels in the three main schools during the spring season.

In spring, CO ranged from non-detectable levels to 1.0 mg m^{-3} (**Figure 5.2**) and did not reach 12.5 mg m^{-3}, the recommended exposure limit (RSECE, 2006). During the autumn and the winter, the hourly average of CO was also below the exposure limit (**Table 5.2**). CO is odourless and colourless, and it interferes with the distribution of oxygen in the

body (Chaloulakou et al., 2003). CO is one of the most characteristic traffic pollutants usually observed in urban areas. However, in this study, the average outdoor concentrations of CO were lower than those indoors, for all seasons. Concomitant increases of CO_2 and CO concentrations, especially at the C school, were observed during spring daily measurements (**Figure 5.2**). CO is emitted when wood, coal and fossil fuels are burned incompletely. It is also emitted naturally when plants decay. In human breath, CO is detectable in small quantities in the exhaled air of healthy people (Zayasu et al., 1997).

Total VOC concentrations measured by the automatic monitor could provide information about the influence of indoor sources, such as aerosol sprays, solvents, cleaning agents, pesticides, paints, furniture and repellents. In a typical school-day in spring, the indoor average values ranged from 0.1 ± 0.034 mg m^{-3} to 0.3 ± 0.33 mg m^{-3} (**Table 5.2**) and did not exceed the recommended value of 0.6 mg m^{-3}. (RSECE, 2006) However, in autumn, the indoor average hourly values ranged from 0.5 ± 0.3 mg m^{-3} to 1.5 ± 0.1 mg m^{-3}. At the A school, part of the indoor VOCs may come from the outdoor environment, which presented 3.2 mg m^{-3}. In the case of the B and C schools, additional indoor sources or inadequate ventilation ratios may have contributed to higher indoor levels compared to outdoors. Examples of additional indoor sources could be glues and paints used by children in art classes. Pegas et al. (2010) and Zhang et al. (2006) also identified an art classroom with a relatively high level of VOCs. Casey et al. (1995) reported total VOC measurements made in two elementary schools at Las Vegas, Nevada, during the autumn/winter seasons. Before the installation and operation of heat recovery ventilators (HRVs) in Las Vegas schools, the only means of ventilation was infiltration, and the total VOC levels ranged from 0.8 to 2.0 mg m^{-3}. After the HRVs were operational, concentrations of total VOC were reduced to 0.75 and 0.45 mg m^{-3} in the two classrooms. Thus, a possible solution to decrease the total VOC concentrations in classrooms is the use of HRVs or other ventilation systems.

In most schools, the total fungal and total bacterial colony-forming units in both indoor and outdoor air (**Table 5.2**) were above the AMV of 500 CFU m^{-3} defined by the Portuguese Legislation, Decree-Law 79/2006 (RSECE, 2006). Generally, the indoor culturable bacterial levels were higher than outdoor levels at all schools in any season.

Most bioaerosols detected indoors have an outdoor source. They are introduced into the indoor environment through natural (open windows and doors) and mechanical ventilation systems. They also are brought indoors on an individual's shoes and clothing (Gots et al., 2003). High indoor bacteria counts were probably due to several factors, including high seasonal level of bioaerosols in outdoor air, indoor micro-climate with high temperatures, human activities, such as breathing, sweating and movement causing particle resuspension, high occupancy loading, poor hygienic condition of occupants, inadequate ventilation rates, movement of textiles, food products, etc (Lee et al., 2002; Mentese et al., 2009). Mentese et al. (2009) evaluated bacteria and fungi levels in various indoor and outdoor environments in Ankara. The highest total bacteria counts were found in kindergartens, primary schools, restaurants, high schools, and homes, while the highest mould levels were observed in kitchens, bathrooms, and offices. In elementary schools of Lisbon, the lowest bacteria and fungi counts were generally found in winter. This seasonal variation in the colony counts with maximum concentration in spring and a winter minimum were also observed in previous studies (Medrela-Kuder, 2003). In winter, the low temperature and small amounts of fungal spores or bacteria in infiltrating outdoor air result in lower bioaerosol counts. The relationship between fungi and SBS symptoms in children has been reported (Cooley et al., 1998; Handal et al., 2004; Garret et al., 1998). The most effective way to manage bioaerosols in a building is to eliminate or limit the conditions that foster their establishment and growth. One of the methods is to prevent moisture due to condensation by increasing surface temperature and/or reducing the moisture level in air (humidity). Also, efficient cleaning protocols could be implemented as a preventive action to control airborne microorganisms.

Generally, indoor total VOC concentrations were markedly higher than those observed outdoors (**Figure 5.3** and **5.4**), except at the A school, in spring. This school had the most spacious and well-ventilated classrooms and the lowest occupancy ratio. With the drop in temperature in autumn and winter, the rooms remained longer with closed windows to maintain thermal comfort; this may have contributed to a gradual accumulation of pollutants. Ventilation is defined by ANSI/ASHRAE Standard 62-1999 (ASHRAE, 1999) in four steps: (1) entry of outside air, (2) conditioning, (3) mixture of air in the indoor environment, and (4) exhaustion of a portion of indoor air. If any of the four steps fails, ventilation will be inadequate and a consequent accumulation of pollutants will occur. The

high winter levels in the N school are probably related to the existence of toilets in front of the classrooms, which were used by the cleaning staff to wash mops, buckets, etc, and as storage room of cleaning products. During the spring/summer and autumn periods, the cleaning staff used outdoor installations for these activities. The indoor VOC accumulation is suspected to be one of the SBS causes (Daisey et al., 2003).

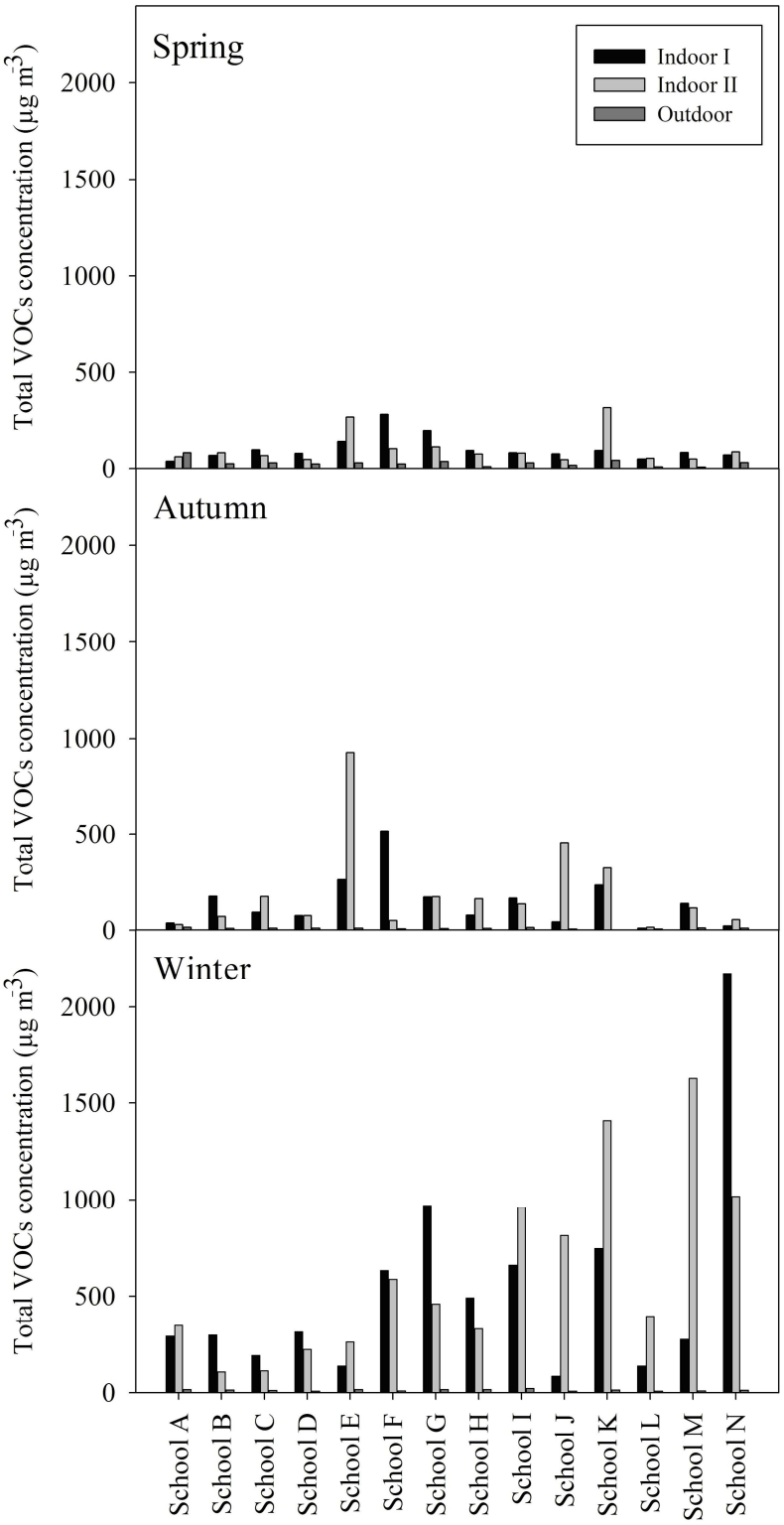

Figure 5.3 - Indoor (2 classrooms) and outdoor VOC concentrations (sum of all compounds identified) during spring, autumn and winter.

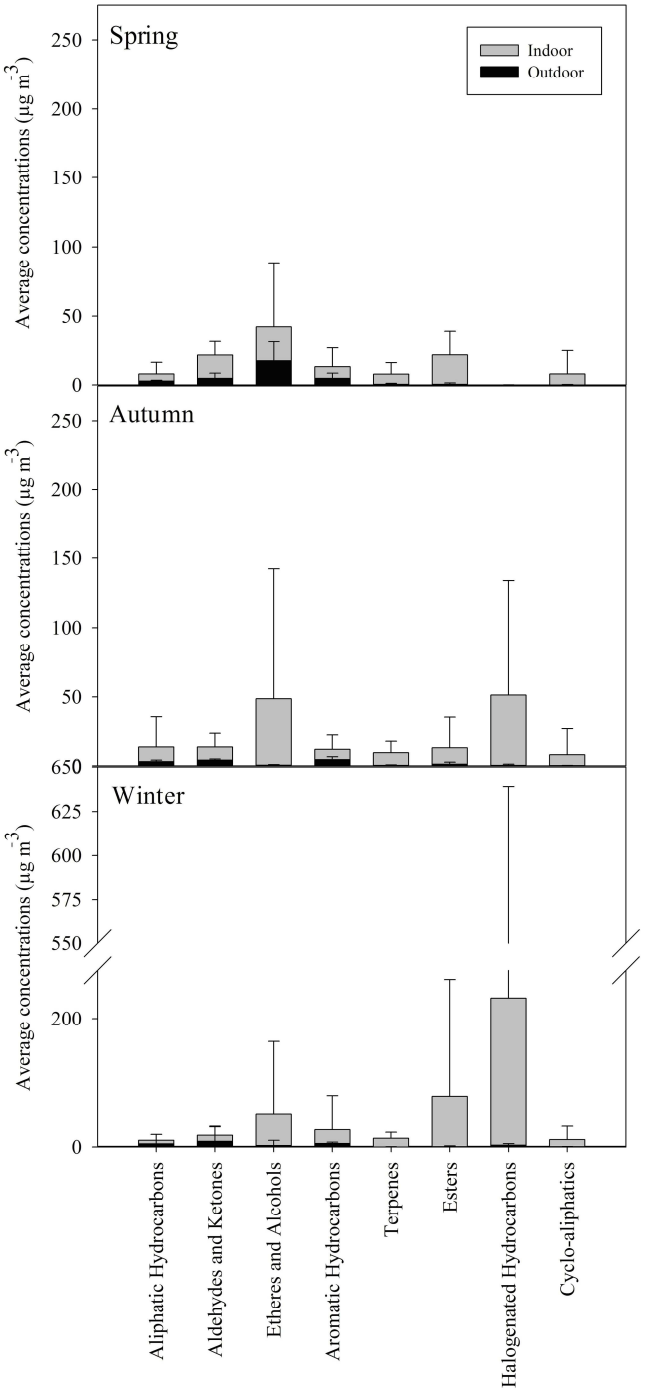

Figure 5.4 - Average concentrations (µg m^{-3}) of all individual VOCs and carbonyls in all schools.

The groups of VOC and carbonyl compounds identified were as follows: aliphatic hydrocarbons (pentane, 2,2-dimethylbutane, 2-methylpentane, *n*-hexane, isooctane, *n*-heptane, octane, nonane, and *n*-decane); aldehydes and ketones (formaldehyde, acetone, 4-methyl-2-pentanone, acetaldehyde, propynaldehyde, and benzaldehyde); ethers and alcohols (methanol, ethanol, isopropanol, butanol, 2-ethoxyethanol, methylcyclohexanol, and 1-propanol); aromatic hydrocarbons (benzene, ethylbenzene, *m*+*p*-xylene, styrene, *o*-xylene, and naphthalene); terpenes (α-pinene, (+)-sabinene, β-pinene, (+)-3-carene, γ-terpinene, isoprene, limonene, and eucalyptol); esters (methyl acetate, ethyl acetate, propyl acetate, and *n*-butyl acetate); halogenated hydrocarbons (dichloromethane, and 1,2-dichloropropane); and cyclo-aliphatics (cyclohexane, and methylcyclohexane) (**Figure 5.4**). VOC compounds showed a substantial seasonal variation (**Figure 5.4**). The sum of the individual VOC concentrations in indoor air varied from 37 to 317 μg m^{-3} in spring, whereas levels in autumn and winter ranged from 11 to 922 μg m^{-3} and from 84 to 2175 μg m^{-3}, respectively. Highest concentrations occurred during the coldest months. This seasonal pattern is in accordance with the results of the AIRMEX study, which examined the principal air contaminants present in public buildings in 11 European cities, including indoor environments frequented by children, like schools and kindergartens (Kotzias et al., 2009). In our study, the sum of individual VOC concentrations in outdoor air were in the ranges 6-80 μg m^{-3}, 5-50 μg m^{-3} and 7-22 μg m^{-3} in spring, autumn and winter, respectively. Thus, outdoor VOCs did not represent the major contribution to indoor levels. All buildings contain a large variety of chemical sources, including synthetic carpet, consumer products, paints, adhesives, furnishing, clothing, building materials, cleaning products, synthetic insulation, among others (Guo et al., 2004).

Indoor and outdoor benzene, toluene, ethylbenzene and xylenes (BTEX) concentrations are summarised in **Table 5.3**. BTEX are of particular interest due to their known carcinogenic effects (Kotzias et al., 2009). For all BTEX compounds, in any season, the indoor concentrations were generally higher than those measured outdoors. The mean benzene concentration was low at the majority of schools, ranging from values below the detection limit to a maximum in winter of 2.89 μg m^{-3}. For this pollutant, the indoor and outdoor levels do not differ appreciably. All measurements were below the limit value of 5 μg m^{-3} (annual mean) set by the European Commission. However, as it is a carcinogenic compound, the WHO has not yet established a guideline or safe value (WHO,

2000). At most sampling places, toluene, ethylbenzene, *m*+*p*-xylene and *o*-xylene were identified in both indoor and outdoor samples, but with higher concentrations in the indoor environments. This may indicate additional indoor sources and/or accumulation of such pollutants in the classrooms. Ethylbenzene and xylenes have been only detected in indoor environments during the coldest seasons at the H, J, L and M schools, suggesting a probable indoor source. Toluene, xylenes and ethylbenzene could be originated from indoor sources, such as tobacco smoke, solvent-based paints, floor adhesives, PVC flooring, carpeting, printed material, and consumer products (Mendell, 2007). Toluene levels were very similar to those found in schools of Curitiba, Brazil (Godoi et al., 2009). The highest toluene concentrations detected in Lisbon are in the same range of those observed in schools of Oporto, Portugal (Madureira et al., 2009). After a smoking ban was imposed in public places, in 2007, it was not expected to detect toluene from tobacco smoke. However, Mulcahy et al.(2010) found that the levels of tobacco smoke exposure have been reduced in workplaces after the ban, but have not been eliminated. The infiltration from outdoors and the exhaled breath of smokers can contribute to pollutant accumulation indoors.

Table 5.3 - Overview of indoor and outdoor BTEX concentrations for fourteen schools in Lisbon during spring, autumn and winter.

			BTEX (μg m^{-3}) Spring					BTEX (μg m^{-3}) Autumn					BTEX (μg m^{-3}) Winter				
			Benzene	Toluene	Ethylbenzene	m+p-Xylene	o-Xylene	Benzene	Toluene	Ethylbenzene	m+p-Xylene	o-Xylene	Benzene	Toluene	Ethylbenzene	m+p-Xylene	o-Xylene
School A	**Indoor**	**I**	0.30	1.98	0.73	0.95	0.99	0.40	1.95	0.00	0.84	0.73	1.26	4.95	0.91	2.01	1.47
		II	0.29	2.20	0.84	1.78	1.25	0.38	2.00	0.39	1.20	0.56	0.94	3.14	0.54	0.84	0.40
	Outdoor		0.38	5.31	2.67	6.68	2.53	0.45	3.45	1.02	3.12	0.94	1.04	4.24	0.86	2.11	0.66
School B	**Indoor**	**I**	0.31	2.12	0.54	1.04	1.89	0.53	2.66	0.52	1.32	1.21	2.08	19.3	1.25	2.38	4.44
		II	0.34	6.45	0.73	0.70	0.82	0.57	2.36	0.36	1.04	1.43	1.01	4.13	0.62	1.26	5.24
	Outdoor		0.31	1.56	0.39	0.86	0.24	0.48	1.81	0.41	0.83	0.29	1.13	2.46	0.25	0.31	-
School C	**Indoor**	**I**	0.34	2.14	1.66	3.54	4.96	0.63	3.80	1.85	3.63	3.47	1.15	4.11	1.07	2.10	5.71
		II	0.33	1.96	1.39	3.04	3.45	0.49	2.91	1.82	4.18	5.01	1.05	4.76	1.05	1.72	3.35
	Outdoor		0.37	1.74	0.57	1.4	0.47	0.48	1.94	0.38	1.10	0.41	1.18	2.75	0.51	0.53	0.13
School D	**Indoor**	**I**	0.36	2.83	1.11	1.86	0.55	0.45	2.85	0.60	1.26	1.04	0.99	7.43	0.92	2.07	1.06
		II	0.28	1.99	0.33	0.87	0.34	0.39	3.32	0.44	1.06	0.99	1.26	3.09	0.58	0.73	0.58
	Outdoor		0.29	1.24	0.34	0.77	0.23	0.45	1.53	0.35	0.81	0.28	0.96	1.84	0.26	0.30	-
School E	**Indoor**	**I**	0.37	5.34	2.58	6.18	2.99	0.48	14.0	3.75	8.52	9.59	0.87	6.20	1.80	3.87	18.1
		II	0.29	7.31	4.37	9.38	5.42	0.68	16.4	4.53	11.9	16.6	0.87	4.96	1.29	2.99	26.3
	Outdoor		0.35	1.91	0.62	1.32	0.46	0.61	2.52	0.49	1.33	0.36	1.17	3.50	0.59	1.01	0.06
School F	**Indoor**	**I**	0.30	1.63	0.59	1.01	0.52	0.74	4.60	0.82	2.83	23.0	0.73	3.19	0.36	0.95	-
		II	0.22	1.45	0.5	0.92	0.56	0.70	3.70	0.67	2.32	-	0.94	2.36	0.71	0.88	22.2
	Outdoor		0.29	1.41	0.44	0.89	-	0.55	1.87	0.33	0.83	0.24	1.19	2.51	0.23	0.31	-
School G	**Indoor**	**I**	0.27	4.47	14.2	19.7	7.90	0.41	2.36	1.45	3.91	-	1.00	5.48	1.02	2.16	6.77
		II	0.28	2.91	1.58	3.28	6.38	0.46	3.82	1.84	-	8.49	1.00	6.43	1.08	3.26	18.9
	Outdoor		0.36	1.84	0.48	1.16	0.38	0.55	2.15	0.29	0.78	0.18	1.44	3.57	0.52	1.46	0.55
School H	**Indoor**	**I**	0.26	1.98	0.97	2.20	0.93	0.50	2.14	0.33	0.98	-	0.96	8.69	3.00	5.31	5.20
		II	0.23	1.81	0.73	1.70	0.63	0.61	2.44	0.34	1.12	0.64	1.19	5.71	0.87	1.88	1.04
	Outdoor		0.27	1.28	0.33	0.99	0.34	0.38	1.35	0.29	0.40	-	1.28	3.36	-	-	-
School I	**Indoor**	**I**	0.41	5.55	2.60	5.35	5.06	0.78	4.35	2.63	7.60	3.80	0.96	5.20	37.7	109	40.3
		II	0.41	3.21	1.17	2.39	3.60	0.72	3.98	1.84	5.87	4.04	0.94	5.75	54.4	160	110
	Outdoor		0.26	1.79	0.48	1.14	0.35	0.47	2.22	0.60	1.84	0.59	1.19	3.14	0.77	1.73	0.69
School J	**Indoor**	**I**	0.29	1.72	0.60	0.94	2.00	0.31	2.17	0.42	0.64	0.40	0.91	2.70	0.54	0.56	-
		II	0.32	1.59	0.29	0.92	0.56	0.33	3.49	1.06	0.85	-	1.06	3.67	1.61	2.00	0.69
	Outdoor		0.26	0.87	0.90	0.62	0.2	0.34	1.53	0.21	0.25	-	1.20	1.82	-	-	-
School K	**Indoor**	**I**	0.32	3.13	1.18	2.65	0.79	0.51	14.09	0.44	1.25	0.55	1.91	10.0	1.46	2.09	4.57
		II	0.49	2.61	13.97	40.0	9.71	0.68	23.30	1.78	4.26	3.26	2.89	17.8	2.31	5.11	7.38
	Outdoor		0.45	5.74	0.43	1.17	0.37	l.	l.	l.	l.	l.	1.41	3.59	0.42	0.68	-
School L	**Indoor**	**I**	0.28	1.42	0.58	1.33	7.18	0.38	1.52	0.32	0.51	0.35	1.04	2.54	0.86	1.50	4.71
		II	0.31	5.50	0.48	1.15	2.40	0.39	1.54	0.36	0.42	0.55	1.08	4.03	0.46	0.70	1.88
	Outdoor		0.33	1.42	0.64	1.00	0.27	0.41	1.51	-	0.33	-	1.42	2.19	-	-	-
School M	**Indoor**	**I**	0.94	4.34	1.00	1.81	0.95	0.35	5.83	0.62	1.22	0.67	0.95	3.61	1.16	-	-
		II	0.28	1.47	0.47	0.96	0.36	0.40	3.29	0.47	0.84	0.27	2.10	5.78	-	1.35	-
	Outdoor		0.22	1.35	0.31	0.97	0.27	0.44	1.53	0.25	0.47	0.19	1.26	2.10	-	-	-
School N	**Indoor**	**I**	0.31	1.52	0.74	1.60	4.87	0.47	2.04	0.55	0.97	0.93	2.28	8.86	2.61	3.81	11.7
		II	0.28	2.01	1.22	2.80	13.5	0.48	2.08	0.63	1.62	-	0.96	3.68	1.50	2.96	14.2
	Outdoor		0.40	1.60	0.44	0.98	0.27	0.50	1.85	0.44	0.75	0.24	1.31	2.87	0.51	0.78	-

Notes: - not identified; l. lost.

In winter, the highest indoor VOC concentrations were found in the F, G, I, K, M and N schools. A possible indoor source in the K school was vinyl flooring and floor adhesives, which are described as emitter materials, especially of benzene, toluene, xylenes, styrene, and ethylbenzene, among others (Mendell, 2007). For the other schools, some old architectural finishes and consumers products could contribute for the accumulation of these VOC contaminations (Mendell, 2007).

Carbonyl compounds are toxic and present carcinogenic health effects. They are the most important chemical contaminants affected by chemical and physical processes in the environment (Cerón et al., 2007). Carbonyls are emitted from incomplete combustion of biomass and fossil fuel, and formed indirectly by atmospheric photo-oxidation of VOCs (Pang and Mu, 2006). In all studied places, the air concentrations for aldehydes inside the buildings were higher than outside. Four carbonyls were identified in Lisbon schools: formaldehyde, acetaldehyde, propinaldehyde and benzaldehyde. Formaldehyde was by far the most abundant carbonyl species. Indoor and outdoor concentrations of formaldehyde in spring, autumn and winter are shown in **Figure 5.5**. Unlike VOCs, in general, both indoor and outdoor formaldehyde concentrations in spring were higher than those in colder months. Formaldehyde could be evaporated under high temperature from building materials and furniture. Moreover, its photochemical production is more active in the hottest seasons, even in indoor environment (Pang and Mu, 2006). Indoor formaldehyde concentrations ranged widely: 3.4-42.3 $\mu g\ m^{-3}$ (spring), 3.1-26.2 $\mu g\ m^{-3}$ (autumn), and 6.3-23.8 $\mu g\ m^{-3}$ (winter). Therefore, the indoor concentration of formaldehyde was higher in spring than measured in autumn and winter. The same relationship between formaldehyde concentrations and season has been reported in studies of residential microenvironments in China (Wang et al., 2007). In 185 houses from Perth, Australia, Dingle and Franklin (2002) used a validated passive sampling technique and found that within homes there was no significant difference in formaldehyde concentrations measured among the rooms. However, according to the same study, it seems that formaldehyde concentrations are significantly affected by season and age of the buildings. The highest values were obtained in newer homes in summer (Dingle and Franklin, 2002). The levels of formaldehyde in Korean schools, most of which are housed in buildings from 1960s and 1970s, were measured and related to the age of the constructions by Sohn et al. (2007). Schools less

than one year old showed a higher average value of formaldehyde (0.16 ppm) than schools that were 1-3 years old (0.12 ppm), 3-5 years old (0.07 ppm) and more than ten years old (0.07 ppm). In this study, school C possessed the oldest building. High levels of formaldehyde in other schools are likely associated with other sources and renovating activities of old buildings. The highest level of formaldehyde was observed at school G. The high levels may be related to the fact that this institution is located in the vicinity of major motorways with very intense traffic. It should be also noted that the ceilings of the school G, H and J were painted during the Shrovetide period and new furniture was purchased just one month before the sampling campaign. There are many evidences indicating that children can be more sensitive to formaldehyde toxicity than adults. It is considered to be a chemical of concern at levels exceeding 1 μg m^{-3}, a concentration more or less corresponding to background levels in rural areas (Kotzias et al., 2009).

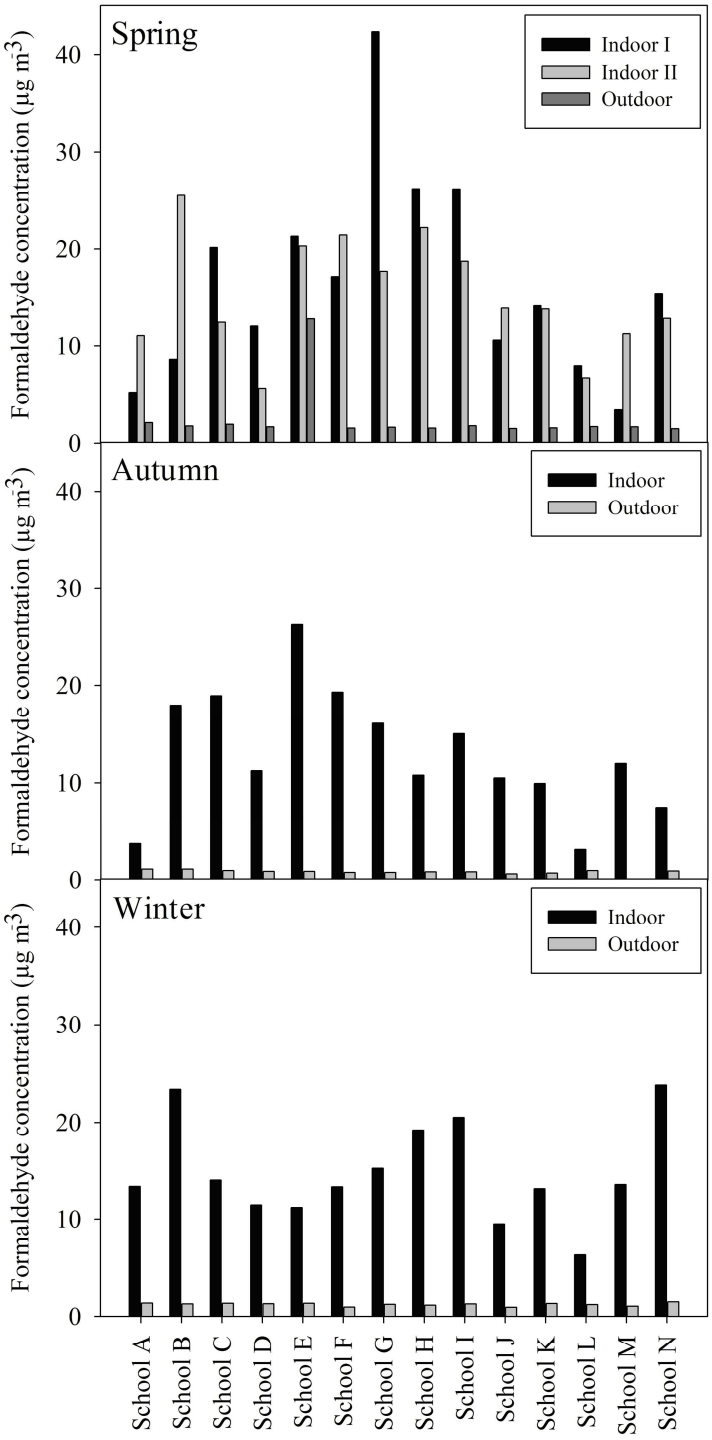

Figure 5.5 - Formaldehyde concentration in fourteen schools during spring, autumn and winter**.**

Descriptive data on indoor and outdoor concentrations of NO_2 are given in **Table 5.4**. The NO_2 concentrations were always higher outdoors than indoors, probably as a result of vehicular exhaust emissions from nearby traffic. Indoor NO_2 average levels were within the intervals 15-37 μg m^{-3}, 12-46 μg m^{-3}, and 10-34 μg m^{-3} during the spring, autumn and winter, respectively. It should be remembered, however, that these data were obtained by passive sampling, representing average concentrations of several days. Therefore, they do not show possible peaks, which may contribute to harmful effects through exposure over short periods of time. The same recommendation could be assigned for carbonyls and VOC compounds. In general, the I/O NO_2 ratios ranged between 0.35 and 1, never exceeding the unity. Because NO_2 is reactive, its removal from the indoor environment may occur not only by dilution, convection or gaseous diffusion processes, but also by gas phase mechanisms and reactions on the inner surfaces of materials (e.g. furniture) (Ugucione et al., 2009).

Table 5.4 - Indoor and outdoor NO_2 concentrations in fourteen schools in Lisbon during spring, autumn and winter.

NO_2 atm concentration (µg m^{-3})									
	Spring			Auntumn			Winter		
	Indoor	Outdoor	I/O	Indoor	Outdoor	I/O	Indoor	Outdoor	I/O
School A	31.0	36.5	0.85	31.1	34.7	0.90	34.4	34.4	1.00
School B	35.2	37.2	0.95	35.1	38.3	0.92	33.6	40.5	0.83
School C	32.6	45.9	0.71	34.1	41.2	0.83	29.4	41.3	0.71
School D	33.3	39.4	0.85	31.5	34.7	0.91	30.3	34.3	0.88
School E	14.9	41.6	0.36	12.4	35.2	0.35	24.0	35.2	0.68
School F	33.5	35.7	0.94	45.8	46.6	0.98	23.4	32.7	0.71
School G	21.7	42.4	0.51	21.4	39.0	0.55	15.9	36.2	0.44
School H	34.0	37.5	0.91	35.5	36.3	0.98	18.6	38.0	0.49
School I	37.4	41.5	0.90	35.1	41.9	0.84	17.3	34.1	0.51
School J	20.2	25.1	0.81	22.9	34.9	0.65	10.2	22.8	0.45
School K	29.6	45.7	0.65	32.2	50.0	0.64	18.5	30.1	0.61
School L	32.2	39.1	0.82	39.6	46.2	0.86	18.9	22.9	0.82
School M	35.5	39.1	0.91	36.6	36.9	0.99	16.3	25.3	0.65
School N	30.7	35.9	0.85	40.7	50.1	0.81	21.0	27.5	0.76

The International Study of Asthma and Allergies in Childhood (ISAAC) written questionnaire was applied to the same school population of this study. Information on asthma and rhinitis prevalence, as well the risk factors related to these respiratory diseases, can be found in Pegas et al. (2011). A statistically significant increase in the prevalence of rhinitis and wheeze was observed among primary schoolchildren in Lisbon (Pegas et al., 2011). Children spend more time in schools than in any other place, except at home. Having pets at home was suggested as a significant risk factor for rhinitis, but not smoking exposure, mould, plush toys, diet (except egg consumption), breastfeeding or other house conditions (Pegas et al., 2011).

5.4 Conclusions

Indoor and outdoor comfort parameters and microbiological counts were monitored in three main elementary schools, while indoor and outdoor concentrations of NO_2, VOCs and carbonyls were measured, for the first time, in fourteen elementary schools in Lisbon, during May and June 2009 (spring period), November 2009 (autumn period), and February 2010 (winter period). The CO_2 concentrations and the bioaerosol counts greatly exceeded the AMV of 1800 mg m^{-3} and 500 CFU m^{-3}, respectively, in all three seasons. The daily profiles of CO_2 suggest that the classrooms are inadequately ventilated. The high amounts of bioaerosols in both indoor and outdoor environments may derive from several factors, including human activities. Most of the assessed VOCs and carbonyls occurred at I/O ratios above unity, in all seasons, showing the important influence of indoor sources and building conditions in IAQ. However, it has been observed that higher indoor VOC concentrations occur often in the colder months, while carbonyl concentrations were higher in warm months. Schools located near traffic busy streets presented the highest outdoor and the smallest indoor NO_2 levels, possibly because the windows and the doors were always closed, or because NO_2 indoor concentrations decayed by gas-phase processes or by reactions on the inner surfaces of furniture.

Some improvements should be made to reduce the risks of exposure, such as the development of low-VOC-emission materials and consumer products indoors, the decrease of the number of students in each classroom, the usage of air cleaners in indoor environments, and humidity control. Increasing the ventilation rate by means of mechanical or natural systems can play a key role in improving the indoor air quality.

Additional studies are needed to determine the extent of IAQ problems in schools. It would be important to use active samplers in future studies to obtain both daily and monthly profiles aiming at evaluating additional indoor sources and the short-term exposure to pollution peaks. More studies are also necessary focusing on the monitoring of the relations between symptoms and measured exposures to multiple specific pollutants. Furthermore, quantitative information is required on exposure-health response relationships for specific pollutants suspected of causing health problems, in order to

afford a sound basis for establishing standards for schools and for assuring cost effective mitigation actions.

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Chapter 6

6. INDOOR AND OUTDOOR CHARACTERISATION OF ORGANIC AND INORGANIC COMPOUNDS IN CITY CENTRE AND SUBURBAN ELEMENTARY SCHOOLS OF AVEIRO, PORTUGAL

Published

Pegas, P.N., Nunes, T. Alves, C.A., Silva, J.R., Vieira, S.L.A., Caseiro, A., Pio, C.A., 2012. Indoor and outdoor characterisation of organic and inorganic compounds in city centre and suburban elementary schools of Aveiro, Portugal. Atmospheric Environment 55, 80-89.

Abstract

Pollutants inside school buildings may affect children's health and influence learning performance and attendance. This study investigated pollutant concentrations inside and outside school buildings at different locations (city centre and suburban) in Aveiro, Portugal, between April and June 2010. The aim was to evaluate simultaneously comfort parameters (temperature, relative humidity, CO_2 and CO) and indoor and outdoor concentrations of VOCs, NO_2, PM_{10} and bioaerosols. PM_{10} samples were analysed and characterised, for the first time, for the water soluble inorganic ions (WSII), organic carbon (OC), elemental carbon (EC), carbonates, and detailed organic speciation. The CO_2 and bioaerosol levels were higher than the acceptable maximum values to the occupants' comfort. Concentrations of the traffic tracer NO_2 were higher outdoors. The daily indoor PM_{10} levels were always higher than those outdoors, except on weekends, suggesting that the physical activity of pupils and class works highly contributed to the emission and resuspension of particles. Almost all identified VOCs showed I/O ratios higher than one, which denotes an important contribution from indoor sources at both schools. The suburban school was more exposed to industrial emissions than the institution located in the city centre. Especially at the city centre, infiltration of outdoor particulates leads to contamination of school indoor environment with vehicle emissions and biomass burning smoke likely coming from biofuel use in nearby restaurants and bakeries.

Key words: indoor air school, particulate matter, inorganic pollutants, organic pollutants.

6.1. Introduction

It has been shown that indoor air quality (IAQ) is usually worse than the outdoors air (Godoi et al., 2009; Jo and Seo, 2005; Kotzias et al., 2009; Lee and Chang, 2000; Pegas et al., 2010; Pegas et al., 2011a,b; Yang et al., 2009). People are exposed to a multitude of chemical and biological stressors, some of which cause health problems (allergy, asthma, sensory irritation, hypersensitivity pneumonitis, lung cancer, etc.) (Bernstein et al., 2008; Jie et al., 2009; Rios et al.; 2009; Samet and Spengler, 2003). On the other hand, some indoor air pollutants, such as dust and water vapour, accumulate on equipments, increasing the chance of an electrical breakdown (Lohbeck, 2008). Results of many studies demonstrate a significant and causal correlation between improving the indoor environment and gains in productivity and health (Fisk, 2000; Fisk and Rosenfeld, 1997; Kats et al., 2003; Kumar and Fisk., 2002; Mendell and Heath, 2005; Mudarri and Fisk, 2007; Seppanen et al., 2007).

Children, as result of the immaturity of immunity system and of growing processes, are more fragile and susceptible to indoor pollution effects (Mendell and Heath, 2005). Children in scholar age spend an important fraction of their time indoors in schools. In Portugal school buildings are frequently old and degraded, potentiating negative health effects in their young occupants.

As result of predictable impact of school IAQ in children health several studies have been performed worldwide in this topic (Daisey et al., 2003; Mendell and Heath, 2005). The pollutants most commonly measured in elementary school studies are gaseous compounds, which comprise total or speciated volatile organic compounds, formaldehyde and nitrogen dioxide, as well as biological agents including airborne fungi and bacteria (e.g. Blondeau et al., 2004; Godoi et al., 2009; Jo and Seo, 2005; Lee and Chang, 2000; Meklin et al., 2002; Pegas et al., 2011a,b; Yang et al., 2009). Comparatively to these traditional pollutants, indoor concentrations of particles at schools have been sparsely investigated. In spite of the various studies performed worldwide to assess the pupils' exposure to indoor particles, only a few aimed at characterising their chemical composition, and this was mainly focused on the elemental content (e.g. Almeida et al., 2011; Molnár et al., 2007; Oeder, et al., 2012; Stranger et al., 2008). Nevertheless,

practically nothing is known about the organic speciation and the respective sources of particles in the indoor air of schools. Due to their carcinogenic potential, only polycyclic aromatic hydrocarbons (PAHs) in the indoor air of residences, offices or commercial spaces have been characterised in a number of studies (Chalbot et al., 2006; Johannesson et al., 2009; Jung et al., 2010; Naumova et al., 2002, 2003; Ohura et al., 2004).

In the present study, in addition to traditional measurements, a detailed chemical characterisation of particles occurring in both indoor and outdoor environments of elementary schools was performed. As far as we know, the abundances of several classes of organic compounds in airborne particles in schools were obtained for the first time. Such information is important as it appends to the emergent global-wide dataset of IAQ in educational buildings.

6.2. Material and Methods

6.2.1. Study design

This study investigated, for the first time, pollutant concentrations inside and outside school buildings at different locations in Aveiro, Portugal. Comfort parameters (temperature, CO_2 and CO), microorganisms, NO_2, VOCs and PM_{10} concentrations in two elementary schools (city centre and suburban location) were measured between April and June 2010.

Aveiro is a coastal city with approximately 60,000 inhabitants. It is situated on the shores of a coastal lagoon. An industrial complex is located 10 km to the north of the city. The city centre school is located at 40º 38’ 16.76’’N; 8º 39’ 09.85’’W. This school started its activities in the sixties. It is surrounded by commercial and residential buildings and in front of the school there is a car parking and busy road. The main classroom studied has wood floor, water based paint covering the walls, blackboard and chalk, white board and markers and wood windows. The suburban school is located at 40º 39’ 0.09’’N; 8º 38’ 25.06’’W. This school started its activities in 2000/2001. The school is located on the

outskirts of the city in a rural area with a mixture of cultivated and abandoned farm fields. Some automobile paint and repair shops are located about 100 m west of the school. A peripheral motorway, at a lower altitude level, is approximately 500 m far. Residential neighbourhoods are found to the east. The main classroom studied presents similar characteristics to those already described for the other school. The main difference is the aluminium windows. Both school buildings are naturally ventilated.

6.2.2. Sample collection and analytical methods

Continuous measurements of temperature, relative humidity (RH), CO_2 and CO were performed with an automatic portable Indoor Air IQ-610 Quality Probe (Gray Wolf® monitor) in one classroom of each school, throughout two weeks. The equipment was supplied with a factory calibration certificate, but it was further checked prior to its use, with appropriate calibration kits.

Taking into account that the National System for Energy and Indoor Air Quality Certification of Buildings (DL 79/2006, *Regulamento dos Sistemas Energéticos de Climatização de Edifícios* – RSECE) restricts the bioaerosol measurements to bacterial and fungal colony-forming units per cubic metre of air (CFU m^{-3}), only viable and culturable fungi and bacteria were quantified. Viable microorganism levels were monitored by liquid impinger sampling (May and Harper, 1957) in the classrooms and playgrounds, during one day in each school. The flow rate was set at 2.5 L min^{-1}. Sampling took one hour at each sampling place. Five replicates of 150 L of air from each classroom and playground were collected and analysed to confirm the validity of results. The Petri dishes were incubated for 5 and 7 days for bacterial and fungal, respectively, in dark boxes with constant ambient temperature (25^{o}C).

NO_2 concentrations were passively monitored during one week-period, for two weeks, in four classrooms and playgrounds of each school. The diffusive samplers with steel grids impregnated with triethanolamine chemiadsorb NO_2, as nitrite, which was quantified by visible spectrophotometry (Bhugwant and Hoareau, 2003).

Radiello® passive samplers were used for VOC monitoring in the classrooms and at the playgrounds, during two weeks. VOCs were extracted from the exposed samplers with 2 mL carbon disulfide (CS_2 from Aldrich) containing 2-fluorotoluene (from Aldrich) as an internal standard. The glass vials were shaken for approximately 30 min. The analyses of the extracts were performed by gas chromatography (Thermo Scientific Trace GC Ultra) coupled to a flame ionisation detector. More details of the method can be found in Pegas et al. (2010).

In each school, on working days, daily sampling of PM_{10} was performed, simultaneously in one classroom and outdoors. Both indoors and outdoors, two parallel samples were obtained by using 4 low volume samplers. On the weekends, a 48-hour sampling time was adopted. The PM samples were collected onto pre-baked (6 h at 500ºC) quartz filters 47 mm in diameter. The particulate matter sampling programme was carried out over a 2 week-period in both schools. PM_{10} mass concentrations were quantified following the EN 12341 method. After mass weight, the PM_{10} filters were stored in a freezer until chemical analysis. One of the parallel PM_{10} filters was used for the WSII determination, while the respective pair was devoted to the organic speciation, after carbonate and OC/EC analysis.

For the determination of water soluble inorganic ions, small parts of the filters were extracted with ultra pure Milli-Q water. Dionex AS14 and CS12 chromatographic columns with Dionex AG14 and CG12 guard columns coupled to Dionex AMMS II and Dionex CMMS III suppressors, respectively for anions and cations, have been used.

The carbon fractions, EC and OC, were analysed by a home-made thermo-optical transmission system described in detail elsewhere (Alves et al., 2011). Carbonates present in PM_{10} samples were analysed through the release of CO_2, and measurement by the same non-dispersive infrared analyser coupled to the thermo-optical system, when a punch of each filter was acidified with orthophosphoric acid (20%) in a free CO_2 gas stream.

Two to three filters sampled during the same day of the week for the same local were combined to meet the limits of detection from speciated organic compounds. Thus, an “average” organic composition for each day of the week was obtained. The combined filters were extracted together by refluxing 300 mL of dichloromethane (Fisher Scientific)

for 24 h to obtain non-polar and semi-polar, and, to a lesser extent, polar compounds. Taking into account that the extraction efficiency of dichoromethane for polar compounds is around 75% (Gonçalves et al., 2011a), after filtration, the pieces of filter were extracted 3 times with methanol (Fisher Scientific) (75 mL for 10 min, each extraction) in an ultrasonic bath to guarantee a 100% recovery of polar compounds. All the 4 extracts were then combined, vacuum concentrated and dried under a gentle nitrogen stream. The total organic extracts were subsequently separated into five different organic fractions by flash chromatography with silica gel (230–400 mesh, 60 Å Merck Grade 9385) and various solvents of increasing polarity. Following each elution, the different fractions were vacuum concentrated and evaporated under an ultra pure nitrogen stream. Before injection, the fractionated extracts that included more polar compounds were derivatised to trimethylsilyl ethers. Finally, the extracts were analysed by gas chromatography-mass spectrometry (GC–MS). The GC–MS system was accurately calibrated using about 150 high purity individual compounds at four/five different concentration levels. All samples and authentic standards were injected with two internal standards: tetracosane-d50 (Sigma-Aldrich) and 1-chlorohexadecane (Merck). Additionally, the EPA 8270 semi-volatile internal standard mix (Supelco), containing six deuterated compounds (1,4-dichlorobenzene-d4, naphthalene-d8, acenaphthene-d10, phenanthreme-d10, chrysene-d12, perylene-d12), has been used for PAH analysis. The methodology for the extraction, flash chromatography and GC–MS analysis was previously described in detail by Alves et al. (2011).

The normality was checked for all variables by Q-Q plots and by Shapiro-Wilk tests (Brown and Hambley, 2002). When deviations from normality were observed, then the non-parametric Mann-Whitney *U* test was preferred rather than the Student's *t*-test to evaluate the significance of differences between variables (Brown and Hambley, 2002). A difference between two means was considered to be statistically significant when the *p-value* of the two-tailed Mann-Whitney *U* test was lower than 0.05. All statistical computations were conducted with the R software (*http://www.r-project.org/*).

6.3. Results and discussion

6.3.1. Comfort parameters, gaseous pollutants and microorganisms

The indoor average temperatures during the occupation periods were very similar in both schools: 23 ± 0.6^{o}C (city centre school) and 23 ± 0.5^{o}C (suburban school). The average values obtained for the relative humidity were 57 ± 2% and 46 ± 3%, respectively, for the city centre and suburban schools. In addition to meteorological specificities during the sampling campaigns in each school, this small difference may be related to the better insulation of the more recent building that composes the suburban institution. The ANSI/ASHRAE Standard 55-2004 specifies the temperature and humidity ranges that are comfortable for 80% of people engaged in chiefly sedentary activities. The operative temperature acceptable ranges are 20–23ºC in winter and 23–26ºC in summer. Acceptable RH levels should range from 30 to 60%. The "comfort zone" limits the growth of microorganisms.

Carbon dioxide is commonly measured as a screening tool to evaluate if adequate volumes of fresh outdoor air are being introduced into indoor air. The National System for Energy and Indoor Air Quality Certification of Buildings establishes an acceptable maximum value (AMV) of 1800 mg m^{-3} for buildings in Portugal (RSECE, 2006). **Figure 6.1** depicts the variation of indoor CO_2 concentrations in a typical working day at both schools. A strong correlation of the CO_2 level with occupancy has been observed. During the occupation period, in the city centre school, the CO_2 levels ranged widely from 899 to 2540 mg m^{-3}, while in the suburban school, values were between 833 and 1859 mg m^{-3}. High indoor CO_2 levels are normally considered as indicative of inadequate ventilation. Outdoor "fresh" air ventilation is important because it can dilute contaminants that are produced in the indoor environment, such as odours released from people and pollutants emitted from the buildings, equipments, furnishings, and human activities. Adequate ventilation can limit the build up of these pollutants. It is these other contaminants and not usually CO_2 that may lead to IAQ problems and complaints.

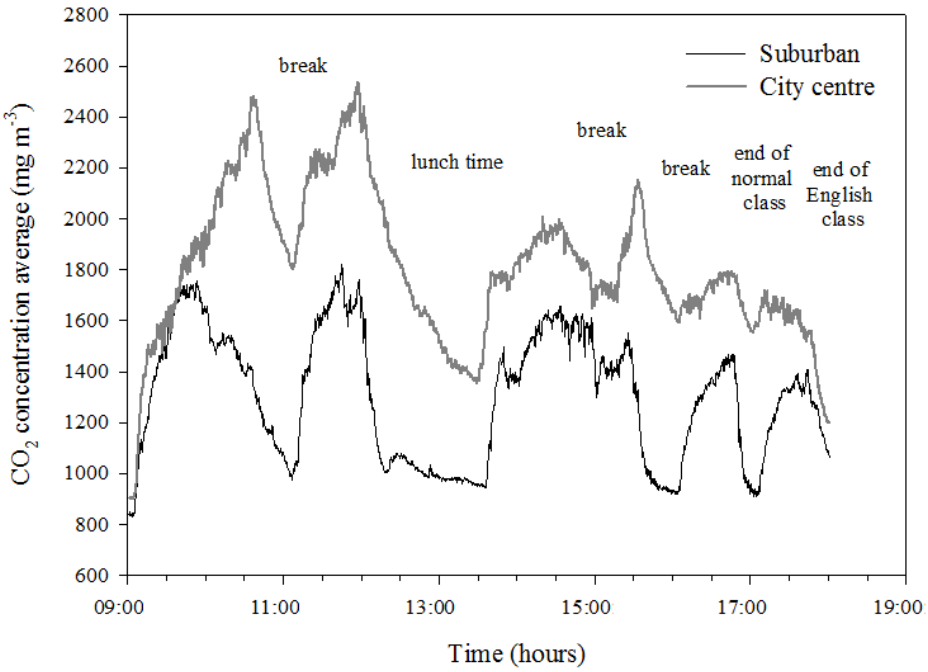

Figure 6.1. Classroom CO_2 concentration (mg m^{-3}) during a typical occupation period.

The total bacterial colony-forming units in both indoor and outdoor air (**Figure 6.2**) were above the AMV of 500 CFU m^{-3} defined by the Portuguese Legislation, Decree-Law 79/2006 (RSECE, 2006). These high CFU values are in agreement with measurements carried out in Lisbon elementary schools in spring, where indoor bacterial levels were also higher than outdoor levels at all institutions, regardless of season (Pegas et al., 2011a). The elevated levels of indoor bacteria have been primarily attributed to the number of occupants. Increased human shedding of skin cells, ejection of microorganisms and particulates from the respiratory tract, and the transport of bacteria on suspended dust particles from floor surfaces probably account for the strong positive correlation between occupancy levels and the concentration of bacteria in internal air (Goh et al., 2000; Moschandreas et al., 2003). High bacterial levels are also associated with excess moisture in indoor environments, especially in damaged buildings (Meklin et al., 2002).

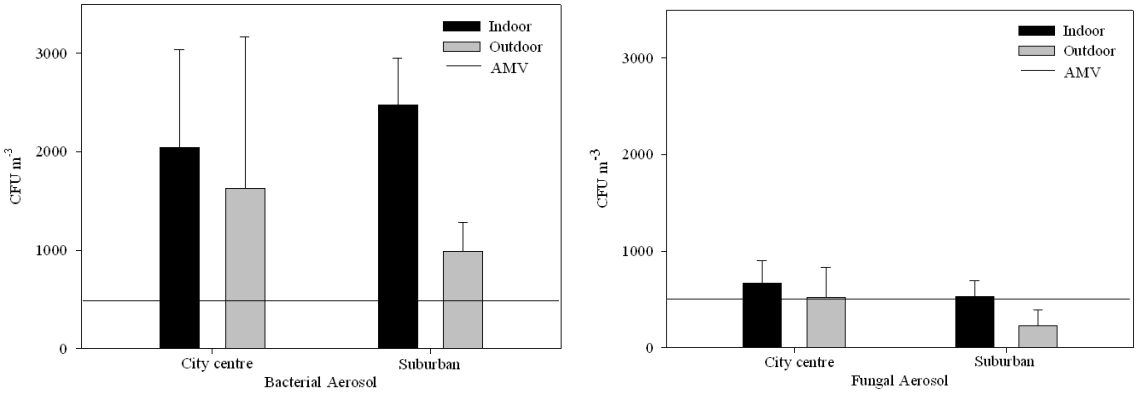

Figure 6.2. Indoor and outdoor bioaerosol levels in both city centre and suburban schools.

Comparable NO_2 concentrations were obtained in both schools. Levels were below the annual and hourly limit values (lower thresholds) of 26 μg m^{-3} and 100 μg m^{-3}, respectively, for the protection of human health, stipulated by the Air Quality Directive 2008/50/EC. The I/O average NO_2 ratio was 0.70 ± 0.06 in the city centre school, and 0.48 ± 0.23 in the suburban school. NO_2 concentrations were higher outdoors than indoors (**Table 6.1**), probably as a result of vehicular exhaust emissions from nearby traffic.

Table 6.1. NO_2 concentration in city centre and suburban schools.

		NO_2 concentration ($\mu g\ m^{-3}$)	
		City centre	Suburban
Week 1	Indoor I	14.02 ± 1.17	14.18 ± 1.19
	Indoor II	16.34 ± 1.17	16.57 ± 0.99
	Indoor III	16.46 ± 0.98	14.31 ± 1.02
	Indoor IV	12.81 ± 0.59	12.92 ± 0.59
	Outdoor	20.68 ± 1.37	20.93 ± 1.39
Week 2	Indoor I	13.39 ± 0.43	11.82 ± 1.64
	Indoor II	11.82 ± 0.33	10.63 ± 0.30
	Indoor III	13.13 ± 0.28	11.83 ± 0.26
	Indoor IV	13.13 ± 1.82	12.04 ± 0.38
	Outdoor	18.77 ± 1.44	16.85 ± 1.29

In general, concentrations of VOCs were higher indoors than outdoors for both schools (**Table 6.2**). The outdoor sum of identified VOCs was significantly lower (about 10 $\mu g\ m^{-3}$) for both schools. Higher indoor levels of many VOC species were also registered in previous studies involving 14 elementary schools of the Portuguese capital, Lisbon (Pegas et al., 2010, 2011a,b). In the present study, the very high dichloromethane concentrations in the indoor air of both schools deserve consideration. In a Canadian household study carried out by Zhu et al. (2005), very high dichloromethane indoor levels, up to 400 $\mu g\ m^{-3}$, were also measured. The National Occupational Health and Safety Commission (NOHSC) established an eight-hour time weighted average exposure limit in the workplace of 174 mg m^{-3}. Household products containing dichloromethane could possibly be the main sources of dichloromethane in indoor air. Dichloromethane is found in adhesives, spray paints, automotive cleaners, and varnish removers Among the consumer products that may contain dichloromethane are aerosol propellants, aerosol air fresheners and deodorants, furniture polish and cleaners, hairsprays, household hard surface cleaners (aerosol and liquid), household insecticides, household tints and dyes, shoe polish and cleaners, etc.

Table 6.2. VOC concentrations (μg m^{-3}).

Compounds	City centre		Suburban	
	Indoor	I/O	Indoor	I/O
Methanol	0.95	2.11	-	-
Ethanol	1.10	-	0.80	-
Acetone	2.33	1.13	1.26	1.75
Isopropanol	-	-	7.55	-
Pentane	0.64	1.02	2.92	7.49
Dichloromethane	156	43.3	115	-
2-Methylpentane	0.58	1.05	-	-
n-Hexane	0.86	1.28	2.13	10.65
Butanol	0.50	-	1.03	-
Benzene	-	-	0.31	0.84
Cyclohexane	2.53	-	0.41	0.65
Isooctane	0.30	-	0.00	-
2-Ethoxyethanol	-	-	0.70	-
Methylcyclohexane	0.60	-	0.54	-
Toluene	2.11	1.26	3.44	4.78
n-Butyl-acetate	1.22	-	1.43	-
m,p-Xylene	0.60	-	0.32	-
Nonane	-	-	0.80	-
α-Pinene	2.57	-	3.66	-
Sabinene	-	-	0.70	-
Eucalyptol	2.09	-	2.07	-
Sum of identified VOCs	175	-	145	-

6.3.2. Particles and their carbonaceous and ionic contents

It has been observed that the 24-hour PM_{10} values frequently exceed the lower threshold of 25 μg m^{-3} stipulated by the European Directive for outdoor air (**Table 6.3**). Yet, concentrations did not exceed the limit value of 150 μg m^{-3} established by the Portuguese legislation for indoor air (RSECE, 2006). However, it should be taken into account that, in this study, a 24-hour sampling schedule was followed, while classes are

only held 8 hours a day (9:00 to 18:00). Thus, measurements may have underestimated the students' exposure to PM_{10}, as it can be seen from **Table 6.4**, where rough estimations of PM_{10} concentrations during school hours are presented. The estimation of the PM_{10} concentrations for the occupation period was derived from the following mass balance:

$$PM_{10}^{Indoor(24h)} = \frac{\left(PM_{10}^{IndoorOccupation}\right)^{(8h)} + \left(PM_{10}^{OutdoorUnoccupied}\right)^{(16h)}}{24} \quad (6.1)$$

Yip et al. (2004), in an investigation conducted in Detroit elementary schools and homes, observed a 2-fold increase in indoor PM_{10} concentrations after changing the sampling time from 24 to 8 hours. The daily indoor PM_{10} levels were always higher than those outdoors, except on weekends (**Table 6.3 and 6.4**), suggesting that the physical activity of the pupils leads to resuspension of coarse particles and greatly contributes to enhance PM_{10} in classrooms (Almeida et al., 2011). The estimated PM_{10} concentrations for the occupation periods suggest that the high levels are due to class activities, either by resuspension or by the introduction/production of new particulate matter (soil material brought in shoes, blackboard dust, skin flakes, cloth and furniture fragments, viable moulds and bacteria, and insects, for example) (**Table 6.4**). Whilst the results indicated an important background contribution to indoor PM_{10} from penetration of outdoor particles, these indoor sources contributed substantially to indoor concentrations and were the dominant apportioners. In statistical terms, the indoor PM_{10} concentrations of the city centre school were significantly higher than those outdoors (*p-values* of 0.0007944), while no significant difference was observed between the indoor and outdoor levels of the suburban school (*p-value* of 0.1064). On the other hand, it was observed that the outdoor PM_{10} levels of the suburban school were significantly higher than the outdoor values of the city centre school (*p-value* of 0.004205).

Table 6.3. Average concentrations of PM_{10}, carbonates, OC, EC and soluble ionic species ($\mu g\ m^{-3}$) in both schools.

Parameters			City centre			Suburban		
			Indoor	Outdoor	I/O	Indoor	Outdoor	I/O
PM_{10}		WD	49.2 ± 9.46	23.4 ± 10.3	2.40 ± 0.88	72.8 ± 28.8	43.4 ± 11.5	1.84 ± 1.06
		WE	13.0 ± 4.66	17.6 ± 6.31	0.74 ± 0.00	20.4 ± 2.4	22.9 ± 6.43	0.91 ± 0.15
carbonates		WD	0.57 ± 0.34	0.04 ± 0.01	16.3 ± 9.72	0.97 ± 0.78	0.08 ± 0.11	19.8 ± 20.2
		WE	0.03 ± 0.00	0.02 ± 0.00	1.84 ± 0.20	0.32 ± 0.42	0.02 ± 0.02	10.3 ± 11.1
OC		WD	14.1 ± 2.71	4.98 ± 2.35	3.35 ± 1.37	13.7 ± 5.00	4.36 ± 1.96	3.84 ± 2.70
		WE	4.60 ± 0.67	4.34 ± 1.37	1.14 ± 0.51	6.84 ± 5.38	1.45 ± 0.98	7.73 ± 8.93
EC		WD	1.70 ± 0.50	1.42 ± 0.54	1.36 ± 0.65	0.99 ± 0.74	0.68 ± 0.75	1.36 ± 1.37
		WE	1.32 ± 0.61	0.58 ± 0.55	3.28 ± 2.06	0.36 ± 0.51	0.18 ± 0.25	1.02 ± 1.44
Soluble ionic species	chloride	WD	0.67 ± 0.60	0.93 ± 1.05	1.67 ± 3.62	0.99 ± 0.72	2.37 ± 1.77	0.57 ± 0.62
		WE	0.48 ± 0.41	1.37 ± 1.13	0.35 ± 0.01	0.67 ± 0.22	1.49 ± 0.08	0.45 ± 0.13
	nitrate	WD	1.02 ± 1.00	1.86 ± 1.40	0.61 ± 0.37	1.04 ± 0.59	2.04 ± 1.48	0.68 ± 0.71
		WE	0.57 ± 0.21	1.30 ± 0.69	0.46 ± 0.08	0.53 ± 0.01	1.06 ± 0.05	0.50 ± 0.02
	sulphate	WD	1.27 ± 0.79	1.96 ± 1.25	0.70 ± 0.22	2.87 ± 1.47	3.46 ± 2.14	1.01 ± 0.82
		WE	1.03 ± 0.02	1.48 ± 0.61	0.76 ± 0.30	2.11 ± 0.57	2.11 ± 0.57	1.00 ± 0.00
	sodium	WD	0.90 ± 0.60	1.17 ± 0.99	1.09 ± 0.98	2.69 ± 1.73	3.81 ± 1.75	0.78 ± 0.57
		WE	0.73 ± 0.58	1.55 ± 1.14	0.45 ± 0.04	1.24 ± 0.10	2.10 ± 0.12	0.59 ± 0.08
	ammonia	WD	0.51 ± 0.43	0.69 ± 0.35	0.68 ± 0.44	0.74 ± 0.54	0.89 ± 0.49	0.81 ± 0.49
		WE	0.43 ± 0.14	0.45 ± 0.21	0.99 ± 0.16	0.39 ± 0.33	0.53 ± 0.20	0.66 ± 0.37
	potassium	WD	0.26 ± 0.05	0.19 ± 0.10	1.55 ± 0.58	0.26 ± 0.11	0.19 ± 0.07	1.69 ± 1.14
		WE	0.12 ± 0.01	0.20 ± 0.04	0.62 ± 0.07	0.10 ± 0.03	0.09 ± 0.05	1.28 ± 0.97
	magnesium	WD	0.09 ± 0.06	0.14 ± 0.12	0.69 ± 0.21	0.15 ± 0.08	0.36 ± 0.18	0.46 ± 0.20
		WE	0.08 ± 0.06	0.19 ± 0.14	0.43 ± 0.00	0.07 ± 0.03	0.17 ± 0.05	0.40 ± 0.07
	calcium	WD	1.05 ± 0.20	0.33 ± 0.19	3.94 ± 1.66	0.74 ± 0.31	0.51 ± 0.28	1.84 ± 1.50
		WE	0.08 ± 0.04	0.22 ± 0.16	0.39 ± 0.12	0.19 ± 0.10	0.18 ± 0.08	1.36 ± 1.20

WD - week day, WE - weekend.

Table 6.4. Indoor and outdoor PM_{10} concentration during all day long (24h) and estimated indoor occupation (8h).

	City centre PM_{10} concentration ($\mu g\ m^{-3}$)				Suburban PM_{10} concentration ($\mu g\ m^{-3}$)			
	Indoor (24h)	Outdoor (24h)	I/O	Estimated Indoor Occupation (8h)	Indoor (24h)	Outdoor (24h)	I/O	Estimated Indoor Occupation (8h)
WD 1	54.13	16.21	3.34	130.0	49.76	49.30	1.01	50.67
WD 2	44.94	15.07	2.98	104.7	59.17	37.52	1.58	102.5
WD 3	48.75	19.53	2.50	107.2	51.02	37.49	1.36	78.07
WD 4	73.99	22.32	3.31	177.3	89.09	36.73	2.43	193.8
WD 5	40.73	20.19	2.02	81.80	73.06	39.74	1.84	139.7
WD 6	52.79	19.44	2.72	119.5	91.27	36.09	2.53	201.6
WD 7	45.56	12.44	3.66	111.8	97.41	56.28	1.73	179.7
WD 8	47.50	17.21	2.76	108.1	108.6	67.08	1.62	191.6
WD 9	53.88	39.66	1.36	82.32	96.56	40.69	2.37	208.3
WD 10	45.49	43.50	1.05	49.46	101.4	22.57	4.49	259.1
WD 11	47.44	35.80	1.33	70.73	-	-	-	-
WD 12	35.47	19.42	1.83	67.58	-	-	-	-
WE 1	9.714	13.13	0.74	*	18.69	18.35	1.02	*
WE2	16.31	22.06	0.74	*	22.11	27.44	0.81	*

WD - week day; WE - weekend; lost sample (-); without occupation (*).

Our results are in line with findings of previous studies carried out in elementary schools in different regions of the world (Almeida et al., 2011; Blondeau et al., 2004; Diapouli et al., 2008; Fromme et al., 2008; Halek et al., 2009; Oeder et al.,2012; Stranger et al., 2008). It has been shown that fine particulate matter is the size fraction most strongly associated with morbidity, but some studies have demonstrated that PM_{10} may also have negative effects on children's health (Schwartz and Neas, 2000; Smith et al., 2000; Weinmayr et al., 2010).

Taking into account that the main component of chalk used in both schools is calcium carbonate ($CaCO_3$) and not calcium sulphate ($CaSO_4$), and thus assuming there is no indoor source of sulphate, the indoor-generated PM_{10} can be calculated by the infiltration ratio for sulphate (Fromme et al., 2008), as follows:

$$C_{ig} = C_i - \frac{\beta^{PM}}{\beta_{sulph}} \times \frac{C_i^{sulph}}{C_o^{sulph}} \times C_o \qquad (6.2)$$

where C_{ig} is the sum of indoor-generated PM_{10}, C_i is the total indoor PM_{10} concentration, β^{PM}/β^{sulph} is the ratio between the increase of indoor PM_{10} per outdoor PM_{10} (linear relationship) and the increase of indoor sulphate per outdoor sulphate (linear relationship), C_i^{sulph} is the indoor sulphate concentration, C_o^{sulph} is the outdoor sulphate concentration, and C_o is the outdoor PM_{10} concentration (Fromme et al., 2008).

Applying the measured values, it has been observed that 74 ± 23% of the total PM_{10} in the city centre school was generated indoors rather than being carried inside from outdoors, while highly variable contributions were obtained for the suburban school.

Generally, the concentration of particulate water soluble inorganic ions (**Table 6.3**) was higher outdoors (30% and 32% of the PM_{10} mass at the city centre school and at the suburban school, respectively) than indoors (13% and 18% of the PM_{10} mass at the city centre and at the suburban school, respectively), suggesting that the main sources of inorganic material are external. Indoor sulphate was the dominant water soluble ion, representing 22% and 30% of the total concentrations of all analysed ions, in the city centre and suburban schools, respectively. The indoor sulphate levels in the suburban school were significantly higher than the indoor levels in the city centre school (*p-value* of 0.000981). The outdoor sulphate levels at the suburban school were found to be significantly higher than those observed at the city centre institution (*p-value* of 0.02751). The chloride levels in the downtown school accounted for 12% and 13% of the total ionic concentrations in the indoor and outdoor air, respectively. In the suburban school, the chloride levels represented 10% (indoors) and 17% (outdoors) of the total ionic mass concentrations. The outdoor chloride levels of the suburban school were significantly higher than the indoor levels at the city centre school (*p-value* of 0.005109). As observed in other coastal towns, such as Salina Cruz, Mexico (Baumgardner et al., 2006), the amounts of chloride ion likely have a strong contribution from sea spray. The school situated on the outskirts of the city is more exposed to this natural input. The calcium levels were significantly higher in the indoor environment of the city centre school than those observed outdoors (*p-value* of 0.00129). The higher indoor levels are probably related to the use of chalk on the blackboard. This observation is corroborated by the high carbonate (CO_3^{2-}) concentrations in the classrooms. The indoor carbonate concentrations

were about 16-20 times the amounts found outdoors during the weekdays. Carbonates represented approximately 1.2% of the PM_{10} mass for both schools. Magnesium represented one of the less abundant ions in the indoor environment. The outdoor magnesium concentrations at the suburban school were significantly higher than those measured indoors (*p-value* of 0.0006122), and the suburban outdoor levels were higher than those of the corresponding environment at the city centre school (*p-value* of 0.001759).

Carbonaceous components (EC and OC) presented higher levels inside than outside (**Table 6.3**). Indoor OC sources seem to be mainly related to student room occupancy and their activities, like small particles of paper, skin debris and clothing fibres. OC constituted the major mass fraction, accounting for almost 30% and 20% of PM_{10} in the city centre and suburban schools, respectively. Elemental carbon contributed, on average, to 3.4% and 1.6% of the particle mass in these two educational establishments. The indoor OC concentrations were found to be significantly higher than those outdoors for the city centre and suburban schools (*p-value* of 3.4e-05 and 4.404e-05, respectively). EC indoor concentrations observed in the city centre school were statistically higher than the values measured in the classroom of the suburban building (*p-value* of 0.002417). The outdoor levels obtained for the inner-city institution were also significantly higher than those measured at the playground of the suburban establishment (*p-value* of 0.003145).

6.3.3. Organic speciation of particles

The chromatographically resolved organic compounds in the particulate phase encompassed aliphatics, PAHs, *n*-alkanols, sugars, polyols, and several types of acids (**Figure 6.3**). Besides *n*-alkenes, the aliphatic fraction comprised *n*-alkanes that exhibited a lack of odd-to-even carbon number predominance with C_{max} at C_{26}, C_{28} and C_{29}. Carbon preferences indices close to 1 (**Table 6.5 and 6.6**), together with the presence of petrogenic tracers (e.g. hopanes), whether in classrooms or in outdoor air, reflect the contribution of vehicular sources (Alves, 2008). The influence of traffic emissions on the indoor air quality is corroborated by the values of diagnostic ratios between PAHs (**Figure 6.4**), which fall in the ranges reported for catalyst-equipped vehicles (Alves, 2008; Bi et al.,

2003; Callén et al., 2011). In some days, however, the PAH ratios reflect the influence of industrial emissions on the PM_{10} collected in the suburban school. The BaP dose equivalent (*BaPE*) for each PAH is calculated by multiplication of the measured concentrations by the respective potency equivalent factor (*PEF*). The *PEF* values were taken from Delgado-Saborit et al. (2011), who presented a compilation of data based on a literature review. The BaP dose equivalent is then calculated as a sum to express the carcinogenicity of the mixture:

$$BaPE = \sum PAH_i \, xPEF_i \tag{6.3}$$

The levels of carcinogenic PAHs (**Figure 6.5**) were in the typical ranges reported for USA and Europe (Callén et al., 2011; Jung et al., 2010; Mantis et al., 2005) and much lower than those measured in Asia (e.g. Fang et al., 2002). The *PEFs* were also used to calculate the proportion of total carcinogenic potential represented by each individual PAH:

$$\left(\%Carc.Potential\right)_i = \frac{\left(RCxPEF\right)_i}{\sum_{i=1}^{N}\left(RCxPEF\right)_i} x100 \tag{6.4}$$

where *RC* is the ratio of the individual PAHs to the carcinogenic marker BaP. **Figure 6.5** shows the individual carcinogenic activity for both indoor and outdoor environments. The compound that contributes most to the total carcinogenic potential of the PAH mixture was always BaP, with average values higher than 61%. Its contribution to total carcinogenicity was slightly higher indoors than outdoors. The second or third highest contributors were benzo[k]flouranthene and chrysene with average shares of 12-14% and 12-16%, respectively. While the contribution from chrysene was higher outdoors, that of

benzo[k]flouranthene did not show any clear pattern. The carcinogenic risk was calculated as follows:

$$Carcinogenic\,risk = PAH_i x PEF_i x UR \quad (6.5)$$

where *UR* represents the cancer unit risk, i.e. the excess cancer risk associated with an inhalation of 1 µg m^{-3} of a compound. It is obtained by multiplication of the cancer potency factor for BaP [3.9 (mg kg^{-1} $d^{-1})^{-1}$] by the reference child inspiration rate per day (12.4 m^3) and dividing by the reference child body weight (21 kg) multiplied by a conversion factor from mg to ng of 10^6 (Bari et al., 2011; Elert et al., 2011). The carcinogenic risk to occupants from the suburban and city centre schools was found to be in the ranges 4.4×10^{-8}-2.4×10^{-7} and 1.2×10^{-7}-2.3×10^{-7}, respectively. In general, USEPA considers excess cancer risks that are below about one chance in a million (1×10^{-6}) to be so small as to be negligible.

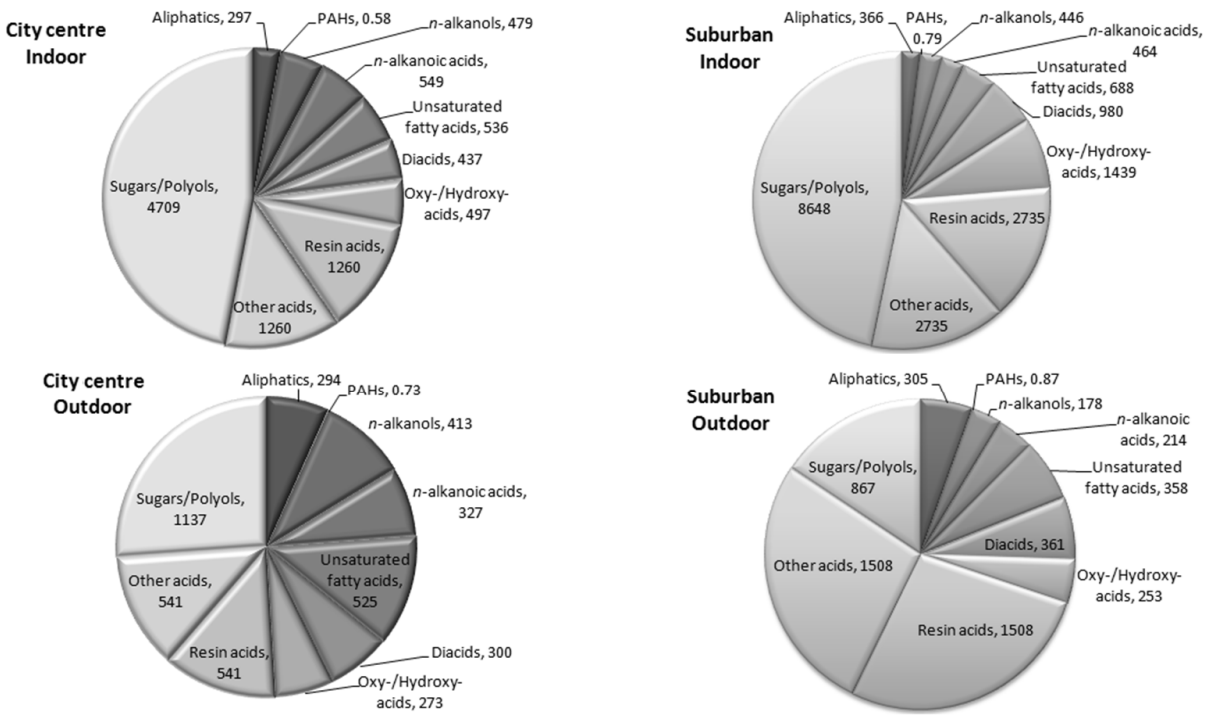

Figure 6.3. Concentrations (ng m^{-3}) of the dominant organic classes detected in PM_{10}.

Table 6.5. Average concentrations of some organic tracers (ng m^{-3}) on working days (WD) and weekends (WE).

		City centre				Suburban			
		Indoor		Outdoor		Indoor		Outdoor	
TRACER	SOURCE/PROCESS	WD	WE	WD	WE	WD	WE	WD	WE
Levoglucosan	Biomass burning	333	138	80.0	150	121	19.2	48.9	16.5
Galactosan	Biomass burning	160	16.9	24.5	27.4	84.5	8.8	14.4	8.37
Mannosan	Biomass burning	137	15.8	22.1	23.9	77.4	8.82	15.5	7.91
Dehydroabietic acid	Conifer biomass burning	17.2	5.79	12.1	19.9	399	12.2	19.4	5.15
Stearin	Cooking	98.7	44.8	62.1	5.23	293	44.3	59.8	20.3
Palmitoleic acid	Cooking	488	320	506	234	638	259	299	173
Hopanes	Vehicle exhausts	15.0	8.3	75.5	70.4	4.68	3.43	0.57	0.38
Squalene	Skin desquamation	10.2	4.26	-	-	1.71	-	0.53	-
Benzoic acid	Photo-oxidation of PAHs	139	129	95.7	33.2	222	6.88	113	59.7
Pinic acid	Photo-oxidation of pinenes	143	77.4	203	158	122	91.7	170	103

– not detected; WD: week day; WE: weekend

Table 6.6. Carbon preferences index (CPI) and homologues with the highest concentrations.

		City centre		Suburban	
		Indoor	Outdoor	Indoor	Outdoor
	CPI	1.24±0.06	1.04±0.12	1.07±0.28	1.02±0.07
n -Alkanes	$\mathbf{C_{max}}$	C_{29}, C_{28}	C_{29}, C_{28}, C_{26}	C_{30}, C_{29}, C_{26}	C_{29}, C_{28}
	CPI	4.41±1.17	8.96±3.29	6.50±1.92	14.9±13.4
n -Alkanols	$\mathbf{C_{max}}$	C_{18}	C_{18}	C_{18}	C_{18}
	CPI	6.16±4.62	6.33±4.24	3.65±1.08	3.13±1.78
n -Alkanoic acids	$\mathbf{C_{max}}$	C_{16}	C_{16}	C_{24}, C_{26}, C_{12}	C_{16}, C_{14}, C_{16}

CPI – ratio between concentrations of odd to even numbered homologs, in the case of *n* -alkanes; even to odd ratios in the case of *n* -alkanols and *n* -alkanoic acids

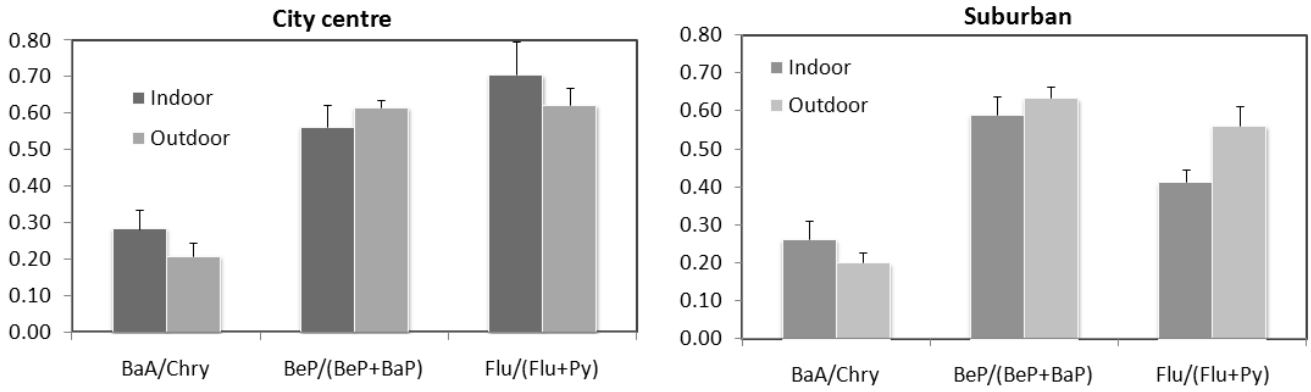

Figure 6.4. PAH ratios (BaA - Benzo[a]anthracene; Chry – Chrysene; BeP – Benzo[e]pyrene; BaP – Benzo[a]pyrene; Flu – Fluoranthene; Py – Pyrene)

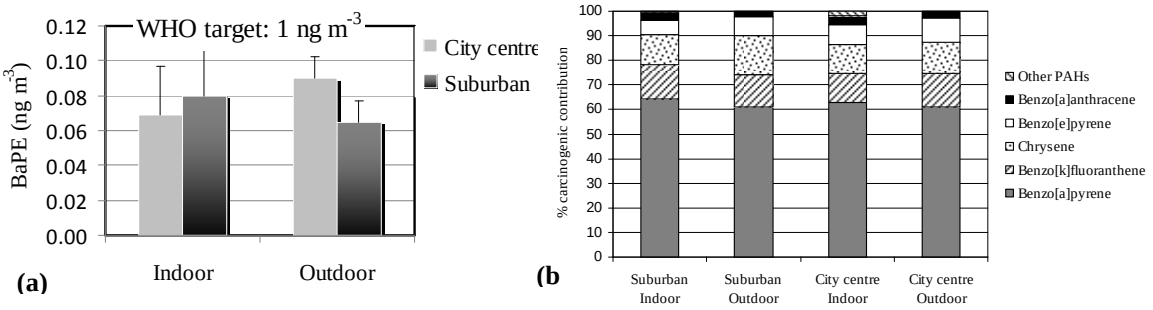

Figure 6.5. (a) Benzo[a]pyrene equivalent concentrations and the World Health Organization target value (WHO, 2010); (b) individual carcinogenic activity for both indoor and outdoor environments.

Besides *n*-alkanes, homologues series of *n*-alkanols (C_{10}-C_{30}) and *n*-alkanoic acids (C_6-C_{28}) were also present in the aerosol samples. The strong even carbon number predominance reflects a dual biogenic origin: (i) waxes from terrestrial vegetation, in the case of the higher weight homologs, and (ii) microbial lipids, in the case of homologues < C_{20}.

Among acids, unsaturated compounds, such as palmitoleic ($C_{16:1}$), oleic ($C_{18:1}$) and linoleic ($C_{18:2}$), were one of the most representative groups. The presence of these acids in atmospheric particles has been attributed to cooking emissions (He et al., 2004). Due to their reactivity, these fatty acids are often used as an indication of the ageing of the aerosols. For most days, the $C_{18:0}/C_{18:1}$ and $C_{18:0}/C_{18:2}$ concentration ratios were lower than 0.6, whether indoors or outdoors, indicating recent genesis of the unsaturated fatty acids (Alves et al., 2007). In spite of the presence of constituents from cooking fumes in the particulate matter, the contribution of this source to VOCs is not so obvious. It should be noted, however, that the dominant VOCs emitted during cooking activities were not searched for in the present study. In fact, it has been reported that formaldehyde, acetaldehyde, and low molecular weight alkanals, 2-alkenals, 2-alkanones and dicarbonyls are major VOCs in emissions from cooking (Fullana et al., 2004; Schauer et al., 2002).

Alkanedioic acids, ranging from the C_3 (propanedioic) to the C_9 homologue (nonanedioic) were detected in PM_{10}. Dicarboxylic acids < C_{10} may be originated from vehicle emissions, meat cooking, biomass burning or atmospheric oxidative processes (Alves et al., 2007). The presence of some diacids in PM_{10} may be associated with vegetation detritus as they are present in the guttation fluids, fruits and tissues of plants. Additionally, they may be originated from the ozonolyis of sporopollenin of spores and pollen grains (Oliveira et al., 2007; and references therein). Indoor concentrations were higher than those measured in the school yards, suggesting accumulation of these constituents inside the buildings and/or that part of them can be generated indoors. Significant amounts of other oxygenated species, some of which are thought to be photo-oxidation products of volatile organic compounds, from both biogenic and/or anthropogenic origin, were identified in the PM_{10} samples. These include hydrocarboxylic acids, oxocarboxylic acids and terpene diacids. The global outdoor levels in the suburban schools were 3-times higher than those measured in the city centre establishment, although

the indoor values were comparable. Benzoic acid, a secondary product from photochemical degradation of aromatic hydrocarbons such as toluene emitted by automobiles (Ho et al., 2011), was one of the secondary organic aerosol (SOA) products observed in samples. Most of the homologous ketocarboxylic acids (e.g. oxobutanoic and oxopentanoic), also detected in this study, are secondarily produced via atmospheric photo-oxidation of organic precursors and/or primarily formed by fossil fuel combustion and biomass burning and further oxidised into diacids (Wang et al., 2009). Pinic and pinonic acids, which represent photo-oxidation products of terpenes emitted from vegetation (Alves, 2008, and references therein), were present at higher concentrations outdoors. These pinene derivatives have been detected in ventilation ducts, where they can be formed at ambient levels of ozone and precursors (Fick et al., 2004). The presence of precursors in indoor air may have two sources, either from the outdoor environment or from recirculated indoor air.

The occurrence of resin acids (isopimaric, abietic and dehydroabietic) in the indoor air indicates infiltration from the outdoor environment. These constituents are markers from gymnosperm (mainly conifer) fuel combustion (Gonçalves et al., 2011b). Conifer wood processing can be pointed out as another possible source of resin acids (Eriksson et al., 2004). The wood dust released into the air contains these diterpenic acids, which are the main constituents of the oleoresin of the coniferous tree species. The presence of carpentry workshops and sawmills in the vicinity of the suburban school may explain the higher levels observed in comparison with the city centre institution. Resin acids may also be originated from a turpentine factory located on the outskirts of the city. Turpentine is produced from distilling the resinous gum from pine trees. Frequently, during the late afternoon and the first few hours of the night, the prevailing winds transport the plume to the city, and usually affect more the suburban school than the city centre school.

Saccharides in atmospheric particles originate from different source types. Microorganisms, plants and animals can release into the atmosphere primary saccharides (monosaccharides including glucose, fructose, xylose and disaccharides, such as sucrose and trehalose), whereas fungi, lichens and bacteria produce saccharidic polyols, also denoted as sugar alcohols, such as arabitol, mannitol and sorbitol (Caseiro et al., 2007). Anhydrosaccharides, on the other hand, such as levoglucosan derived from cellulose, and galactosan and mannosan, derived from hemicelluloses, are the primary thermal

degradation products of structural polysaccharides present in biomass (Gonçalves et al., 2011). The average I/O obtained in the city centre and suburban schools for the global concentrations of sugars and polyols were, respectively, 4.1 and 5.7, reflecting the representativeness of bioparticles in the indoor air.

Levoglucosan is commonly used as a tracer for wood combustion in urban atmosphere (e.g. Oliveira et al., 2007). However, taking into account that the sampling campaign was carried out in spring, emissions from residential wood combustion for heating purposes are thought to represent a minor contribution. Levoglucosan was detected in Chinese cooking source profiles (He et al., 2004; Hou et al., 2008). The high temperature during cooking processes would lead to the emission of levoglucosan due to thermal degradation of vegetable cellulose. Spices such as *Cumimum cyminum* and *Capsicum* (powder of dry vegetables) used as condiments can also decompose to form levoglucosan (Hou et al., 2008). Thus, in addition to woodstoves and/or open-hearth cooking in restaurants in the school surroundings, food preparation in these commercial spaces may likely contribute to levoglucosan emissions. The open field burning of garden and agriculture residues may represent an additional source of anhydrosugars and other compounds to the aerosol, especially in the suburban school.

Organophosphate esters and six phthalate esters were detected in PM_{10} from both schools. Both groups of these semi-volatile compounds are widely incorporated as additives into plastic materials used in the indoor environment, thus contributing to the indoor exposure to industrial chemicals. I/O ratios ranging from 4 to 14 and from 1 to 9 were obtained in the city centre and suburban schools, respectively.

Squalene, a constituent of skin flakes (Weschler et al., 2011), was almost exclusively found in indoor samples, pointing out skin desquamation as a major source.

6.4. Conclusions

Comparison of weekday and weekend data demonstrated that school activity and indoor sources increase loadings of many gas and particle pollutants. Almost all of the identified

VOCs showed I/O ratios higher than one, and especially dichloromethane, suggesting the presence of important indoor sources in both schools. The daily profiles of CO_2 suggest that the classrooms are inadequately ventilated, which likely favours accumulation of pollutants in indoor air. Vehicle emissions contributed to I/O NO_2 ratios lower than 1 and to PAH ratios typical of this source. However, the benzo[a]pyrene equivalent concentrations were lower than the WHO target value and the carcinogenic risk to occupants from the suburban and city centre schools was found to be negligible. Only 26% of PM_{10} were of ambient origin. Indoor sources of organic matter have a strong impact on indoor PM_{10} concentrations (small particles of paper, skin and cloth particles). All the carbonaceous fractions showed a significant enrichment in the indoor environment. Chalk used in classrooms could explain the higher indoor concentrations of carbonate. Outdoor particulate infiltration leads to direct transportation into indoors of vehicle emissions and biomass burning smoke likely coming from solid fuel use in restaurants and bakeries. The effect of cooking activities in the restaurants on the indoor air particulate level in city centre school nearby is important. The cooking activities around this school release significant amounts of oily fumes from kitchens to outdoor air, which infiltrate into the classrooms. The suburban school was more exposed to industrial emissions than the city centre institution.

This type of study should be extended to other schools in order to be better able to sustain IAQ management strategies, and to apply source apportionment methodologies. Future investigations should also evaluate the toxicological aspects related to the PM exposure in schools in comparison to PM exposure in outdoor air.

6.5. References

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Chapter 7

7. COULD HOUSEPLANTS IMPROVE INDOOR AIR QUALITY IN SCHOOLS?

Published

Pegas, P.N., Alves, C.A., Nunes, T., Bate-Epey, E.F., Evtyugina, M., Pio, C.A., In Press. Could houseplants improve indoor air quality in schools? Journal of Toxicology and Environmental Health, Part A [ISSN: 1093-7404].

Abstract

Previous studies performed by the National Aeronautics Space Administration (NASA) indicated that plants and associated soil microorganisms can be used to reduce indoor pollutant levels. This study investigated the ability of plants to improve indoor air quality in schools. A nine-week intensive monitoring campaign of indoor and outdoor air pollution was carried out in 2011 in a primary school of Aveiro, Portugal. Measurements included temperature, CO_2, CO, concentrations of volatile organic compounds (VOCs), carbonyls and particulate matter (PM_{10}) without and with plants in a classroom. PM_{10} samples were analysed for the water soluble inorganic ions, as well for the carbonaceous fractions. After hanging 6 potted plants from the ceiling, the mean CO_2 concentration decreased from 2004 to 1121 ppm. The total VOC average concentrations in the indoor air during periods of occupancy without and with the presence of potted plants were, respectively, 933 and 249 $\mu g\ m^{-3}$. The daily PM_{10} levels in the classroom during the occupancy periods were always higher than those outdoors. The presence of potted plants likely favoured a decrease of about 30% in PM_{10} concentrations. Our findings corroborate the results of NASA studies suggesting that plants can clean indoor air and make interior breathing spaces healthier.

Key words: indoor air quality, VOCs, carbonyls, PM_{10}, plants, school.

7.1. Introduction

Various studies have demonstrated that plants can be used to remove pollutants from indoor air (e.g. Liu et al., 2007; Matsumoto and Yamaguchi, 2007; Wolverton et al., 1989; Wood et al., 2006). Plants have been pointed out as an attractive and cost effective way to improve indoor air quality (IAQ). Indoor potted-plants have been shown to remove most types of airborne pollutants arising from either outdoor or indoor sources. The benefits of plants on attendance and wellbeing of building occupants has been documented (Berg, 2002; Fjeld, 2002).

This issue arose when the National Aeronautics Space Administration (NASA) tried to find ways to reduce pollutants inside future space habitats (NASA, 1974). Wolverton et al. (1984, 1985, 1989) placed potted plants inside sealed plexiglass chambers, injecting substances commonly found in indoor air. The results showed that leaves, soil, and plant-associated microorganisms have an important function in reducing indoor air pollutants (cigarette smoke, organic solvents, and bioaerosol).

In schools, IAQ is often much worse than outdoor air quality (Kotzias et al., 2009; Pegas et al., 2010; Pegas et al., 2011a, b). Studies carried out by the USA Environmental Protection Agency (EPA) indicate that indoor air pollutant concentrations may be 2-5 times, and occasionally more than 100 times, higher than outdoor levels.

There are several reasons to consider IAQ at primary schools a public concern. One is that children breathe higher volumes of air, relatively to their body weights. Children's physiological vulnerability to air pollution arises from their narrower airways and the fact that their lungs are still developing. Also, many children breathe through their mouths, bypassing the nasal passages' natural defences. Thus, children are more likely to suffer the consequences of indoor pollution. Another reason for environmental deficiencies in schools is due to chronic shortages of funding, which contribute to inadequate operation and maintenance of facilities (Mendell and Heath, 2005).

Previous measurements of particulate matter (PM_{10}), volatile organic compounds (VOCs) and carbonyls carried out in elementary schools in Lisbon revealed indoor/outdoor

(I/O) ratios above unity, showing the influence of indoor sources, building conditions and inappropriate ventilation on IAQ, and indicating the need to take decisive remedial actions (Almeida et al., 2011; Pegas et al., 2010; Pegas et al., 2011a, b). The main purpose of the present study was to assess the effectiveness of three common species of houseplants in the fight against rising levels of air pollution in classrooms.

7.2 Material and Methods

7.2.1 Study design

This study investigated the effectiveness of potted plants suggested by NASA (NASA, 1974) in reducing the air pollutant concentrations in classrooms. A school located in the city centre of Aveiro, Portugal, was selected to carry out this study. The selected school is located at 40º 38' 16.76''N; 8º 39' 09.85''W. This school started its activities in the sixties. It is surrounded by commercial and residential buildings and in front of the school there is a car parking and a busy road. The main classroom studied has wood floor, water based paint covering the walls, black board and chalk, white board and markers and five wood windows. The area of the room was 52.5 m^2. The number of students in the classroom is around 25.

Comfort parameters (temperature, relative humidity, CO_2 and CO), VOCs, carbonyls and particulate matter < 10 μm (PM_{10}) concentrations were measured between February and May 2011, 3 weeks without plants (February 28th to March 20th 2011) and 6 weeks with potted plants indoors (March 21st to May 28th 2011).

Dracaena deremensis (Striped dracaena or Janet Craig), *Dracaena marginata* (Red-edge Dracaena, Madagascar dragon tree or Marginata) and *Spathiphyllum* (Mauna loa or Peace lily) were the selected houseplants, since in test-chamber studies (Orwell et al., 2004; Tarran et al., 2002; Wolverton et al., 1989; Wood et al., 2002; Wood et al., 2006) they have been found to be reliably effective in removing benzene, toluene, ethylbenzene and xylenes (BTEX).

The potted-plants were all of similar size, weight and age. In classrooms, they were placed on metallic holders to ensure there was enough height from the floor and a free space under the pot for air circulation (about 30 cm). The number of potted-plants was defined according to the area of the classroom. The Associated Landscape Contractors of America (ALCA) recommendation is one plant per 9.29 m^2. Thus, six potted-plants (300 mm diameter pots) were placed in the selected classroom.

7.2.2 Sampling and analytical methods

Continuous measurements of temperature, relative humidity (RH), CO_2, CO and total VOCs were performed with an automatic portable Indoor Air IQ-610 Quality Probe (Gray Wolf® monitor) and a TSI monitor, simultaneously in the classroom and at the playground, respectively, during 9 weeks.

Every week, during 9 weeks, passive samplers for VOCs and carbonyls (Radiello®) were used to obtain indoor and outdoor average concentrations. Another set of Radiello passive samplers were only exposed from 8:30 AM to 17:30-18 PM to obtain VOC and carbonyl concentrations for the occupancy periods.

VOCs adsorbed in activated charcoal cartridges were extracted with 2 mL of carbon disulfide (CS_2) containing the internal standard, in accordance with the Radiello® procedure. Analyses were performed by gas chromatography (Thermo Scientific Trace GC Ultra) coupled to a flame ionisation detection (GC/FID). The equipment was calibrated before and during the analyses of samples by injecting standard solutions of all compounds identified in CS_2 (Pegas et al., 2010).

Carbonyls were extracted with 2 ml of acetonitrile during 30 minutes and the extract filtered through 0.45 μm membrane disc filters (filtration kit RAD 174) and injected into the high-performance liquid chromatography (HPLC) system. The carbonyl concentrations were quantified with external calibration curves constructed from standard solutions - Aldehyde/ketone-DNPH TO11/IP-6A Mix (USEPA, 1999).

Active sampling of carbonyls was performed during two days in the first period without plants (March 24th and 25th) and during two days in the second period with plants (May 25th and 26th). Carbonyl active collection involved a sampling train consisting of a Thomas pump to draw in air at a flow rate of 2 L min^{-1} for a sampling time of one or two hours in agreement with the classroom cycles, through silica gel cartridges, impregnated with 2,4-dinitrophenylhydrazine reagent (Sep-Pak® DNPH-Silica Cartridges), a dry gas meter to measure the volume of air and ozone scrubbers to minimise ozone interferences. The analytes were extracted with 5 mL of acetonitrile by filtration through gravity feed elution and the extract collected in 3 mL vials and later analysed by high-performance liquid chromatography (HPLC) with UV detection at absorption wavelength at 360 nm (ASTM, 1997).

Two low volume samplers were used to collect simultaneously indoor and outdoor PM_{10} on a daily basis, during the occupancy period, from 8:30 AM to 17:30-18 PM, over a period of 9 weeks. The PM_{10} samples were collected onto pre-baked (6 h at 550ºC) quartz filters 47 mm in diameter. Before weighting, the filters were conditioned in a desiccator at least for 24 hours in a temperature and humidity-controlled room. Before and after sampling, the gravimetric determination was performed with a microbalance Mettler Toledo AG245 (readability 0.1mg/0.01mg). Filter weights were obtained from the average of ten measurements, with weight variations less than 5%.

The elemental and organic carbon (EC and OC) content in PM_{10} was analysed by a home-made thermal-optical transmission system, after passive exposure of sampled filters to HCl vapours to remove carbonate interferences. This procedure was at first developed by Carvalho *et al.* (2006) and recently adapted by Alves *et al.* (2011). Carbonates present in PM_{10} samples were analysed through the release of CO_2, and measured by the same non-dispersive infrared analyser coupled to the thermo-optical system, when a punch of each filter was acidified with orthophosphoric acid (20%) in a free CO_2 gas stream (Alves *et al.* 2011).

For the determination of water soluble inorganic ions (WSII), a filter fraction (2 discs of 13 mm of diameter) were extracted with ultra pure Milli-Q water. Dionex AS14 and CS12 chromatographic columns with Dionex AG14 and CG12 guard columns coupled

to Dionex AMMS II and Dionex CMMS III suppressors, respectively for anions and cations, have been used.

To evaluate the significance of differences between variables, the non-parametric Mann-Whitney *U* test was preferred rather than the Student's *t*-test (Browm and Hambley, 2002). A difference between two means was considered to be statistically significant when the *p-value* of the two-tailed Mann-Whitney *U* test was lower than 0.05. All statistical computations were conducted with the R software (*http://www.r-project.org/*).

7.3 Results and discussion

The indoor average temperature ranged from18.7±1.99^{o}C in the first period of the study, without plants, to 24.0±2.22^{o}C in the second period, with plants. The RH values did not change appreciably throughout the campaign (55.9±8.32% and 51.7±7.98%). The CO concentrations in the classroom were always low (0.05±0.04 ppm). However, the CO_2 levels (**Figure 7.1**) were significantly different between the period without (2004±580 ppm) and with plants (1121±600 ppm) in the classroom (*p-value* of 0.001). Many studies demonstrated that high levels of CO_2 could cause a negative influence on students' learning ability (Coley and Greeves, 2004; Shendell et al., 2004; Smedje et al., 1996). It should be noted, that during the entire campaign the windows were kept closed. During the hottest days, three exceptions to this condition were registered, when one or two windows were partially opened for a few minutes. Taking into account that these extents of time with higher natural ventilation represented less than 5% of the occupancy period, the possible dilution effect of concentrations was considered negligible.

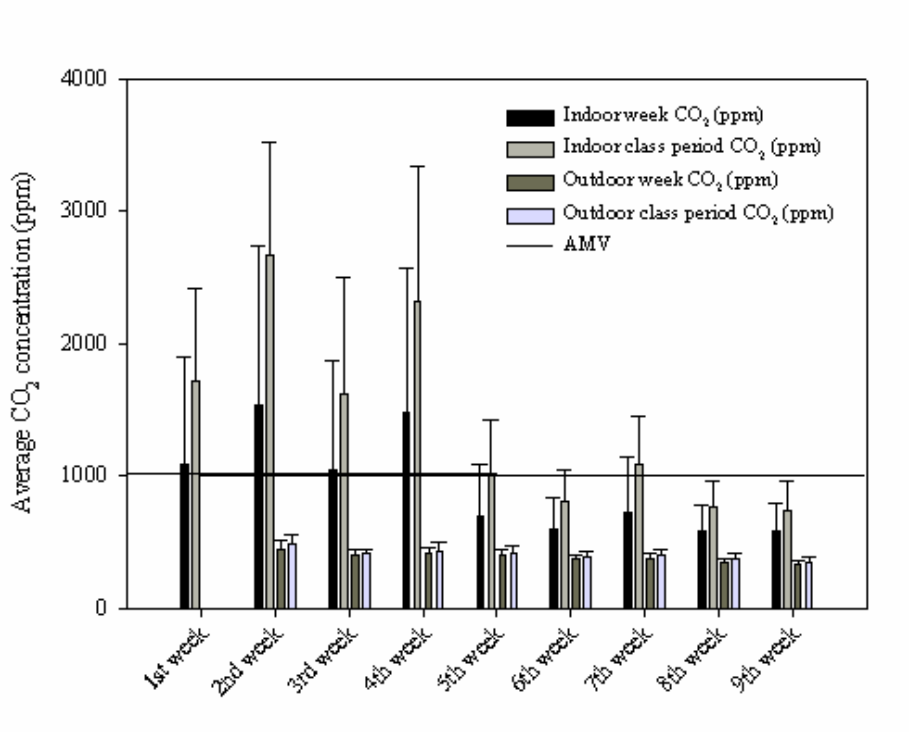

Figure 7.1. Indoor and outdoor average CO_2 concentration week by week.

The National System for Energy and Indoor Air Quality Certification of Buildings establishes an acceptable maximum value (AMV) for the CO_2 concentrations of 1000 ppm in indoor environments in Portugal (RSECE, 2006). Over the period without plants, as well during the week of their acclimatisation, the CO_2 concentrations were always much higher than the AMV. High indoor CO_2 levels are normally considered as indicative of inadequate ventilation. Based on indoor and outdoor CO_2 concentrations, it is possible to estimate ventilation rates under different degrees of window openings or when they are fully closed. When unoccupied there is no CO_2 emission from the tenants, so the ventilation rate can be obtained by:

$$Q = -\frac{V}{t} \times \ln\left(\frac{C_t - C_{ext}}{C_0 - C_{ext}}\right) \tag{7.1}$$

where C_t is the indoor concentration of CO_2 at time t (ppm), C_{ext} the concentration of CO_2 in the external air (ppm), C_0 the concentration of CO_2 in the indoor air at time 0 (ppm), Q

the ventilation rate of air entering the space (m^3 s^{-1}), *V* the volume of the classroom (m^3) and *t* is the interval since *t*=0 (s) (Griffiths and Eftekhari, 2008).

The estimated ventilation rates ranged from 11 to 23 L s^{-1}. The maximum ventilation value, which corresponds to about 0.9 L s^{-1} per person, represented only 35% of the minimum value of 2.5 L s^{-1} per person recommended by the ANSI/ASHRAE Standard 62-1999, and only 10% of that recommended by RSECE (8.33 L s^{-1} per person). The CO_2 levels measured from the 5^{th} week onwards, during the occupancy periods, were not as high as those of the first three weeks, in the absence of plants (**Figure 7.1**). Tarran et al. (2007), in a study aiming at evaluating the capacity of indoor plants to remove pollutants, reported that CO_2 concentrations were reduced by about 10% in air-conditioned offices and by about 25% in naturally ventilated rooms.

Concentrations of VOCs were always higher indoors than outdoors, including nighttime periods (**Figure 7.2**). A concentration decrease during the non-occupancy period was observed. Higher indoor levels of many VOC species were also registered in previous studies involving 14 elementary schools of the Portuguese capital, Lisbon (Pegas et al., 2010, 2011a, b). The VOC concentrations during teaching periods ranged from 933 ± 577 μg m^{-3} in the absence to 249 ± 74.2 μg m^{-3} in the presence of plants. The difference between VOC levels without and with plants was statistically significant (*p-value* of 0.035). The approximately 73% reduction of VOC concentrations observed in this study is in line with the results of previous investigations in 60 offices by Wood et al. (2006), who tested the effectiveness of potted-plant and root-zone microcosms with and without air-conditioning. It has been observed by these authors that the root-zone microcosm could substantially reduce high concentrations of VOCs within 24 hours. In the current study, the decrease of indoor VOC levels was observed whether in samples obtained during school hours or in weekly samples continuously exposed. The main difference between the two sets of samples is the magnitude of concentrations. VOC levels in weekly samples continuously exposed, as obtained in previous works in Portugal (Pegas et al., 2010, 2011a,b), do not truly reflect the levels of exposure. Outside the room, the VOC levels remained almost uniform over the entire sampling period (**Figure 7.2**). Methylacetate, 1,1,1-trichloroethane and isopropanol were systematically more abundant in the classroom. Acetone, methanol and 1,1,1-trichloroethane were prevalent outdoors. These compounds

may derive from both indoor and outdoor sources, including felt pens, personal care products, PVC cement and primer, various adhesives, contact cement, model cement, degreasers, aerosol penetrating oils, brake cleaner, carburettor cleaner, commercial solvents, electronics cleaners, spray lubricants, etc. (Mendell, 2007).

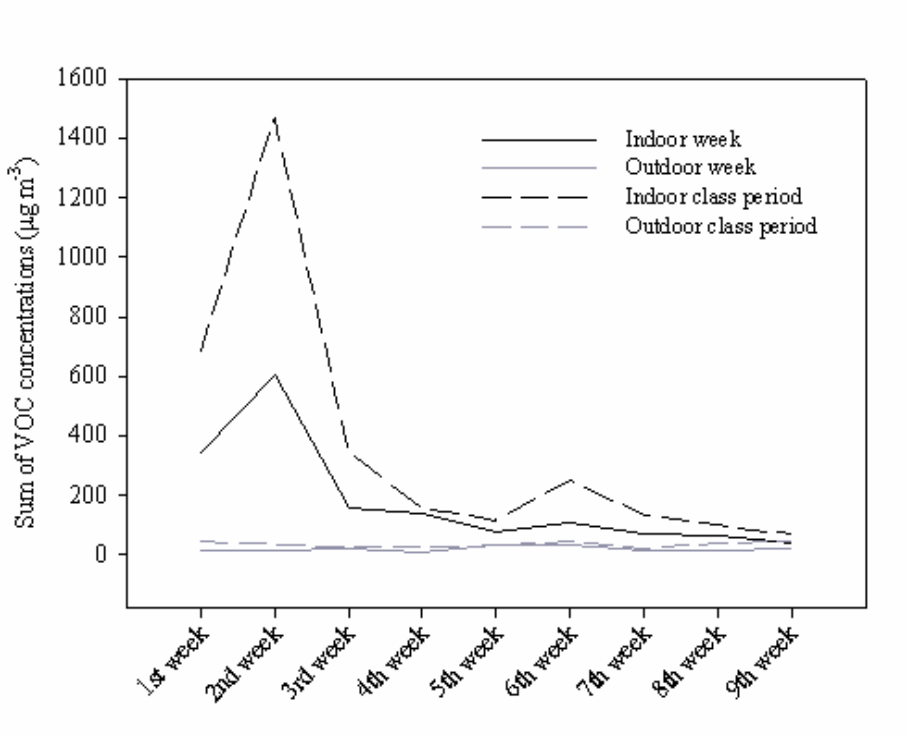

Figure 7.2. Indoor and outdoor concentrations of all VOCs identified.

Among all monitored VOCs, BTEX are of particular interest due to their known carcinogenic effects (Kotzias et al., 2009). Ethylbenzene showed a decrease from levels in the 1.48-2.53 μg m^{-3} range during the period without plants to values below the detection limit during the period with potted-plants indoors. The average toluene concentrations were 7.62 ± 1.73 μg m^{-3} and 4.09 ± 0.66 μg m^{-3}, respectively, when plants were absent or present, showing a decrease of about 57%. A reduction of 80% between the two periods was observed in *m*+*p*-xylene and *o*-xylene concentrations. Benzene is a carcinogenic compound to which the WHO has not yet established a guide or safe value (WHO, 2000).

The average benzene concentration was 1.09 ± 0.21 μg m^{-3} in the absence of plants, decreasing to 0.84 ± 0.03 μg m^{-3} during the presence of potted vegetation, which represents a decline of almost 15%. Outdoor toluene, ethylbenzene, *m+p*-xylene and *o*-xylene levels were significantly lower than air concentrations in the classroom, reflecting the contribution of indoor sources. Although Wolverton (1989) has found a reduction in benzene concentration in controlled chambers of 77.3, 79.5 and 79.0% for the species Janet Craig, Marginata and Peace Lily, respectively, in the classroom, this reduction did not exceed 15%. However, it is important to note that the chamber experiments refer to static testing, where pollutants are injected and then their decay is measured. A classroom is an open system and there are many other cross-factors influencing concentration values. The benzene levels were always within the same order of magnitude or smaller than the outside concentrations, denoting that the major contribution is likely from the outdoor environment.

Carbonyl compounds are the most important chemical contaminants affected by chemical and physical processes in the environment (Cerón et al., 2007). Among the five carbonyls identified in the indoor environment, butyraldehyde (40.8 ± 2.20 μg m^{-3}) and formaldehyde (22.6 ± 3.54 μg m^{-3}) were the most abundant in the classroom in the absence of plants. Formaldehyde is a ubiquitous pollutant that could be found in almost all indoor and outdoor environments. Formaldehyde indoor sources include pressed wood products and furniture, insulation, combustion and tobacco smoke, some textiles and glues. **Figure 7.3** shows that there was a significant decrease in the sum of carbonyl concentrations after hanging potted plants from the ceiling in the classroom (*p-value* of 0.035). During the first three weeks without plants, the sum of aldehyde concentrations ranged from 81.3 to 94.3 μg m^{-3} at an average temperature of 18.7 ± 1.90 ºC. Between the fifth and ninth weeks, with plants in the classroom, the concentrations of total carbonyls ranged from 57.4 to 68.7 μg m^{-3} at an average temperature of 24.8 ± 1.35 ºC. Even with increasing temperature, a decrease in carbonyl concentrations of up to 40% was registered. Normally, the carbonyl concentrations increase with increasing temperatures due to evaporation from building materials (Pang and Mu, 2006). In chamber studies with controlled conditions, the decrease in formaldehyde concentration due to the effect of plants ranged from 47 to 70% (Wolverton et al., 1989). Results from active sampling in office environments suggested that achieving an 11% reduction in formaldehyde levels in a real life situation would

require the equivalent of one plant to each m^3 or 2.4 plants to every m^2 (Dingle et al., 2000). **Table 7.**1 presents results from active samplings carried out before and after having plants in the classroom. An approximately 40% decrease in the indoor concentrations of the four carbonyl compounds measured by active sampling, whose determination was also done by passive sampling, was observed. The outdoor levels increased with increasing temperature.

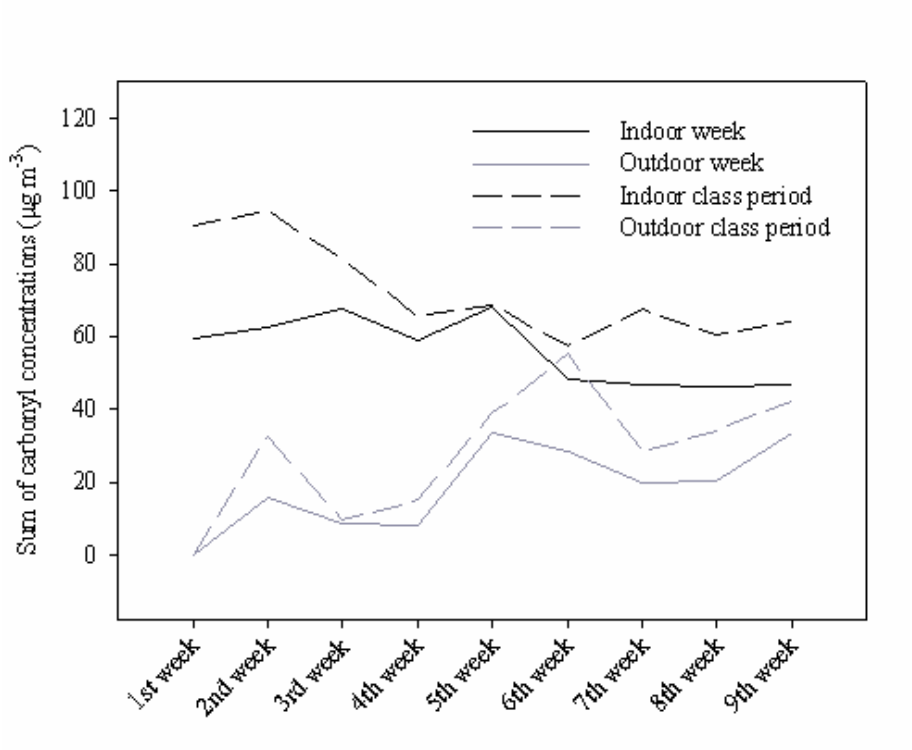

Figure 7.3. Indoor and outdoor concentrations of all carbonyls identified (passive sampling).

Table 7.1 Active sampling of carbonyls.

	Sum of carbonyl concentrations (µg m^{-3})			
	Without Plants		With Plants	
	Average	STDEV	Average	STDEV
Indoor	**52.9**	3.89	**32.1**	11.9
Outdoor	**16.3**	3.86	**27.5**	28.1

Atmospheric particles have been associated with increased respiratory symptoms (Delfino, 2002; Simoni et al., 2002; Weisel, 2002). Indoor PM_{10} may carry toxic pollutants and reaction products into the airways, inducing inflammatory responses through the generation of oxidative stress (Leem et al., 2005). In this experiment, the daily indoor PM_{10} levels were always higher than those outdoors (**Figure 7.4**), suggesting that the physical activity of the pupils leads to emission/resuspension of coarse particles and greatly contributes to enhanced PM_{10} in classrooms (Almeida et al., 2011). Lohr and Pearson-Mims (1996) reported an approximately 2% reduction in PM_{10} levels in a computer lab and in an office after introducing plants into these building environments. A statistically significant decrease in PM_{10} levels was observed in our study (*p-value* of 0.001). The indoor PM_{10} mean values ranged from 137 ± 7.70 μg m^{-3}, without plants, to 91.2 ± 13.2 μg m^{-3}, with plants (**Figure 7.4**). The outdoor PM_{10} mean values ranged from 28.2 ± 5.78 μg m^{-3} in the first period to 38.2 ± 14.4 μg m^{-3} in the second period of the campaign. Even with an increase of about 35% of outdoor PM_{10} concentration, there was a reduction of about 34% in the indoor levels. This could be related to the gravitational settling of particles onto foliage and potting soil. Lohr and Pearson-Mims (1996) suggested that the plants do not simply block the fall of particles. Plants may also remove particulate matter through impaction of particles carried across their foliage by eddy currents.

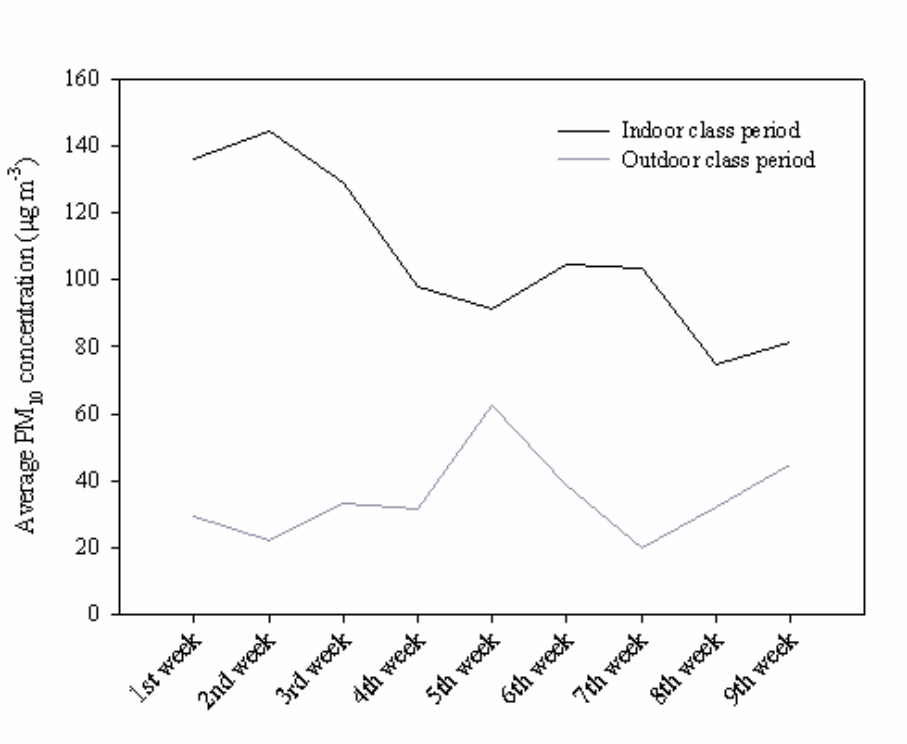

Figure 7.4. Indoor and outdoor PM_{10} concentrations week by week.

On average, the organic carbon represented a mass fraction of PM_{10} of 30.0% indoors. A lower mass fraction was obtained outdoors (OC/PM_{10}=21.3%). The total carbon (TC = OC + EC) levels were higher indoors than outdoors (**Figure 7.5**). Clearly, OC is enriched in indoor, as compared to outdoor air. An indoor enhancement of OC/EC ratios is likely to be due to indoor sources of organic compounds, such as submicron fragments of paper, skin debris and clothing fibres, among others. A decrease from 36.9 ± 4.81 μg m^{-3} to 24.6 ± 6.32 μg m^{-3} in the OC concentrations have been observed between the periods without and with plants, respectively (*p-value* of 0.001), whereas no significant difference was found outdoors. There was no significant difference in EC levels between the two periods of the campaign and between the indoor and outdoor air (**Figure 7.5**).

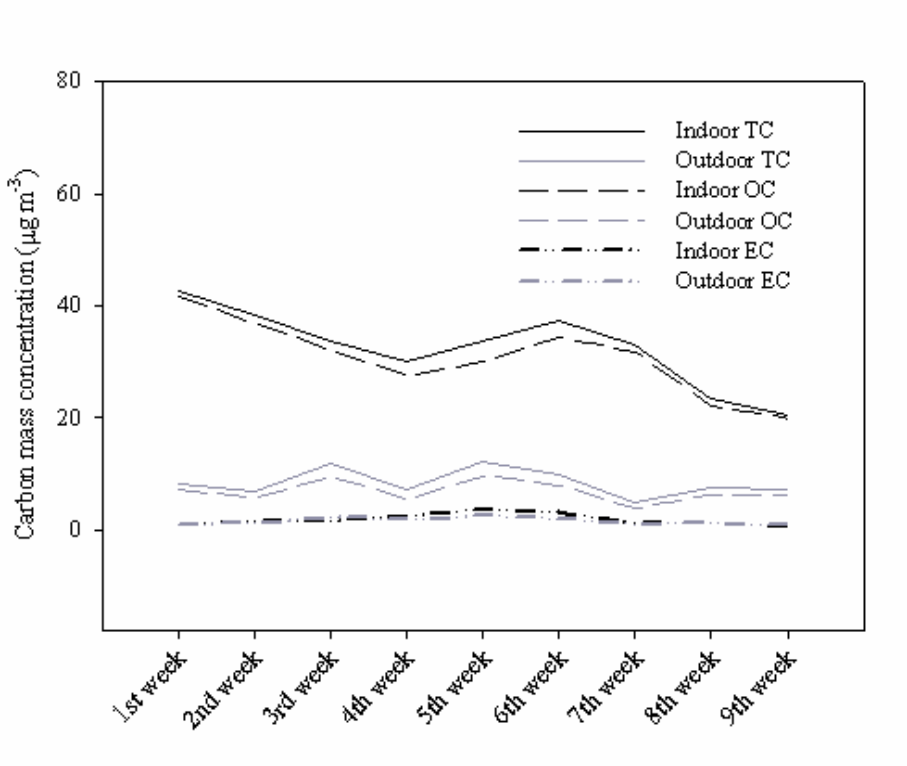

Figure 7.5. Indoor and outdoor carbon mass concentration week by week.

The water soluble ions contributed, on average, to 20.4% and 14.1% of the particle mass in the classroom and playground, respectively (**Figure 7.6)**. Carbonate was the dominant ion of indoor-sampled particles, representing, on average, 10.2% of the mass of all analysed ions. Carbonate levels in the indoor air ranged from 21.8 ± 1.33 μg m^{-3}, without plants, to 6.93 ± 2.31 μg m^{-3}, in the presence of plants (*p-value* of 0.004). The reduction of carbonate levels was followed by a concomitant reduction in calcium levels from 4.25 ± 0.66 μg m^{-3} to 2.78 ± 0.81 μg m^{-3}, without and with plants, respectively (*p-value* of 0.004). Compared with other soluble ions, the calcium mass fractions were higher in the indoor environment (2.76% of the PM_{10} mass) than those observed outdoors (0.76% of the PM_{10} mass). The higher indoor levels are probably related to the use of chalk crayons on the blackboard. This observation is corroborated by the high carbonate concentrations in the classrooms. The indoor carbonate concentrations were about 10 times

the amounts found outdoors during the weekdays. Magnesium represented one of the less abundant ions in the indoor and outdoor environments. The outdoor sodium and chloride levels were about 2 times higher than the indoor levels, probably because these two ions likely have a strong contribution from sea spray. A statistically significant reduction in levels of nitrate, sulphate and ammonia between periods in the absence and presence of plants was observed (*p-value* of 0.001, 0.001 and 0.001, respectively). Atmospheric PM, and especially some of its constituents (e.g. nitrates and ammonium) may affect vegetation directly following deposition on foliar surfaces or indirectly by changing soil chemistry. Indirect effects through the soil, however, are usually the most significant because they can alter nutrient cycling (Grantza et al., 2003; Prajapati, 2012).

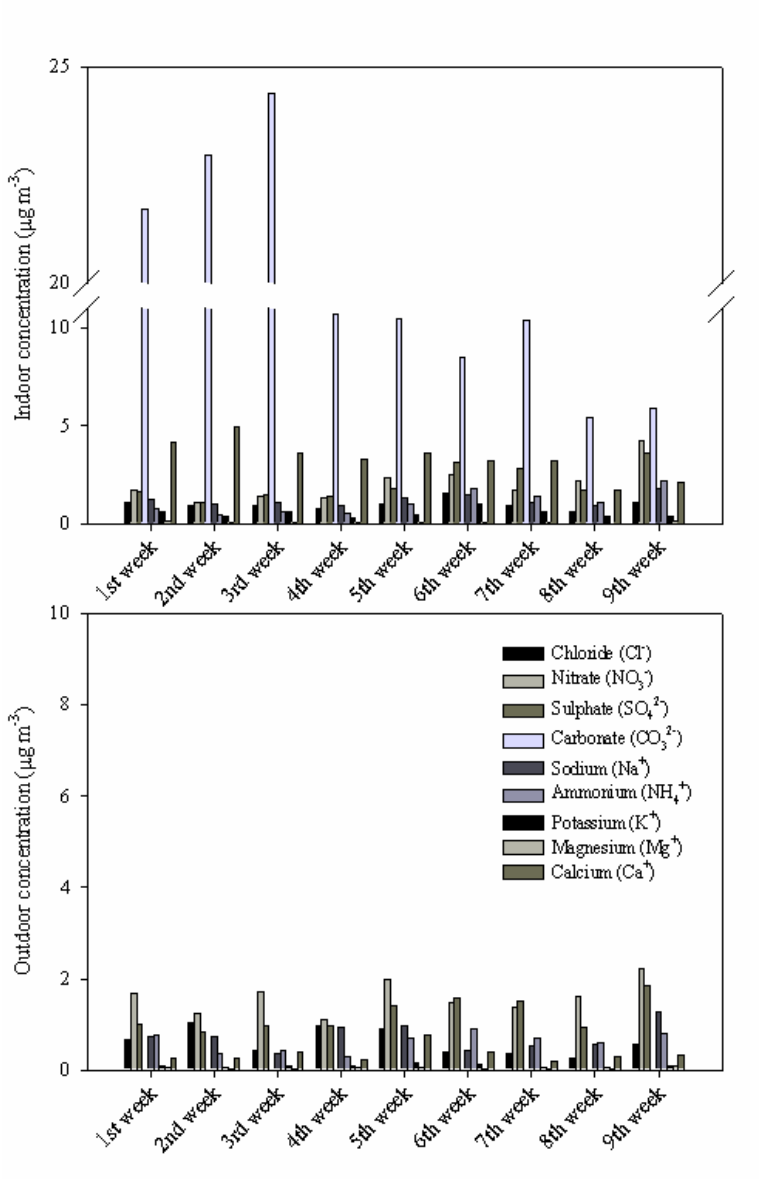

Figure 7.6. Indoor and outdoor soluble ion concentrations week by week.

7.4 Conclusions

This study tried to determine if common houseplants are useful in improving overall indoor air quality. In spite of some possible confounding factors (e.g. variable ventilation rates throughout the monitoring campaign) that could lead to misinterpretation of results, it seems that plants do have the ability to remove ordinary pollutants from the

air. After the placement of six potted-plants in the classroom, a statistically significant reduction in CO_2, VOCs, carbonyl, PM_{10}, OC, nitrate, sulphate, ammonia, calcium, and carbonate concentrations was observed. The decrease in indoor air pollutant levels resulting from the use of plants may represent a low-cost solution to reduce exposure to many compounds and lifetime risk, and further improve performance, attendance and welfare of students and teachers in classrooms. This simple measure does not invalidate, however, the adoption of other abatement or preventive strategies, such as to the use low VOC emitting materials and consumer products, lowering the occupancy rates in classrooms, use of air cleaner and humidity control systems, and increasing the ventilation rates (through natural openings or mechanical devices).

Taking into account that the rate at which the plants metabolise the air pollutants depends on the growing conditions and that the removal performance depends on the plant species, further research is needed. This study provides some clues that this is an important issue to pursue, especially as it may relate to potential human health effects.

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Chapter 8

8. GENERAL CONCLUSIONS

Indoor and outdoor concentrations of VOCs, carbonyls, NO_2, PM_{10}, OC, EC, carbonates, water soluble ions, organic compounds in PM_{10}, microbiological components and comfort parameters (CO_2, CO, temperature and RH) were measured in elementary schools in Lisbon and in Aveiro in different periods between December 2008 and May 2011. The results suggest that IAQ in schools is worse than that of outdoor air, in line with what has been reported for many regions worldwide.

The ANSI/ASHRAE Standard 55-200418 recommends indoor temperature ranges from 20 to 23ºC in the autumn/winter seasons and from 23 to 26ºC in the spring/summer seasons. The suggested indoor RH values are in the 30–60% range. The winter temperatures in classrooms were not satisfactory since average values of 14ºC and 18º were, respectively, obtained in Lisbon and Aveiro, during the occupancy periods. In Lisbon schools, either in autumn or in winter, uncomfortably high values of relative humidity were registered, likely contributing to mould thriving. Thermal comfort is a key component of quality of indoor environments. Elements such as lack of heating systems, lack of adequate ventilation, high humidity levels, and poorly performing building envelopes can contribute to poor thermal comfort. If these elements are not addressed, schools leave both teachers and students in an environment in which they must adapt to poor comfort levels. This can be distracting to students and teachers, and likely reduce their productivity.

The Portuguese Legislation (Decree-Law 79/2006) defines a maximum value of 500 CFU m^{-3} indoors. However, taking into account the conditions found in schools, it is very difficult, if not impossible, to control the amounts of airborne microorganisms in indoor air. According to the present results, there seems to be a seasonal variability in bioaerosol concentrations. There is a trend towards a higher indoor microbial concentration in the warmer season with respect to colder periods. In all seasons and in both cities, the bacterial and fungal colony forming units surpassed the Portuguese guidelines. Microorganisms in indoor air originate not only from the activities of occupants, but also from contaminated building materials, furnishings, and from outdoor air. Thus, inadequate

ventilations, poor hygienic conditions in schools, overcrowded classrooms and high RH values favour microbial growth.

At concentrations occurring in most indoor environments, CO_2 build up can be considered as a surrogate for other occupant-generated pollutants, and for ventilation rate per occupant, but not as a causal factor in human health responses. Whether ASHRAE or the Portuguese legislation recommend that CO_2 levels do not exceed 1000 ppm or 1800 mg m^{-3}. The average CO_2 levels in Lisbon and Aveiro schools were about 2000 mg m^{-3}, with peaks of 3000 mg m^{-3}. During the test of houseplants inside a classroom, a statistical significant decrease of the CO_2 levels was observed, showing the positive effect of phytoremediation on IAQ. Improving ventilation rates and the presence of recommended plants may contribute to the decrease of CO_2 levels and to prevent other contaminants from accumulating. Concomitant increases of CO_2 and CO concentrations suggest a direct relationship between increasing concentrations and classroom occupancies. It should be noted, however, that CO levels were always lower than 1 mg m^{-3} in all schools, i.e. were far below the threshold of 12.5 mg m^{-3} stipulated by the Portuguese legislation and the WHO guidelines.

Generally, the NO_2 concentrations were higher outdoors than indoors, probably as a result of vehicular emissions from nearby traffic and other combustion processes in the urban environment. The indoor NO_2 average levels ranged from 10 to 46 μg m^{-3} showing lower values during the winter, possibly because the windows and the doors were always closed, isolating the classroom environment of emissions from the outside, or because NO_2 indoor concentrations decayed by gas-phase processes or by reactions on the inner surfaces of furniture. Even if the NO_2 concentrations were lower in the classrooms; in some schools, the average values exceeded the WHO recommendation of 40 μg m^{-3}.

Most of the assessed VOCs occurred at I/O ratios above unity, in all seasons, showing the important influence of indoor sources and building conditions on IAQ. However, it has been observed that higher indoor VOC concentrations occur often in the colder months in Lisbon schools. The winter VOC concentrations ranged from 84 to 2175 μg m^{-3}, the autumn concentrations ranged from 11 to 922 μg m^{-3}, and finally, the spring VOC concentrations ranged from 37 to 317 μg m^{-3}. Higher levels in wintertime are probably related to the fact that classrooms remained longer with closed windows to

maintain thermal comfort, contributing to a gradual accumulation of pollutants from indoor and outdoor sources. The outdoor pollutants have the capacity of entering buildings and they suffer accumulation inside the room, due to low air exchange rates. Higher temperatures in the warmer seasons, together with enhanced ventilations due to opening of windows by users, likely favoured both the volatilisation and dilution of VOCs. In Aveiro, the indoor VOC concentrations were always higher during the occupancy period. A reduction of 73% of indoor VOC levels was observed after placement of plants in one classroom.

In all studied places, the indoor carbonyl concentrations were higher than those outside. Generally, formaldehyde was the most abundant carbonyl compound found in schools. In Lisbon, the indoor formaldehyde levels were higher in spring (3.4 – 42.3 μg m^{-3}) than those measured in autumn (3.1 26.2 μg m^{-3}) and winter (6.3 – 23.8 μg m^{-3}). Carbonyl concentrations were higher in warmer months, due to increased emissions from furniture with increasing sun-light intensity. In Aveiro, even with a substantial increase in temperatures (from 18.7 to 24.8ºC), a decrease in carbonyl concentrations of 40% was observed following the placing of plants in one classroom (81.3-94.3 μg m^{-3} to 57.4 - 68.7 μg m^{-3}).

The daily indoor PM_{10} levels (72.8 – 49.2 μg m^{-3}), measured in schools of Aveiro, were always higher than those outdoors (43.4 – 23.4 μg m^{-3}), except on weekends, suggesting that the physical activity of students and class works highly contributed to the emission and re-suspension of particles. Using the measured sulphate content on PM filters as an indicator for ambient PM sources, it was estimated that only about one quarter of PM_{10} was of ambient origin. Indoor sources, such as re-suspension by physical activities, soil particles brought in shoes, blackboard dust, skin flakes, cloths and furniture fragments, bioaerosol and insects, have a strong impact on indoor PM_{10} concentrations. The presence of plants in the room contributed to a reduction of about 34% in the indoor levels (from 137 to 91 μg m^{-3}), even with an increase of about 35% of outdoor PM_{10} (from 28 to 38 μg m^{-3}). This could be related to the capacity of houseplants attract and retain particles by gravitational settling onto foliage and potting soil.

OC was the particulate component contributing most to the indoor PM_{10} concentrations measured in schools in Aveiro. Indoor OC sources seem to be mainly

related to student room occupancy and their activities, such as small particles of paper, skin debris and clothing fibres. A decrease in the OC average concentration was observed between the periods without (36.9 μg m^{-3}) and with plants (24.6 μg m^{-3}), whereas no significant difference was found outdoors. The average EC indoor concentrations observed in the city centre school of Aveiro (1.7 μg m^{-3}) were higher than those measured in the indoor air of the suburban school (0.99 μg m^{-3}), denoting a lower influence of traffic emissions on the outskirts. A possible indoor source of EC in primary schools could be graphitic pencil largely used by children. There was no difference in EC levels without and with plants indoors.

The PM_{10} mass fraction of soluble inorganic ions was higher outdoors (30% and 32%) than indoors (13% and 18%) for the city centre and the suburban school, respectively, suggesting that the main sources of inorganic material are from outside. Carbonate was the dominant ion of indoor-sampled particles. Chalk used in classrooms could explain the higher indoor concentrations of carbonate, calcium and potassium. The reduction of carbonate levels from 21.8 μg m^{-3} to 6.93 μg m^{-3} was followed by the concomitant reduction in calcium levels, from 4.25 μg m^{-3} to 2.78 μg m^{-3}, without and with plants, respectively. Nitrate, sulphate and ammonia concentrations also decreased after the placement of recommended potted plants in one classroom of the city centre school of Aveiro.

In Aveiro, the influence of traffic emissions on the IAQ is corroborated by the values of diagnostic ratios between PAH, which fall in the ranges reported for catalyst-equipped vehicles. In some days, however, the PAH ratios reflected the influence of industrial emissions on the PM_{10} collected in the suburban school. Homologous series of *n*-alkanes and n-alkanols ($C_{10} - C_{30}$) and *n*-alkanoic acids ($C_6 - C_{28}$) were present in samples. It was observed a strong even carbon number predominance, which reflects a dual biogenic origin: waxes from terrestrial vegetation and microbial lipids. The average concentrations of some organic tracers for biomass burning (levoglucosan, galactosan and mannosan) were higher indoors than outdoors for both school locations. The input of biomass burning tracers was more pronounced at the city centre school, showing the contribution of nearby restaurants and bakeries for the elevated PM_{10} levels. Stearin and palmitoleic acid, organic tracers for cooking process, showed an important activity around the city centre school due

to significant amounts of oily fumes from kitchens to outdoor air, which infiltrate into the classroom. At the suburban school, this contribution was smaller.

A possible mitigation measure to decrease indoor air pollutant levels is the use potted plants in a number proportional to the volume of the room. This could be a low-cost solution to reduce exposure to many compounds (like CO_2, VOCs, carbonyl, PM_{10}, OC, nitrate, sulphate, ammonia, calcium, and carbonate) and lifetime risk, and further improve performance, attendance and welfare of students and teachers in classrooms. However, this simple step can not be isolated and does not invalidate the adoption of other depletion or preventive strategies, like the use of low VOC emitting materials and consumer products, lowering the number of students per classroom, increasing the air exchange rates, and use of air cleaner and humidity control systems. The schools should be built in strategically places or “green areas”, where they are not directly affected by heavy traffic or industry or any other polluting sources at the neighbourhood. Floor covering and wall paint in classrooms should be chosen with particular caution to avoid any adverse effects on the respiratory health of children. New comprehensible instructions for good cleaning practices in schools should be provided and implemented. It is important to create new preventive and legal measures for controlling IAQ, such as imposition of periodic audits. Finally, it is indispensable to educate every one on IAQ. Students, teachers and other staff should have information about sources, effects of contaminated air, and knowledge about operation of the ventilation system (when there is one) or the importance of efficient natural ventilation and indoor air renovation.

Health symptoms, like asthma, rhinitis and wheezing, are not only related to IAQ in schools. The prevalence of children with wheezing and allergic rhinitis has increased in relation to the ISAAC studies of 2002/2003 and 2006 in the same city. The wheezing prevalence ranged from 26.7 to 30.1% between 2002/2003 and 2006, and then to 43.3% in the present study carried out in 2008. The allergic rhinitis also increased from 26.9 to 31.2%, and then to 42.9%, whereas the percentage of asthma cases has decreased slightly, from 9.2 to 7.8% and then to 5.6%. A decrease in the percentage of smoking parents was observed. A small decrease in the number of breastfed children from 82.2% in 2002/2003, to 81.5% in 2006, and to 76.9% in 2008, was also registered. This decrease may be due to the increasing number of women employed. Nevertheless, breastfeeding was not found as a

significant protective factor for respiratory diseases, in statistical terms. Among variables related to eating habits, the only statistically significant correlation with respiratory symptoms was found for egg consumption. The risk of manifestation of allergic rhinitis is 90% higher in children who often eat eggs in comparison with those who never eat this food. Differences in prevalence of respiratory symptoms obtained in several studies may point out exposure to different risk factors, as well as variable racial, environmental, and socioeconomic conditions, and heterogeneous diagnostic criteria.

Future investigation is needed to determine the extent of IAQ problems in school population. Student's exposure to complex mixtures of air pollutants also reflects a complex mixture of microenvironments in which pupils spend their time, such as school, home, public transportation, car or other way to commute, etc. Since children move around, including during school hours, the pollutants and concentrations to which they are exposed to vary according to the period of the day. Thus, the evaluation of an integrated daily exposure to air pollutants by personal and area sampling in different microenvironments is highly recommended.

Epidemiological studies relating pollutant levels in schools and health are in the early stages. More studies are necessary to establish unequivocal causal relationships in order to revise air quality standards and to adopt cost effective mitigation actions. On the other hand, pollutants have been observed to work in a synergistic fashion as two or more substances may have a combined effect. The multiplicative effects consequently make the causation of many cases of environmental illness difficult to identify. Thus, this aspect should be addressed in further studies by multidisciplinary teams.

Source contributions to PM have been modelled for outdoor air pollution. However, an understanding of the relative contributions from important pollutant sources to indoor exposures is necessary for the design and implementation of effective control strategies for IAQ. Detailed emissions profiles have been used in receptor modelling, such as the Chemical Mass Balance (CMB), to apportion the contribution of outdoor sources to particulate matter. The complete inexistence of indoor source profiles invalidates the application of such models to accurately assign the different emission inputs to interior spaces. Thus, the detailed chemical characterisation of emissions from indoor sources/activities should be target in future investigations. Using source apportionment

techniques, epidemiological studies can more clearly examine exposures to indoor sources and indoor penetration of source-specific components, reduce exposure misclassification, and improve the characterisation of the relationship between pollutants and health effects.