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VOLATILE ORGANIC COMPOUNDS: INDOOR LEVELS AND RISK ASSESSMENT

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MASTER IN ENVIRONMENTAL ENGINEERING

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Abstract

The exposure to volatile organic compounds (VOCs) has been associated with various adverse health outcomes. This is especially relevant for indoor environments, where people spend the majority of their time (80-90%), with a large proportion of that being spent at home (70% of indoor time). There are many indoor emission sources of VOCs. As the current trend to increase the energy efficiency of buildings often leads to their air tightening, the respective indoor levels and exposure can be higher than those outdoor. Thus, this work aims to assess the levels of VOCs in indoor air of home environments and to estimate the respective risks considering seven target VOCs (benzene, toluene, trichloroethylene, tetrachloroethylene, pinene, limonene, and xylene). VOCs were collected concurrently in indoor and outdoor air across 64 homes situated primarily in the Porto Metropolitan area. Sampling was conducted by air sampling pumps (AirChek® XR5000 – SKC Ltd., Dorset, UK; air flow of 50 mL/min) with a stainless-steel sorbent tube (Tenax TA; 60/80 mesh). Quantification and determination of total (TVOCs) and individual VOCs were performed by thermodesorption with gas chromatography (GC) and flame ionization detection (FID). Carcinogenic (CR) and non-carcinogenic (HI) risks were assessed according to the US Environmental Protection Agency (USEPA) methodology. The results obtained in this work showed that across 64 homes TVOCs concentrations ranged between 0.050 and 1 617 $\mu g/m^3$ (mean of 217 $\mu g/m^3$), being approximately 5 times higher than the respective levels outdoors. Out of these, 10% of the evaluated homes did not fulfil the Portuguese protective threshold (600 $\mu g/m^3$; set for indoor air quality in public buildings). The majority of the homes (97 %) exhibited I/O ratio higher than one, thus strongly suggesting predominant indoor origin of TVOCs. The large variability of the observed indoor levels was most likely caused by the differences and specificity of indoor emissions sources as well as the seasonal trends. The analysis of non-carcinogenic risk showed a need for potential concerns in the homes, with the total (i.e., the sum of 7 VOCs) exceeding the unity. Limonene, pinene and trichloroethylene exhibited hazard quotient greater than one, with the following order of individual HQ being obtained: limonene > trichloroethylene > pinene > benzene > xylene > tetrachloroethylene > toluene. Carcinogenic risks of trichloroethylene and benzene exceeded (29 and 18 times) the protective USEPA threshold of 10^{-6}. When all seven VOCs were incorporated into risk analysis, the total mean carcinogenic risk exceeded the protective threshold of 10^{-4} for the cumulative exposure with values 300 greater than that threshold. Finally, among the seven VOCs compounds considered in this study tetrachloroethylene and benzene were ranked as the overall most toxic chemicals, though their toxicity profiles differed. While the obtained results showed potential risks due to indoor air exposure to VOCs in the studied homes, the mitigation of VOCs, requires, first of all, identification of their major indoor sources. To ensure safe indoor environments, a complex individual approach is required, fully dependent not only on reducing air pollution levels but also on economic viability for the occupants, their awareness of the issue and knowledge literacy, as well individual health susceptibilities.

Sumário

A exposição a compostos orgânicos voláteis (COVs) tem sido associada a várias consequências adversas na saúde. É especialmente relevante para ambientes interiores, onde as pessoas passam a maior parte do tempo (80-90%), sendo a maioria desse tempo passado em casa (70% do tempo passado em espaços interiores). Existem várias fontes de emissão interna de COVs. Como a tendência atual de aumentar a eficiência energética dos edifícios leva muitas vezes à constrição da regulação do ar em espaços interiores, os respetivos níveis de exposição interior podem ser superiores aos exteriores. Por isso, este trabalho visa avaliar os níveis de COVs no ar interior de ambientes domésticos e estimar os respetivos riscos, considerando sete COVs alvo (benzeno, tolueno, tricloroetileno, tetracloroetileno, pineno, limoneno e xileno). Os COVs foram recolhidos simultaneamente no ar interior e exterior em 64 casas situadas predominantemente na área metropolitana do Porto. A amostragem foi realizada por bombas de amostragem de ar (AirChek® XR5000 – SKC Ltd., Dorset, Reino Unido; fluxo de ar de 50 mL/min) com tubo sorvente de aço inoxidável (Tenax TA; malha 60/80). A quantificação e a determinação de COVs totais e individuais foi realizada por termodessorção com cromatografia gasosa e deteção de ionização por chama. Os riscos cancerígenos (CR) e não cancerígenos (HI) foram avaliados de acordo com a metodologia da Agência de Proteção Ambiental dos EUA (USEPA). Os resultados obtidos neste trabalho mostraram que em 64 casas as concentrações de TVOCs variaram entre 0.050 e 1 617 µg/m^3 (média de 217 µg/m^3). sendo aproximadamente 5 vezes superior aos respetivos níveis no exterior. Destes, 10% dos lares avaliados não cumpriram o limite de proteção português (600 µg/m^3; definido para a qualidade do ar interior em edifícios públicos). A maioria das residências (97%) exibiu razão I/O > 1, sugerindo fortemente a origem interna predominante de TVOCs. A grande variabilidade dos níveis internos observados foi provavelmente causada pelas diferenças e especificidade das fontes de emissões internas, bem como pelas tendências sazonais. A análise do risco não cancerígeno mostrou a necessidade de potenciais preocupações nas residências, com o total (ou seja, soma de 7 VOCs) superando a unidade. Limoneno, pineno e tricloroetileno apresentaram quociente de risco maior que um, obtendo-se a seguinte ordem de HQ individual: limoneno > tricloroetileno > pineno > benzeno > xileno > tetracloroetileno > tolueno. Os riscos cancerígenos do tricloroetileno e do benzeno excederam (29 e 18 vezes) o limite protetor da USEPA de 10^{-6}. Quando todos os sete COVs foram incorporados na análise de risco, o risco total cancerígeno excedeu o limite de proteção de 10^{-4} para a exposição cumulativa com valores 300 vezes superiores a esse limite. Finalmente, entre os sete compostos de COV considerados neste estudo, tetracloroetileno e benzeno foram classificados como os produtos químicos mais tóxicos, embora seus perfis de toxicidade sejam diferentes. Embora os resultados obtidos mostrem riscos potenciais devido à exposição do ar interior aos COVs nas residências estudadas, a mitigação dos COVs exige, antes de tudo, a identificação de suas principais fontes internas. Para garantir um ambiente interior seguro, é necessária uma abordagem complexa, mas individual, totalmente dependente não apenas da redução dos níveis de poluição do ar, mas também da viabilidade econômica dos ocupantes, sua conscientização sobre o problema e alfabetização de conhecimento, bem como suscetibilidades individuais de saúde.

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List of Publications

Scientific meetings with abstract:

Ricardo Rodrigues, Klára Slezáková, Maria do Carmo Pereira, João Paulo Teixeira, Joana Madureira. VOCs in Private Dwellings: Levels and Risk Assessment. IJUP 2022 – Encontro Investigação Jovem U. Porto. Book of abstracts, page 74. May 4 - 6, 2022, Porto, Portugal.

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Nomenclature

Abbreviations

AT	Average Time of Exposure
ATSDR	Agency for Toxic Substances and Disease Registry
BMD	Benchmark Dose
BMDL	Benchmark Dose Lower Limit
CA	Contaminant Concentration in Air
CAA	Clean Air Act
CAS	Chemical Abstracts Service Registry Number
CFC	Chlorine Fluorine Hydrocarbon
CPV	Cancer Potency Value
CR	Carcinogenic Risk
Csb	Cool-summer Mediterranean Climate
CTV Predictor	Conditional Toxicity Value Predictor
DDT	Dichlorodiphenyltrichloroethane
EC	Exposure Concentration
ED	Exposure Duration
EF	Exposure Frequency
ET	Exposure Time
EU	European Union
FID	Flame Ionization Detector
GC	Gas Chromatographer

HAP	Hazardous Air Pollutant
HI	Hazard Index
HQ	Hazard Quotient
IAQ	Indoor Air Quality
IARC	International Agency for Research on Cancer
I/O	Indoors/Outdoors
IRIS	Integrated Risk Information System
IUR	Inhalation Unit Risk
LOQ	Limit of Quantification
NCR	Non-carcinogenic Risk
NO(A)EL	No Observed Adverse Effect Level
NO_x	Nitrogen Oxides
PAH	Polycyclic Aromatic Hydrocarbon
PCB	Polychlorinated Biphenyl
PCE	Perchloroethylene
PMA	Porto Metropolitan Area
RfC	Reference Concentration
PM	Particulate Matter
SD	Standard Deviation
SOA	Secondary Organic Aerosol
SVOC	Semi Volatile Organic Compound
TD	Thermal Desorption
ToxPi	Toxicological Prioritization Index
TNT	Trinitrotoluene
TVOCs	Total Volatile Organic Compounds
USEPA	U.S. Environmental Protection Agency
VOC	Volatile Organic Compound
VVOC	Very Volatile Organic Compound
WHO	World Health Organization

1. Preface

1.1 Relevance and motivation

World Health Organization (WHO) has emphasized "healthy indoor air" as a basic human right (*WHO, 2000*). In western society people spend 80-90% of their time indoors, with a large part of that time being spent in their homes (70% of indoor time) *(Wickliffe et al., 2020)*. The indoor air quality (IAQ) in these settings is extremely variable and depends on many factors. Human activities, building materials and furnishings, and the seasonal effects are all parameters that influence IAQ (*Rösch et al., 2014*). Moreover, the current concerns with increasing number of indoor emissions sources, exposure to mixtures of pollutants, and the role of outdoor air add further complexity to this issue.

Over the past two decades, the needs regarding suitable IAQ have increased as research has linked exposure to indoor air pollutants with various health risks (*WHO, 2010*). Volatile organic compounds (VOCs) are a group of chemical pollutants, many of which have known health effects (*Halios et al., 2022*). Exposure to VOCs has been associated with a wide range of adverse outcomes (liver and kidney dysfunction, neurological impairment, eye and nose irritation, allergy, dizziness, and nausea; *Wang et al., 2022*). While VOCs are a large group of many chemicals, WHO identified 15 VOCs as priority substances (in the framework of a screening tool for the risk assessment from combined exposure to hazardous chemicals), namely: formaldehyde, acetaldehyde, benzene, xylene (as m and p isomers), styrene, toluene, 1,4 dichlorobenzene, ethylbenzene, butyl acetate, tetrachloroethylene, α-pinene, 1,2,3 trimethylbenzene, limonene, naphthalene and trichloroethylene (*WHO, 2021*).

Indoor emission sources of VOCs are numerous and widespread (*Szabados, 2021*). Furthermore, to improve energy efficiency of buildings, the current trend leads to their air tightening (*Kovats and Brisley, 2021*). As such, the respective VOCs may potentially become more common and presumably even more elevated in the indoor air.

1.2 Objectives

The aims of this thesis were:

(1) To evaluate the levels of volatile organic compounds in indoor air of residential environments;
(2) To predict the attributable health risk by assessing carcinogenic and non-carcinogenic risk from exposure to specific target VOCs (benzene, toluene, trichloroethylene, tetrachloroethylene, αpinene, limonene and xylene (o- and p- isomers));
(3) To prioritize the target VOCs using a systematic toxicity prioritization scheme model

1.3 Thesis outline

The thesis is divided into five chapters. The content of each chapter is briefly described below.

Chapter 1 (present chapter) is the preface of the thesis. It explains the relevance and motivation of the work as well as its objectives.

Chapter 2 briefly introduces the significance of VOCs, covering definitions, sources, and their impact on human health, with particular emphasis on indoor environments.

Chapter 3 describes the materials and methods applied in this work. Sites and sampling protocols are detailed, and all analytical methods used to determine the chemical components are also recounted. Risk assessment methodology as well as description of the statistical treatments are provided.

Chapter 4 summarizes the results and discusses the data obtained, considering the proposed main objectives. Exposure assessment and seasonal trends are analysed for total VOCs

(TVOCs) and for target VOCs. The health risk assessment of the seven VOCs is estimated, and their toxicity ranking is established.

Chapter 5 presents the conclusions of the thesis and suggestions for future work.

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2. Volatile organic compounds: an overview

Air pollution has become an important issue regarding environmental preservation, climate change, and public health. According to the WHO each year, when combined, ambient air and indoor air pollution are responsible for nearly seven million premature deaths around the globe. Specifically, the estimates show that annually 3.8 million deaths occur as a result of household exposure to smoke from dirty cooking stoves and to fuels, whereas 4.2 million annual deaths are due to exposure to outdoor air pollution (*WHO, 2022*). Worldwide, 2.6 billion people are exposed to dangerous levels of household air pollution, with residents in low to middle income countries being affected the most. Nine out of ten human beings currently breathe air that exceeds the WHO's guideline limits for pollutants (*WHO, 2022).* Air pollution is defined as the contamination of the indoor or outdoor environment by any chemical, physical or biological agent that modifies the natural characteristics of the atmosphere (*WHO, 2022*). Common indoor and outdoor air pollutants include volatile organic compounds (VOCs), nitrogen oxides (NO_x), ozone (O_3), particulate matter (PM), bioaerosols, heavy metals, and polycyclic aromatic hydrocarbons (PAHs).

VOCs are present both in indoor and outdoor environments. They are air pollutants of considerable concern, due to their potential to adversely affect the health of the people exposed to them. In this chapter, a brief overview of VOCs' significance is described, covering the classification of VOCs, the sources, and their impacts on human health, with particular emphasis on VOCs presence in indoor air.

2.1 Indoor air

As people spend over 90% of their time indoors (70% of which in their homes) (*Wickliffe et al., 2020*), indoor air quality (IAQ) is important for human exposure to air pollutants. The impacts on public health are potentially enormous, as indoor air pollution can be 2 to 5 times greater than outdoor one (*Wickliffe et al., 2020*). Over the last two decades, scientific awareness of IAQ has gradually increased (*Wickliffe et al., 2020*). Indoor air pollution has become an area of public health concern, though its understanding is still limited when compared to ambient air. The spatial and temporal variability of personal indoor air exposure, which is typically not well correlated with outdoor air quality (often based on stationary ambient air monitoring stations), adds to the complexity of indoor air pollution.

The concentration of VOCs in indoor air can be affected by various parameters, such as the number of occupants and their activities, the presence of specific indoor emission sources (such as cigarette smoke or use of cleaning products), physical parameters (temperature and relative humidity) and the characteristics and properties of the indoor spaces (interior design and materials, form and frequency of ventilation (*Holos et al., 2018*) and heating system, presence of animals, plants, etc) as well as seasonal trends. In addition, ambient air pollution has great impacts to indoor air (*Wickliffe et al., 2020*) thus the location and the surrounding environments (urban vs rural) are also relevant. Atmospheric chemistry and the respective transformation processes, mainly related with solar activity, and the presence of ozone and nitrogen oxides also influence the levels of VOCs in indoor air (*Rösch et al., 2014*).

2.2 Classification of volatile organic compounds

Volatile organic compounds (VOCs) are a broad group of carbon-based chemical compounds with high vapour pressure and low water solubility, thus allowing for evaporation at ambient temperature and pressure. VOCs' boiling points can span from less than 0°C to 400°C (*WHO, 1989; USEPA, 2022*). The higher the volatility (lower the boiling point), the more likely the compound is to be emitted (from a product or a surface of origin) into the air. The more volatile compounds are found solely as gases in the air, while the less volatile compounds can be present as solids or liquids (*USEPA, 2022*). Due to their volatility, the primary route of human exposure to VOCs is through inhalation, with ingestion and dermal exposure being less relevant. Many VOCs are the key precursors of secondary organic aerosols (SOA_s), which constitute more than half of fine particles $PM_{2.5}$ (*WVDEP, 2022*). VOCs can react with nitrogen oxides (NO_x) to produce acid rain and tropospheric ozone (O_3), creating haze days and high O_3 episodes that worsen air quality in urban areas (*Liu et al., 2021*). Most VOCs are considered hazardous air pollutants (HAPs), meaning they are toxic air pollutants with the ability to cause cancer or other serious health effects, as well as adverse environmental effects (*WVDEP, 2022*).

VOCs are usually classified by how easily they can be emitted, i.e., by the degree of their volatility. Very volatile organic compounds (VVOCs), also known as very gaseous organic compounds, have boiling points ranging from less than 0°C to 50-100°C and include propane, butane, and methylchloride. Volatile organic compounds (VOCs) have boiling points spanning from 50-100 °C to 240-260°C, and examples include formaldehyde, d-limonene, toluene, acetone, and ethanol. Semi volatile organic compounds (SVOCs) are those with boiling points fluctuating between 240-260°C and 380-400°C. They comprise pesticides, such as DDT (dichlorodiphenyltrichloroethane) and fire retardants, namely PCBs (polychlorinated biphenyl) (*USEPA, 2022*).

2.3 Sources of pollution by VOCs

The main anthropogenic sources of VOCs include oil and gas extraction, processing and combustion, industrial operation emissions, transportation emissions (by gasoline and diesel emissions directly to the air and through fuel combustion), and industrial processes, such as solvent and chemical production (*ALA, 2020*). In indoor air, the emission sources of VOCs are fires and wood burning, building materials, cooking, use of cleaning products and practices, disinfectants, pesticides, fragrances and fresheners, and use of equipment such as printers and photocopiers, and occupant's activities including smoking and burning candles (*Wickliffe et al., 2020*).

2.4 Chemical composition of VOCs

In this study, seven specific compounds were selected and quantified because of their hazardousness to health: benzene; toluene; trichloroethylene; tetrachloroethylene; pinene; limonene; xylenes. The molecular structure for each of these compounds is represented in Figure 2-1.

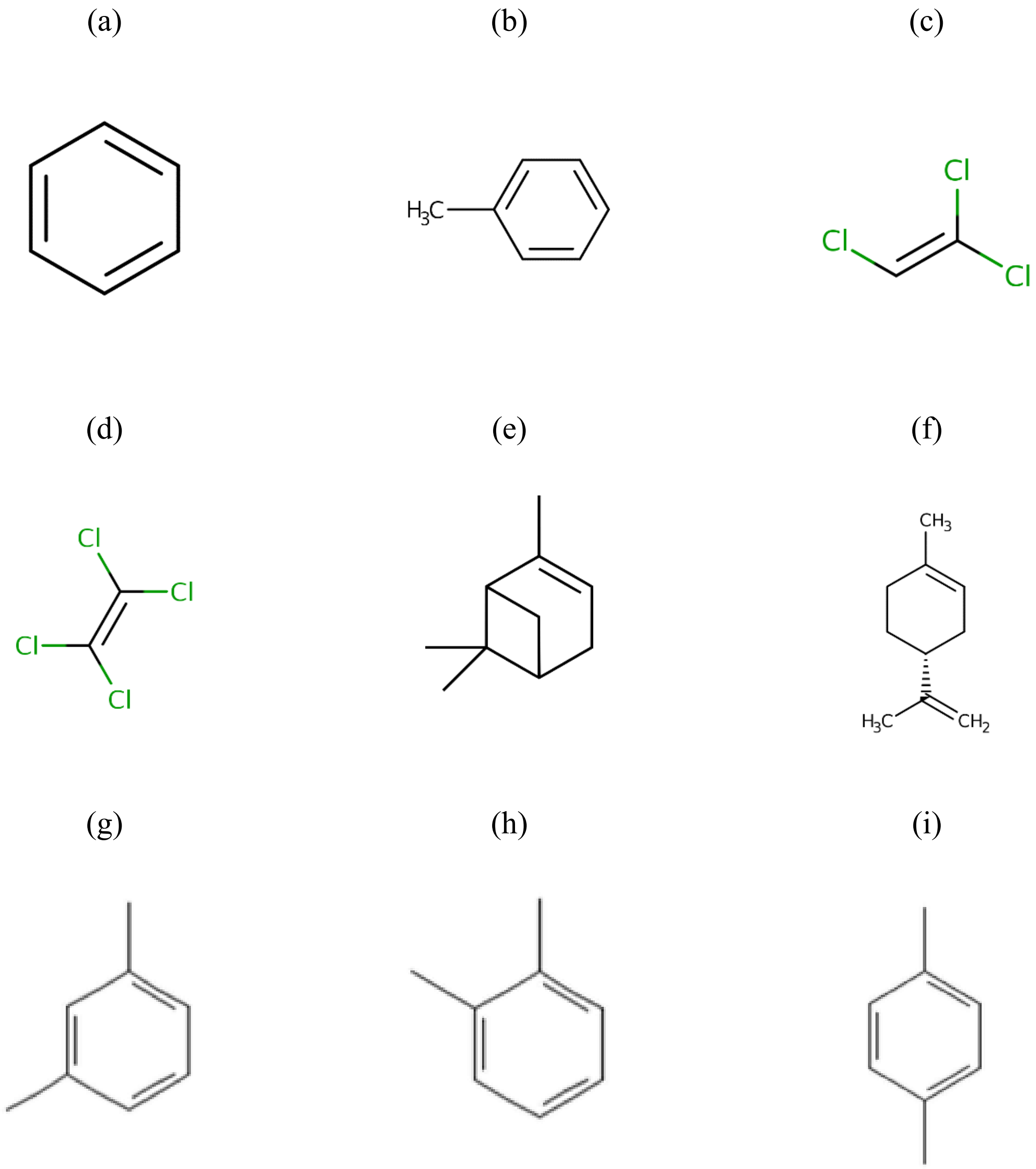

Figure 2-1 – Molecular structure of selected VOCs: (a) benzene; (b) toluene; (c) trichloroethylene; (d) tetrachloroethylene; (e) α-pinene; (f) limonene; (g) m-xylene; (h) o-xylene; (i) p-xylene

2.4.1 Benzene

Benzene (CASRN 71-43-2), also known as benzol, is an aromatic hydrocarbon composed of only carbon and hydrogen atoms, with the molecular formula C_6H_6. Benzene is a natural constituent of crude oil and an elementary petrochemical and a precursor for the manufacture of various industrial chemicals. Benzene is a colourless and highly flammable liquid with a sweet smell, being responsible for the aroma of gasoline (*Folkins, 2000*).

Benzene ranks as one of the top 20 compounds in production volume for chemicals produced in the United States. It is used to produce Styrofoam™ (DuPont, Wilmington, Delaware, United

States) and other plastic polymers, such as synthetic polymers (nylon), fibres and rubbers, as well as cumene, lubricants, dyes, detergents, and various drugs and pesticides (*HHS, 2007*). Thus, the specific emission sources of benzene emission are industrial processes, coal and oil burning, motor vehicle exhaust and evaporation from gasoline service stations (*HHS, 2007*). Tobacco smoke is a particularly prevalent source of benzene in indoor environments, and smokers take in about 10 times the average daily intake of benzene of non-smokers (*HHS, 2007*). Benzene evaporates in the air and reacts with other chemicals, decomposing within a few days, but when it is present in water or soil it breaks down more slowly (*HHS, 2007*).

2.4.2 Toluene

Toluene (CASRN 108-88-3), also known as methylbenzene, toluol, or phenylmethane, is an aromatic hydrocarbon composed of only carbon and hydrogen atoms, with the molecular formula C_7H_8. Toluene is a clear, colourless liquid with a distinctive smell, it is used as a solvent that occurs naturally in crude oil and in tolu balsam. Some uses of toluene include making paints, thinners, polish, lacquers, adhesives, and rubber and in printing and leather tanning processes (*HHS, 2017*). Toluene is also used to produce benzene, nylon, plastics, polyurethane, and trinitrotoluene (TNT), among other chemical compounds. Toluene emissions usually occur from solvent and petroleum products spilling into the air and water surfaces. Evaporation and degradation into other chemicals will occur quickly (*HHS, 2017*).

2.4.3 Trichloroethylene

Trichloroethylene (CASRN 79-01-6), also known as ethylene trichloride, acetylene trichloride, narcogen, trilene, and TCE, is a halocarbon consisting of carbon, hydrogen, and chlorine atoms, with the molecular formula C_2HCl_3. Trichloroethylene is a clear, colourless volatile non-flammable liquid with a sweet chloroform like smell. It is predominantly used as an extraction solvent for greases, oils, fats, and waxes, or as a chemical used to create other chemicals, primarily the refrigerant HFC-134a, for textile processing methods like scouring cotton, wool, and other fabrics, among others (*ATSDR, 2019*). Trichloroethylene is also a key component of adhesives, lubricants, paints, varnishes, and pesticides. Emissions occur naturally through evaporation into the air during degreasing operations. Compounds get degraded by reacting with hydroxyl radicals and persist in the atmosphere for 3 to 7 days (*ATSDR, 2019*).

2.4.4 Tetrachloroethylene

Tetrachloroethylene (CASRN 127-18-4), also known as perchloroethylene (PCE), and tetrachloroethene, is a chlorinated hydrocarbon with the molecular formula C_2Cl_4. It is a non-flammable colourless liquid used as a dry-cleaning agent and metal degreasing agent, and for making other chemicals. Emissions from dry cleaning and consumer products lead to quick evaporation in the atmosphere, but breakdown is slow, with a half-life of 100 days (*ATSDR, 2019*).

2.4.5 Pinene

Pinene (CASRN 80-56-8) is a group of unsaturated bicyclic monoterpenes with the molecular formula $C_{10}H_{16}$. Pinene has two major geometric chiral isomers in nature, α-pinene and β-pinene. Pinene can be found in coniferous plants such as pines, camphorweed, and sagebrush. It is also the main component found in turpentine. Isomer α-pinene reacts with nitric oxides and forms tropospheric ozone. Its reactions with hydroxyl and radicals are a major sink of pinenes in the daytime troposphere (*Montenegro et al., 2012*). Pinene is used in the processes of creating and preserving personal care products, cleaning and household products, perfumes, and air fresheners (*NTP, 2016*).

2.4.6 Limonene

Limonene (CASRN 5989-27-5), also known as dipentene, d-limonene, carvene, and cinene, is a cyclic monoterpene aliphatic hydrocarbon with the molecular formula $C_{10}H_{16}$. It is a colourless liquid with a citrus odour. Once emitted into the air, it is easily oxidised to form various oxidation products, with half-life ranging from a few minutes to 2-3 hours (*DEPA, 2013*). Limonene is used as a flavouring agent in foods and beverages, as a substitute for organic solvents like chlorinated hydrocarbons and chlorine fluorine hydrocarbons (CFCs), as a raw material to produce resins, as an insecticide agent, and as a component in perfumes and fragrances. Limonene can be used to dissolve retained cholesterol gallstones and as an additive to increase transdermal penetration of medical substances. It’s also used as a solvent in dyes and as a degreasing agent for industrial products (*DEPA, 2013*).

2.4.7 Xylenes

Xylenes (CASRN 1330-20-7), also known as xylol are a class of volatile organic compounds with the molecular formula $(CH_3)_2C_6H_4$. The primary xylene isomers are meta-xylene (m-xylene), orto-xylene (o-xylene), and para-xylene (p-xylene). Xylenes are colourless, flammable liquids with a sweet odour. They occur naturally or are synthesized (from petroleum and coal tar). They are used as solvents in printing, rubber, and leather industries, or as cleaning agents, thinners, and varnishers (*HHS, 2007*). Xylenes are also an ingredient in the production of other chemicals, plastics, and synthetic fibres. When emitted into the air, xylenes evaporate rapidly. In ambient air they are degraded by sunlight into less toxic chemicals within a few days (*HHS, 2007*).

2.5 Human health effects

Health effects from VOC exposure vary considerably depending on their concentration in the air and the time of the respective exposure. The toxicity of the chemical compound will influence how great the human health effect will be. Exposure to VOCs can manifest through acute (or short term) exposure (hours to days) or through chronic exposure (years to a lifetime). Chronic inhalation exposure to low levels of VOCs may increase the risk of severe health problems and may worsen pre-existing symptoms of conditions like asthma (*MDH, 2022*). Acute exposure to high concentrations of VOCs includes eye, nose and throat irritation, headaches and dizziness, difficulty to breathe and worsening of asthma symptoms, and nausea and vomiting (*MDH, 2022*). Chronic exposure to high concentrations of VOCs leads to cancer (prominently lung cancer), liver and kidney failure, and central nervous system damage (*MDH, 2022*). Exposure to VOCs also increases the risk of developing cardiovascular disease, elevated blood pressure, and heart failure.

Most health studies relating to VOCs are conducted on single chemical compounds, while the health effects on the exposure to combinations of chemicals (how VOCs are more commonly present in the air) are limited. People with pre-existing respiratory problems, allergies or heightened susceptibility to chemicals, the elderly, and young children are more vulnerable to the effects of VOC exposure. Health risk assessment (HRA) is the process to estimate the nature and probability of adverse health effects in humans who may be exposed to chemicals in contaminated environments, now or in the future, using published toxicity data and estimated exposure concentrations. Chemical compounds are classified by various organizations, such as the International Agency for Research on Cancer (IARC), the Agency for Toxic Substances and Disease Registry (ATSDR), and USEPA Integrated Risk Information System (IRIS). The specific chemicals identified in this study have different routes of exposure and manifest their effects on human health differently, and therefore they are detailed as follows.

2.5.1 Benzene

Inhalation is the main route of exposure to benzene, with gases emitted from products containing benzene, such as glues, paints, furniture wax, detergents, and tobacco smoke (*HHS, 2007*) being among the main sources. Benzene enters the human body through the lungs, but also through the gastrointestinal tract and through the skin, with about half of the concentration that passes through the lungs entering the bloodstream (*HHS, 2007*). When in the bloodstream, benzene can accumulate in the bone marrow and fat and is converted to metabolites in the liver and bone marrow which can cause harmful effects (*HHS, 2007*). Most benzene metabolites are removed through urine (within 48 hours after initial exposure (*HHS, 2007*)), but exposure to high concentrations in a short period (10 000-20 000 ppm) can result in death (*HHS, 2007*). Exposure to low levels can cause drowsiness, dizziness, rapid heart rate, headaches, tremors, confusion, and unconsciousness (*HHS, 2007*). Benzene can cause health consequences in the blood cell tissues and bone marrow, disrupting and decreasing blood components production, leading to anaemia, excessive bleeding, debilitating the immune system, increasing the chance of infection, and lowering the effectiveness of the body’s immune system against cancer (*HHS, 2007*). It can be transferred from the mother’s blood to the foetus during pregnancy (*HHS, 2007*). Benzene is classified by the International Agency for Research on Cancer (IARC) as a “known” human carcinogen (Category A) for all routes of exposure and the tumour site hematologic through leukaemia (*IARC, 2018*).

2.5.2 Toluene

Human exposure to toluene is via inhalation or through ingestion of food containing toluene, however, the majority of the compound is removed from the body within a day, either chemically unchanged or broken down into less harmful chemicals such as hippuric acid, through breathing, sweat or urine (*HHS, 2017*). Toluene can affect the nervous system, which may be temporary, causing headaches, dizziness, and unconsciousness when temporary, or permanent with repeated exposure, through incoordination, cognitive impairment, and vision and hearing loss (*HHS, 2017*). High levels of toluene exposure during pregnancy may lead to developmental effects, such as retardation of mental abilities and growth in children (*HHS, 2017*). According to IARC there is inadequate evidence of the carcinogenicity of toluene in humans (*IARC, 1999*).

2.5.3 Trichloroethylene

The main source of human exposure to trichloroethylene is through drinking trichloroethylene contaminated water, although other sources include dermal contact and inhalation. Most of the trichloroethylene that is inhaled enters the bloodstream and organs. The liver can metabolize the compound into other chemicals and most of the breakdown products are released in urine within a day (*ATSDR, 2019*). In small to moderate concentrations, trichloroethylene may cause headaches, dizziness, and sleepiness, while large concentrations may cause coma and death, as well as damage to the nervous system, kidney damage, and systemic autoimmune disease (*ATSDR, 2019*). IARC considers trichloroethylene as a carcinogenic compound to humans by all routes of exposure, with primary tumour sites located in urinary, hematologic, and hepatic systems, and manifesting as renal cell carcinoma, non-Hodgkin's lymphoma, and liver tumours (*IARC, 2014*).

2.5.4 Tetrachloroethylene

Exposure to tetrachloroethylene can happen through inhalation as well as absorption from direct skin contact, and most tetrachloroethylene incorporated in the body goes to the bloodstream and organs (*ATSDR, 2019*). It takes about 3 days for half the concentration in the body to be eliminated, either through exhalation or through urine (*ATSDR, 2019*). Exposure to this chemical can severely affect the nervous system, liver, kidneys, and the reproductive system (*ATSDR, 2019*). Studies show consequences for both pregnant women and unborn children, possibly causing miscarriage, birth defects and slow growth in infants (*ATSDR, 2019*). Short periods of exposure (hours to 14 days) cause dizziness and sleepiness, headaches, and lack of coordination, whereas long term exposure leads to unconsciousness, change in mood, loss of memory, attention, reaction time and vision, and may lead to death (*ATSDR, 2019*). There is a high risk of cancer correlated to exposure to tetrachloroethylene from all possible routes of exposure, with inhalation exposure causing hepatocellular adenomas and carcinomas (*IARC, 2014*).

2.5.5 Pinene

Pinene is a common pollutant in indoor air, being quickly absorbed by the body after inhalation, creating metabolites that can potentially cause respiratory and skin irritation (*NTP, 2016*). Regarding carcinogenicity, very few studies and data exist for pinene in humans, with weak correlation between respiratory cancer and exposure to pinene found in turpentine and terpene in the studies that do exist (*NTP, 2016*).

2.5.6 Limonene

The primary forms of exposure to limonene are through inhalation, skin contact and ingestion of contaminated food and water, with expulsion of most of the chemical occurring between 24 to 72 hours after entry in the human body. Short term exposure may cause non-bloody diarrhoea, transient proteinuria, tenesmus, and skin irritation, while constant long-term exposure (various weeks) causes gastrointestinal irritation, nausea, and diarrhoea. Currently, there are no conclusive studies in humans on the possible carcinogenicity of limonene, although it has been known to increase the incidence of renal-cell adenomas, carcinomas, and tubular hyperplasia in rat studies (*IARC, 1999*).

2.5.7 Xylenes

Exposure to xylenes occurs primarily by inhalation of contaminated air from gasoline, paint, varnishes, pesticides, cigarette smoke, and especially through work in industrial facilities and laboratories with frequent use of chemicals. The compound is absorbed by the lungs and can leave by exhalation or as breakdown products in urine within 2 to 18 hours after exposure (*HHS, 2007*). Health effects include irritation of skin, eyes, nose and throat, difficulty breathing, impaired lung function, delayed visual stimulus, impaired memory, headaches, lack of muscle coordination, dizziness, confusion, altered sense of balance, stomach discomfort, and damage to liver and kidneys. Short term exposure to high concentrations of xylenes may cause death (*HHS, 2007*). Currently, there is inadequate data on the potential carcinogenicity of xylenes, as human data is not available and animal test data is inconclusive (*IARC, 1999*).

2.6 Legislation

The current protective thresholds for indoor air are encompassed in the Portuguese legislation (DL nº101-D/2020 of December 7th, Portaria nº138-G/2021 of July 1st). For Total VOCs (TVOCs), the limit value of 600 µg/m^3 was defined (with a tolerance margin of 100%). It shall be emphasized that the respective legislation refers only to commercial and public buildings, such as schools and hospitals, and not private households.

The European Union (EU) sets air quality standards in ambient air to protect human health and the environment, defining air quality standards for 12 pollutants: sulphur dioxide, nitrogen dioxide and oxides, particulate matter (PM_{10}, $PM_{2.5}$), ozone, benzene, lead, carbon monoxide, arsenic, cadmium, nickel, and benzo(a)pyrene. The directive is based on standards, guidelines and programmes created by the World Health Organization (*EC, 2022*). In this legislation, TVOCs are represented by benzene with an annual limit of 5 µg/m^3 (*EC, 2022; DL 47/2017*).

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3. Materials and methods

This work was conducted in the framework of the NeoGene project, a cross-sectional birth and post-partum study. The project was approved by the Ethical Committee of Centro Hospitalar de São João, Porto, Portugal (under reference 326/16). It was conducted in compliance with the Declaration of Helsinki and its amendments. Subjects who agreed to participate signed written consent forms and were clearly instructed on the aim of the project and the nature of participation. Authorization for data collection and management was obtained from the Portuguese Data Protection Authority.

3.1 Study region

The study was conducted primarily in Porto Metropolitan Area (PMA). PMA comprises 17 municipalities, being the second largest urban area in Portugal. Furthermore, it is one of the largest metropolitan areas in the EU (2 040 km^2) and constitutes 9.6% of the North region and 2.2% of the national territory (*AMP, 2020*). The resident population is more than 1 700 000 inhabitants (*INE, 2011*) and the population density is around 850 inhabitants/km^2.

The climate of PMA can be defined as Mediterranean climate (subtype Csb, i.e., Cool-summer Mediterranean climate; Köppen-Geiger classification), which represents dry, cool to warm summers, and mild and wet winters, with two transitional seasons (spring and autumn). Most precipitation occurs during autumn and the driest month is July (*CD, 2021*). The highest temperatures are registered in July and August, while December and January are the coldest months. Annual average temperature is 15.1 °C (*CD, 2021*). Topographically the regions are uneven, with an average altitude ranging from 100 m to 200 m (*CD, 2021*).

3.2 Sites description

This study involved the exposure assessment to air pollution in 64 private residences, which was conducted between May 12th, 2018, and February 6th, 2019. The locations of all 64 dwellings are represented in Figure 3-1.

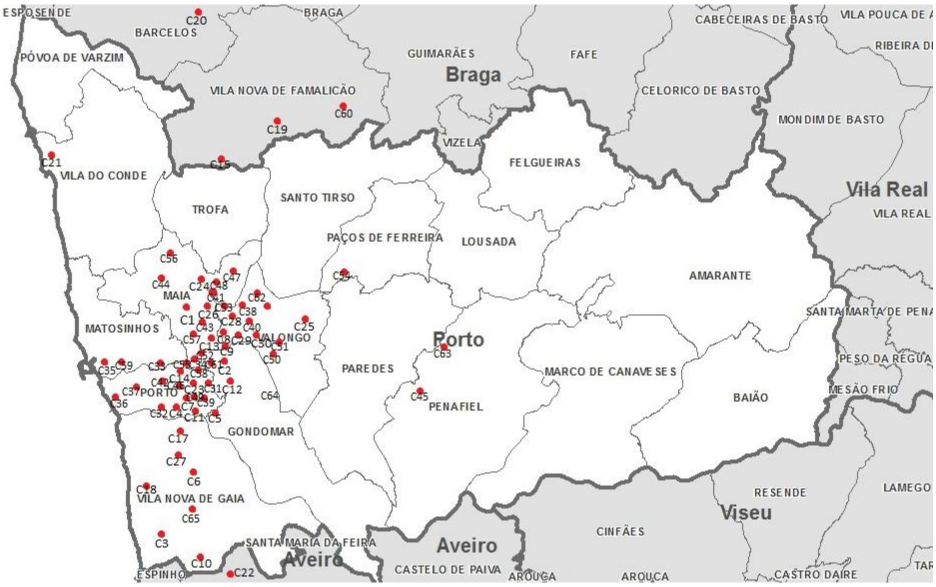

Figure 3-1 – Geographical identification of the 64 homes involved in the study with representation of Porto and the bordering districts

3.3 Walkthrough inspection and checklist of the homes

A standardized walkthrough inspection and a detailed checklist were conducted for each dwelling (Appendix A). Pertinent details regarding potential outdoor pollution sources, construction materials, and other relevant parameters, such as type and frequency of ventilation, type and use of heating and cooling systems, cleaning routines (schedules and procedures), smoking habits, existence of textiles, use of candles and incenses, and available equipment, such as air conditioners or fireplaces were registered. The characteristics of the study sites, obtained through the checklist, are summarized in Table A-1 of Appendix A.

3.4 VOCs collection and quantification

Sampling of VOCs in the air was done for 8 h in each home, concurrently both indoors and outdoors. The indoor air sampling was done predominantly in living rooms, where the subjects spent the most time. In addition, indoor VOCs were collected in the kitchen and bedrooms whenever possible. All samples (both indoors and outdoors) were collected in duplicates, resulting in a total of 122 and 127 measurements of ambient air and indoor air, respectively.

Personal air sampling pumps (AirChek® XR5000 – SKC Ltd, Dorset, UK) were used to collect VOCs (air flow of 50 mL/min). Each sampler was connected to a stainless-steel sorbent tube (Tenax TA; 60/80 mesh) using Tygon® high-purity tubing. Before and after the sampling, air flows were verified using DryCal DC-Lite Gas Flow Calibrators. The equipment setup is shown in Figure 3-2.

Figure 3-2 - Representation of sampling system: (a) AirChek XR5000 (SKC Ltd) pump; (b) Stainless-steel sorbent tube (Tenax TA; 60/80 mesh); (c) Tygon® high-purity tubing

Indoors, the sampling equipment was positioned at least one meter above ground and one meter away from the walls. Outdoors, sample collection was done at a distance of at least one meter from the window.

VOCs analysis and quantification were conducted through thermal desorption (TD) combined with gas chromatography (GC) with flame ionized detector (FID). Through this process, concentrations of total VOCs (TVOCs) and of seven individual VOCs were determined, namely: benzene, toluene, trichloroethylene, tetrachloroethylene, limonene, pinene (α-pinene isomer), and xylenes (m-xylene, o-xylene and p-xylene isomers).

Concentrations of TVOCs were quantified into mass units of toluene through the toluene response factor and then expressed as TVOCs mass concentrations in the sampled air according to the procedure described in international standard ISO 16000-6:2011. The quantification of individual VOCs was carried out also according to the methodology of the ISO 16000-6:2011 standard.

The overall analytical procedure was previously validated by systemic recovery experiments. Limits of quantification (LOQs) were calculated and expressed as the concentration of a compound in air samples. LOQs between 0.050 µg/m^3 and 0.150 µg/m^3 were obtained.

3.5 Statistical analysis

The statistical analyses were conducted using Microsoft Excel 2013 (Microsoft Corporation), and SPSS (Statistical Package for the Social Sciences) (IBM SPSS Statistics 28). Statistical significance was set as $p<0.05$. As obtained data did not display the normal distributions (confirmed by Shapiro-Wilk's test), Spearman correlations (two-tailed) were conducted, to address the relationship between different pollutants. Kruskal-Wallis H tests (one-way ANOVA) for sample distributions were also conducted.

3.6 Risk assessment

Both carcinogenic risks (CR) and non-carcinogenic risks (NCR) for inhalation exposure to VOCs were evaluated in this work. For carcinogenic risk, USEPA defines a threshold of 10^{-6} for an individual compound's risk and 10^{-4} for cumulative risk (combination of all detected compounds). Values exceeding these thresholds indicate a high risk of cancer for those exposed to the analysed compounds.

The carcinogenic risks were calculated as shown in Equation (1) (*USEPA, 2009*):

$$CR_i = EC_i \times IUR_i \qquad (1);$$

where CR represents the cancer risk of compound *i*, IUR is inhalation unit risk (risk per µg/m^3) and EC is the exposure concentration (µg/m^3). The total cancer risk (CR_t), for all VOCs, was then calculated through the sum of the individual CR of each compound. The EC is defined as shown in Equation (2) (*USEPA, 2009*):

$$EC_i = CA_i \times \frac{ET \times EF \times ED}{AT} \times 90\% \quad (2);$$

where CA is the contaminant *i*'s concentration in the air (µg/m^3), ET is the exposure time (h/day), EF is the exposure frequency (day/year), ED is the exposure duration (yrs), and AT is the total average time of exposure (h). In this work, ET for indoor exposure directly at home was considered 15.1 h/day (i.e., 70% of all the indoor time being spent at home (*Wickliffe et al., 2020)).* EF was considered as 350 days/year, assuming 15 days of vacation period (spent outside of the homes*; BLS, 2021)*. ED was 80.7 yrs, based on the average life expectancy in Portugal (*PORDATA, 2022*). AT was calculated by multiplying EF by ED and by 24 hrs/day, resulting in 677 800 hrs which converts to 77.3 yrs of lifetime exposure.

Chemical compounds are classified by various organizations, such as the International Agency for Research on Cancer (IARC), the Agency for Toxic Substances and Disease Registry (ATSDR), and USEPA Integrated Risk Information System (IRIS). Thus, there are various sources and values for the existent risk parameters. In this work, IUR values were retrieved from USEPA IRIS database when available (*USEPA, 2022*). As IUR values were not available for all target VOCs of this study (mainly due to insufficient evidence, inconclusive results, or non-inclusion of a compound in the IRIS program database). When inexistent, IUR values from a conditional toxicity value predictor (CTV Predictor) were used (*Wignall et al., 2018*).

The CTV Predictor *(CTV, 2022)* is an *in-silico* approach for generating toxicity values for chemicals. It predicts a toxicity value with an error of less than a factor of 10 and can be used to quickly assess relative hazards of environmental exposures when data or risk assessments are unavailable (*Wignall et al., 2018*). The CTV Predictor generates a predicted value as well as a lower 95% and an upper 95% value. The lower 95% values were used in this work, assuming "the lowest, i.e., best risk scenario". This was due to the fact that, for the three target VOCs of this study (i.e., benzene, trichloroethylene, and tetrachloroethylene) that are included and assessed by the IRIS program, lower 95% CTV predictions were similar to the figures reported by IRIS. It shall also be noted that for xylenes (defined as the total of three isomers IUR of m-xylene was used in a view that it is the most common form of the three isomers (40-65%) (*Kandyala et al., 2010*). Table 3-1 summarizes IUR values of all compounds used in this study and the database sources of the respective values.

Table 3-1 – Inhalation unit risk values

Compound	IUR (risk per μg/m^3)	Source
Benzene	7.80×10^{-6}	USEPA IRIS[1)]
Toluene	3.15×10^{-4}	CTV Predictor[2)]
Trichloroethylene	4.10×10^{-6}	USEPA IRIS[1)]
Tetrachloroethylene	2.60×10^{-7}	USEPA IRIS[1)]
Limonene	5.18×10^{-6}	CTV Predictor[2)]
Pinene	4.21×10^{-4}	CTV Predictor[2)]
M-Xylene	3.48×10^{-4}	CTV Predictor[2)]

1) US-EPA IRIS Assessments, 2022; 2) CTV – Conditional Toxicity Value Predictor (Wignall et al., 2018)

Non-carcinogenic risk was assessed through the Hazard Index (HI), which represents the sum hazard quotient (HQ) of each compound. USEPA defines HQ < 1 as the compound not having any appreciable risk, while HQ > 1 suggests the occurrence of possible adverse health effects. The HQ calculations were done according to Equation (3) (*USEPA, 2009*):

$$HQ_i = \frac{EC_i}{RfC_i} \quad (3);$$

Where HQ is the hazard quotient of the compound *i*, EC is the exposure concentration (µg/m^3), and RfC is the reference concentration for inhalation (µg/m^3). Similarly to IUR, RfC values were retrieved from the IRIS program of USEPA when available and generated by CTV Predictor when inexistent at IRIS. Table 3-2 summarizes the RfC values used to determine HI and the respective sources.

Table 3-2 – Reference concentration values

Compound	RfC (μg/m^3)	Source
Benzene	30	USEPA IRIS[(a)]
Toluene	5 000	USEPA IRIS[(a)]
Trichloroethylene	2	USEPA IRIS[(a)]
Tetrachloroethylene	40	USEPA IRIS[(a)]
Limonene	9	CTV Predictor[(b)]
Pinene	14	CTV Predictor[(b)]
M-Xylene	100	USEPA IRIS[(a)]

a - US-EPA IRIS Assessments, 2022; b- CTV – Conditional Toxicity Value Predictor (Wignall et al., 2018)

When the determined concentration of a compound was lower than its LOQ, the LOQs value (0.050 µg/m^3 for TVOCs, benzene, tetrachloroethylene, limonene, and xylenes; and 0.150 µg/m^3 for toluene, trichloroethylene, and pinene) were used for the risk assessment. In addition, two more scenarios were explored to assess the carcinogenic and non-carcinogenic risks: LOQ/2, and minimum concentration of a VOC (determined across all the homes of each season).

3.7 Toxicity assessment

The Toxicological Prioritization Index (ToxPi) is a free software (*Reif et al., 2010*) that creates dimensionless toxicity index scores for various chemical compounds. These are based on different toxicity parameters, both standardized (such as RfC and RfD) and experimentally obtained in the laboratory, and the weight given to each of those parameters. This structuring facilitates the prioritization process of chemicals for toxicity testing, which is a primary goal of the USEPA ToxCast™ forecasting program (*Reif et al., 2010*). ToxPi calculated scores represent the toxicity of a compound relative to the other compounds present in the dataset. This software allows for a theoretical general outlook of the toxicity innately associated to a set number of chemical compounds present in a mixture of air, before conjugating the different concentrations and volatility of each VOC in the amalgam. In this study, all seven individual VOCs were analysed through the ToxPi software (including all three xylene isomers).

The following parameters were used for the ToxPi score calculations as they most adequately describe toxicity values for inhalation exposure (*Bayati et al., 2021*): RfC (mg/m^3), IUR (risk per $\mu g/m^3$), CPV – Cancer Potency Value (risk per ($mg/(kg \cdot day)$)), NO(A)EL – reference dose for No Observed Adverse Effect Level; ($mg/(kg\ day)$), BMD – reference dose Benchmark Dose $mg/(kg \cdot day)$), and BMDL – reference dose Benchmark Dose Lower Limit ($mg/(kg \cdot day)$). Each toxicity parameter was given equal weight in the process of calculation. Further, negative log scaling was used for RfC, NO(A)EL, BMD, and BMDL, in order to comply with the convention that greater values correspond to greater toxicity (*Bayati et al., 2021*); IUR and CPV were linearly scaled.

It shall also be noted that the lowest values predicted by CTV for each parameter were used, considering "the best case scenario". Values of all the considered parameters for the seven VOCs are summarized in Table 3-3.

Table 3-3 – Parameters used in ToxPi score calculations

Compound	IUR (risk per μg/m³)	RfC (μg/m³)	CPV (risk per mg/(kg·day))	NO(A)EL (mg/(kg·day))	BMD (mg/(kg·day))	BMDL (mg/(kg·day))
Benzene	7.80×10^{-6} (a)	30 (a)	1.10×10^{-1} (b)	0.41 (b)	0.60 (b)	0.39 (b)
Toluene	3.15×10^{-4} (b)	5 000 (a)	1.53×10^{-2} (b)	1.51 (b)	1.10 (b)	1.04 (b)
Trichloroethylene	4.10×10^{-6} (a)	2 (a)	3.43×10^{-4} (b)	0.33 (b)	0.43 (b)	0.13 (b)
Tetrachloroethylene	2.60×10^{-7} (a)	40 (a)	5.00×10^{-2} (b)	0.37 (b)	0.16 (b)	0.08 (b)
Limonene	5.18×10^{-6} (b)	9 (b)	6.82×10^{-3} (b)	0.81 (b)	1.94 (b)	1.60 (b)
Pinene	4.21×10^{-4} (b)	14 (b)	1.66×10^{-2} (b)	0.79 (b)	1.56 (b)	1.43 (b)
M-Xylene	3.48×10^{-4} (b)	100 (a)	1.34×10^{-2} (b)	1.90 (b)	1.78 (b)	1.71 (b)
O-Xylene	3.58×10^{-4} (b)	100 (b)	1.48×10^{-2} (b)	1.79 (b)	1.71 (b)	1.75 (b)
P-Xylene	3.32×10^{-4} (b)	100 (b)	1.24×10^{-2} (b)	1.88 (b)	1.19 (b)	1.73 (b)

a - USEPA-IRIS database value; b - CTV Predictor value

3.8 References

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4. Results and discussions

The distribution of the data was assessed considering TVOCs and considering each specific VOC (benzene, toluene, trichloroethylene, tetrachloroethylene, pinene, limonene, xylenes). The seasonal trends were determined, for convenience, as starting on the first day of the month after it usually starts, as the following: spring starting on the first day of April, summer starting on the first day of July, autumn starting on the first day of October and winter starting in the first day of January. This resulted in 11 homes with 22 measurements in spring for both indoors and outdoors, 22 homes with 44 measurements in summer for both indoors and outdoors, 21 homes with 42 measurements outdoors and 24 homes with 47 measurements indoors in autumn, and finally 7 homes with 14 measurements in winter for both indoors and outdoors. The seasonal trends were assessed considering mean, maximum, minimum, and median of the concentrations, and 25th and 75th percentile concentrations, both for each season and considering all homes. Table B-1 summarizes registered VOCs concentrations, both indoors and (Appendix B).

4.1 Characterization of VOCs

4.1.1 Indoor VOC levels

Table 4-1 shows the statistics for concentrations of TVOCs and for each specific VOC, indoors. Overall, TVOCs concentrations ranged from 0.050 to 1 617 µg/m^3. The protective threshold of

600 µg/m^3 (DL nº101-D/2020 of December 7th, Portaria nº138-G/2021) was exceeded in six homes, i.e., 10% of the assessed dwellings, and 5% of households exceeded the 100% margin of tolerance (secondary condition) reaching indoor levels of 1 316 – 1 617 µg/m^3. Considering individual VOCs, pinene was the most abundant compound (19% of TVOCs), followed by limonene (18% of TVOCs) and by toluene (7% of TVOCs).

Table 4-2 summarizes the Spearman correlation coefficients (r_s) for indoor VOCs (total and individual compounds), considering all indoor measurements (based on 64 homes). Overall, the results showed positive correlations in 99% of the cases. Strong correlation ($r_s \geq 0.70$) was observed only for TVOCs with xylenes (0.70), whereas benzene, toluene and pinene showed moderate relationships with TVOCs ($0.5 < r_s < 0.70$). Associations of compounds like trichloroethylene and tetrachloroethylene were weak (i.e., $r_s < 0.3$). Considering the relationships between the individual compounds, moderate trends were observed between toluene and xylenes (0.63), between benzene and pinene (0.59), and between benzene and xylenes (0.53).

4.1.2 Outdoor VOC levels

Table 4-3 displays the statistics for concentrations of TVOCs and for each specific VOC in outdoor air. In general, the outdoor TVOCs concentrations were in the range of 4.54 – 194 µg/m^3. Trichloroethylene was the most abundant compound (31% of TVOCs), followed by pinene (16% of TVOCs) and by toluene and limonene (12% of TVOCs).

In the ambient air (Table 4-4) Spearman correlations were slightly different from those in indoor air. Outdoor TVOCs showed moderate correlations ($0.50 < r_s < 0.70$) with benzene (0.66), tetrachloroethylene (0.65), and xylenes (0.66). Benzene and xylenes were strongly linked (0.70), as well as benzene and tetrachloroethylene (0.70). Overall, the several cases of negative relationships for individual compounds in outdoor air were most probably caused by meteorological conditions as well as by atmospheric processes (*Zhang et al., 2021*).

Table 4-1 – Indoor VOC concentrations (µg/m³) in 64 dwellings across four seasons: mean, min, max, median, 25th and 75th percentile

	TVOCs		**Benzene**		**Toluene**		**Trichloroethylene**		**Tetrachloro-ethylene**		**Pinene**		**Limonene**		**Xylenes**	
	Mean (min-max)	Median (P25-P75)	Mean (min-max)	Median (P25-P75)	Mean (min-max)	Median (P25-P75)	Mean (min-max)	Median (P25-P75)	Mean (min-max)	Median (P25-P75)	Mean (min-max)	Median (P25-P75)	Mean (min-max)	Median (P25-P75)	Mean (min-max)	Median (P25-P75)
Spring	141 (0.050-320)	129 (63.8-200)	4.26 (1.36-13.3)	3.24 (1.80-4.57)	2.87 (0.150-6.64)	2.66 (0.150-5.28)	8.15 (0.150-33.8)	9.78 (2.51-11.2)	3.69 (0.050-12.2)	2.70 (0.215-6.64)	32.1 (0.150-123)	15.0 (2.39-38.2)	66.0 (6.78-192)	29.2 (14.3-129)	4.28 (0.664-9.07)	3.76 (1.92-6.58)
Summer	154 (0.218-1315)	84.0 (42.8-114)	1.25 (0.178-3.98)	0.992 (0.380-1.90)	16.2 (0.307-245)	6.85 (2.94-9.59)	24.9 (0.150-463)	7.65 (3.11-11.6)	4.66 (1.86-22.6)	3.89 (2.92-4.54)	57.5 (1.31-252)	20.0 (14.8-67.2)	14.1 (1.49-84.5)	9.00 (4.37-14.6)	7.32 (0.536-36.4)	4.55 (2.39-7.23)
Autumn	244 (63.6-1617)	177 (122-256)	4.78 (0.576-37.5)	2.53 (1.44-5.55)	17.6 (0.234-94.1)	10.8 (5.56-19.0)	6.25 (0.150-37.1)	3.42 (1.47-8.51)	2.82 (0.302-6.26)	2.86 (1.59-3.84)	29.4 (5.30-92.1)	18.4 (11.7-46.0)	40.0 (6.23-294)	17.4 (13.9-32.5)	13.5 (0.563-60.8)	6.16 (3.27-15.5)
Winter	444 (85.3-1319)	293 (188-556)	6.20 (2.41-11.1)	5.18 (3.32-9.96)	21.0 (4.40-51.5)	16.2 (9.63-26.8)	9.70 (0.813-29.9)	9.24 (2.58-10.6)	3.14 (1.32-8.73)	2.83 (1.72-3.81)	36.9 (8.72-143)	21.4 (15.6-24.9)	60.7 (6.92-207)	50.3 (26.2-82.3)	21.7 (2.56-48.0)	18.2 (4.89-37.1)
Total	217 (0.050-1617)	132 (82.9-216)	3.63 (0.178-37.5)	2.23 (1.20-4.36)	19.9 (0.150-245)	7.02 (3.46-14.4)	13.5 (0.150-463)	6.00 (2.05-11.0)	3.66 (0.050-22.6)	3.16 (1.91-4.29)	40.7 (0.150-252)	20.1 (11.0-48.3)	38.0 (1.49-294)	17.2 (9.23-38.6)	10.7 (0.536-60.8)	5.08 (2.69-12.1)

Table 4-2 - Spearman correlation coefficient (r_s) between VOCs in indoor air of 64 dwellings

	TVOCs	**Benzene**	**Toluene**	**Trichloro-ethylene**	**Tetrachloro-ethylene**	**Pinene**	**Limonene**	**Xylenes**
TVOCs	-	-	-	-	-	-	-	-
Benzene	0.61	-	-	-	-	-	-	-
Toluene	0.56	0.31	-	-	-	-	-	-
Trichloro-ethylene	0.17	0.13	0.26	-	-	-	-	-
Tetrachloro-ethylene	0.003	0.31	0.15	0.39	-	-	-	-
Pinene	0.69	0.59	0.14	0.46	-0.93	-	-	-
Limonene	0.37	0.19	0.25	0.32	0.27	0.19	-	-
Xylenes	**0.70**	0.53	0.63	0.37	0.22	0.28	0.50	-

Note: values in bold show strong correlation, i.e., with $r_s \geq 0.70$

Table 4-3 – Outdoor VOC concentrations (µg/m^3) in 64 dwellings across four seasons: mean, min, max, median, 25th and 75th percentile

	TVOCs		**Benzene**		**Toluene**		**Trichloroethylene**		**Tetrachloro-ethylene**		**Pinene**		**Limonene**		**Xylenes**	
	Mean (min-max)	Median (P25-P75)	Mean (min-max)	Median (P25-P75)	Mean (min-max)	Median (P25-P75)	Mean (min-max)	Median (P25-P75)	Mean (min-max)	Median (P25-P75)	Mean (min-max)	Median (P25-P75)	Mean (min-max)	Median (P25-P75)	Mean (min-max)	Median (P25-P75)
Spring	51.2 (14.6-185)	29.5 23.0-51.9)	2.78 (1.21-5.26)	3.22 (1.61-3.41)	1.77 (0.150-6.71)	0.150 (0.150-3.55)	9.87 (0.150-22.0)	11.0 (5.12-12.8)	2.87 (0.050-11.1)	1.70 (0.252-4.53)	6.37 (0.150-47.6)	0.150 (0.150-1.53)	14.3 (1.21-30.8)	17.8 (2.19-25.0)	2.21 (1.03-3.85)	2.28 (1.76-2.49)
Summer	31.5 (4.54-94.5)	20.6 (16.7-43.4)	0.706 (0.203-2.41)	0.477 (0.291-0.736)	3.49 (0.864-9.89)	2.82 (1.91-3.95)	21.3 (1.41-123)	14.0 (8.88-28.0)	2.61 (0.050-7.56)	2.43 (1.92-3.02)	8.94 (0.150-43.6)	5.05 (3.96-10.2)	3.22 (0.983-14.6)	2.29 (1.76-3.26)	2.79 (1.15-7.63)	2.33 (1.74-2.89)
Autumn	33.7 (9.99-120)	23.9 (16.0-46.2)	1.33 (0.050-3.53)	1.12 (0.919-1.76)	5.46 (0.150-16.4)	5.13 (2.14-7.98)	7.60 (0.264-115)	3.35 (1.83-5.44)	0.780 (0.050-5.45)	0.345 (0.083-0.741)	4.70 (1.14-12.0)	3.93 (3.18-5.37)	2.59 (0.050-33.5)	0.755 (0.288-2.37)	2.90 (0.050-7.48)	2.12 (1.37-4.66)
Winter	83.3 (27.1-194)	65.9 (60.4-103)	5.93 (1.22-16.7)	4.30 (1.92-7.40)	15.2 (2.86-42.6)	9.85 (7.42-19.7)	7.18 (1.91-19.7)	5.90 (3.04-8.43)	5.07 (0.050-17.9)	3.73 (0,909-6.55)	7.40 (3.35-15.4)	6.59 (4.84-8.92)	4.54 (0.313-11.0)	3.23 (0.913-8.71)	7.40 (1.47-18.2)	4.98 (2.40-11.6)
Total	41.8 (4.54-194)	26.9 (17.8-52.9)	1.90 (0.050-16.7)	1.21 (0.614-2.06)	5.20 (0.150-42.6)	3.19 (1.85-6.75)	12.9 (0.150-123)	8.11 (3.39-13.3)	2.31 (0.050-17.9)	1.67 (0.337-2.95)	6.84 (0.150-47.6)	4.24 (2.89-7.03)	5.16 (0.050-33.5)	2.14 (1.15-3.36)	3.25 (0.050-18.2)	2.29 (1.62-3.79)

Table 4-4 - Spearman correlation coefficient (r_s) between VOCs in outdoor air of 64 dwellings

	TVOCs	**Benzene**	**Toluene**	**Trichloro-ethylene**	**Tetrachloro-ethylene**	**Pinene**	**Limonene**	**Xylenes**
TVOCs	-	-	-	-	-	-	-	-
Benzene	0.66	-	-	-	-	-	-	-
Toluene	0.31	0.38	-	-	-	-	-	-
Trichloro-ethylene	0.082	-0.90	-0.10	-	-	-	-	-
Tetrachloro-ethylene	0.65	**0.70**	0.20	0.16	-	-	-	-
Pinene	0.37	0.068	0.13	0.21	0.15	-	-	-
Limonene	0.45	0.31	-0.12	-0.45	0.25	0.17	-	-
Xylenes	0.66	**0.70**	0.49	0.08	0.61	0.25	0.032	-

Note: values in bold show strong correlation, i.e., with $r_s \geq 0.70$

4.1.3 Indoors vs. outdoors VOC levels comparison

The results obtained within this study (namely Tables 4-1 and 4-3) showed that indoor concentrations of TVOCs were significantly higher than outdoors (mean 217 vs 41.8 µg/m^3). In addition, based on the values for the Spearman correlations between correspondent indoor and outdoor levels (Table 4-5), the majority of the compounds showed moderate correlations between indoor and outdoor concentrations, being even strongly linked in the case of benzene (0.71). Pinene was the only exception (0.19) and considering its much higher indoor levels (approximately six times higher; Tables 4-1 and 4-3), it seems that this compound originated predominantly from specific indoor sources.

Table 4-5 – Spearman correlation coefficient (r_s) for indoor vs outdoor VOCs

	TVOCs	Benzene	Toluene	Trichloro-ethylene	Tetrachloro-ethylene	Pinene	Limonene	Xylenes
r_s	0.40	**0.71**	0.68	0.56	0.52	0.19	0.54	0.51

Note: values in bold show high correlation, i.e., with $r_s \geq 0.70$

4.1.4 Seasonal concentration trends

4.1.4.1 TVOCs

Considering the evaluation throughout the year, the comparison between indoor and outdoor TVOCs levels is presented in Figure 4-1. As clearly demonstrated, the higher concentrations were observed in winter indoors (mean of 444 µg/m^3 indoors; 83.3 µg/m^3 outdoors), being at 3 times higher than in spring (141 µg/m^3 indoors; 51.2 µg/m^3 outdoors) and summer (154 µg/m^3 indoors; 31.5 µg/m^3 outdoors), and almost twice higher than in autumn (244 µg/m^3 indoors; 33.7 µg/m^3 outdoors). The higher indoor TVOCs levels in winter were most likely caused by lower air temperatures that resulted in less frequent ventilation and consequently reduced air exchange rate (*Hernandez et al., 2020*). At the same time higher and longer occupancy indoors during cold months (*Hernandez et al., 2020*) and additional emissions from indoor sources may have contributed to the increased indoor VOCs in winter. It is noteworthy that the protective threshold of 600 µg/m^3 (DL nº101-D/2020 of December 7th, Portaria nº138-G/2021) was exceeded in indoor air during three seasons, namely summer, autumn, and winter. Overall indoor average concentrations throughout the study (217 µg/m^3), accounting for all 64 houses, were about half of the means estimated for winter. The concentration of TVOCs in outdoor air was the highest during the winter, being about 2.5 times higher than in the summer, when solar radiation is more intensive, and leads to ionization and consequently decomposition of VOCs at a higher rate than in the winter (*Li et al, 2020*).

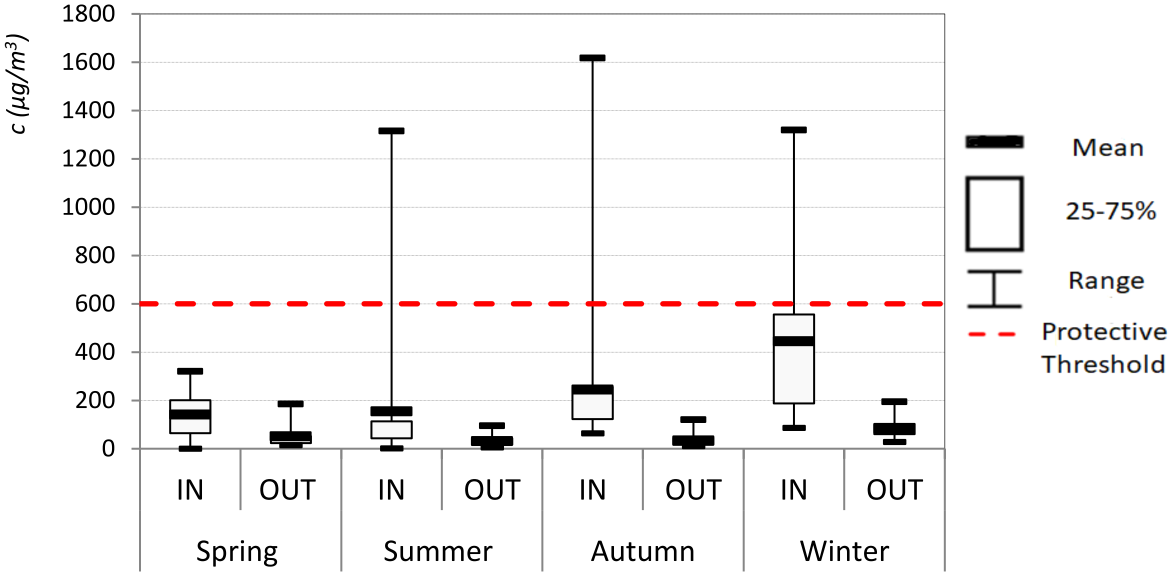

Figure 4-1 – Indoor and outdoor TVOC levels during four seasons at 64 dwellings. Note: red horizontal line represents the protective threshold (600 µg/m^3) as defined in Ordinance No. 138-G/2021. Note: distribution and medians were statistically different across all seasons ($p<0.001$)

The indoor to outdoor (I/O) ratios of TVOCs are shown in Figure 4-2. If I/O <1, then a compound is predominantly originated from penetration of ambient air, whereas if I/O >1, a compound results mainly from indoor sources. The majority of homes (97% of TVOCs) exhibited I/O ratio higher than one, thus strongly suggesting predominantly indoor origin of TVOCs. It is noteworthy that the highest I/O value was registered during the summer. To confirm these findings, further assessments regarding specific indoor sources identification should be performed.

4.1.4.2 Benzene

Mean benzene concentrations were twice higher indoors than outdoors, as show in Figure 4-3. Considering the seasons, the highest concentrations for both indoors and outdoors were recorded during winter (mean 6.20 µg/m^3 and 5.93 µg/m^3, respectively), being three and eight times higher, respectively for indoor and outdoor air than in summer, when the respective levels were the lowest (mean 1.25 µg/m^3 and 0.706 µg/m^3, indoors and outdoors, respectively).

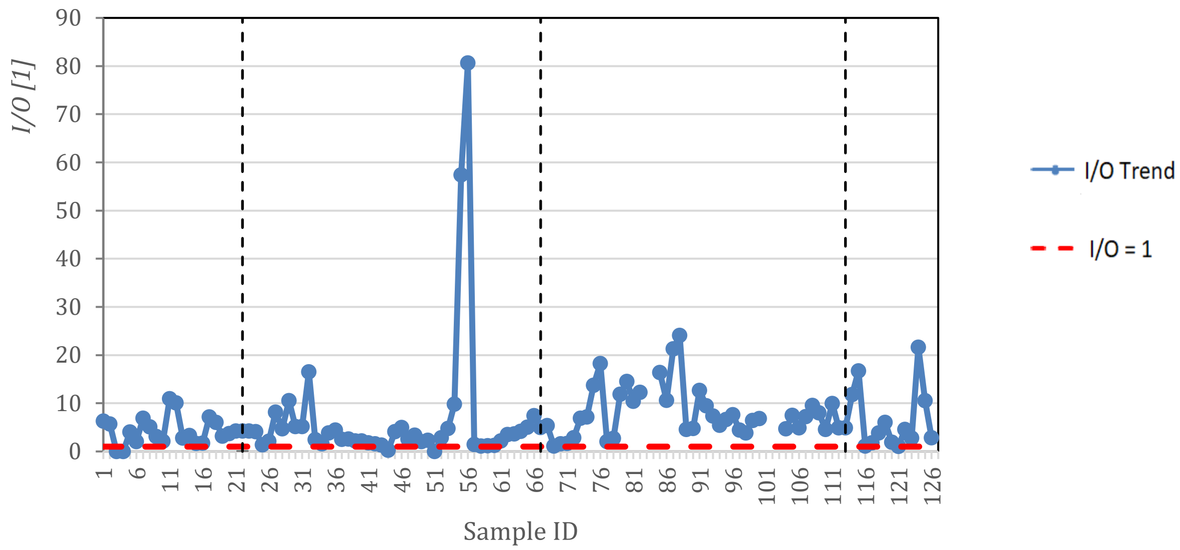

Figure 4-2 – Indoor to outdoor (I/O) ratio of TVOCs at 64 dwellings of the study. Note: red horizontal line represents I/O=1. Note: vertical lines represent separation of calendar seasons

The I/O ratio of benzene, in Figure 4-4, showed similar indoor and outdoor trends, particularly in the spring and summer, though in 77% of homes the indoor concentrations were still higher than outdoor ones. The highest ratios occurred in autumn, with some indoor concentrations being 35 times greater than outdoors.

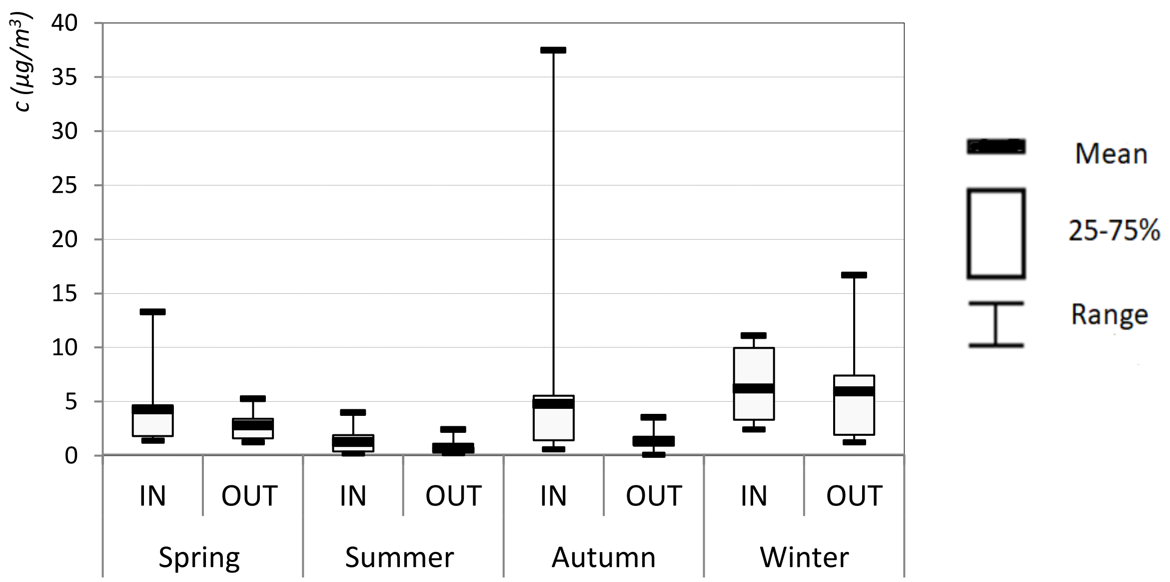

Figure 4-3 – Indoor and outdoor benzene levels during four seasons at 64 dwellings. Note: distribution and medians were statistically different across all seasons (p<0.001)

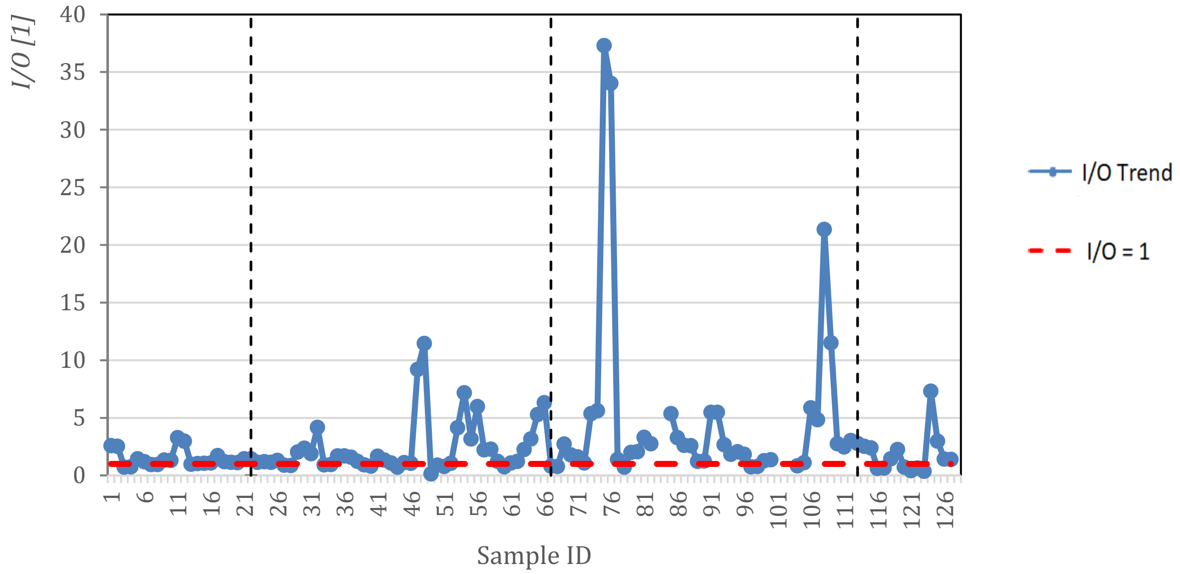

Figure 4-4 – Indoor to outdoor (I/O) ratio of benzene at 64 dwellings of the study. Note: vertical lines represent separation of calendar seasons

4.1.4.3 Toluene

The highest average concentrations of toluene were found during winter, both for indoor and outdoor air (21.0 µg/m^3 and 15.2 µg/m^3, respectively), with the maximum indoor concentration registered in the summer (245 µg/m^3). The seasonal trend, in Figure 4-5, demonstrated low levels of toluene during spring, and in similar ranges for both indoors and outdoors environments (0.150 – 6.64 µg/m^3 and 0.150 – 6.71 µg/m^3, respectively). In autumn, the indoor concentrations of toluene rose, and in winter both indoors and outdoors levels exhibited the highest mean values, being 5 and 3 times higher, respectively, than in spring.

The analysis of the seasonal patterns of I/O ratio for toluene showed several extreme occurrences with values ranging up to 80. It is assumed that this was most likely caused by specific emission sources such as paint thinners, use of nail polish, glues, inks and stain removers (*HHS, 2017*). To confirm these findings, specific source specific analysis (using advanced statistical modelling) should be conducted. In addition, Figure 4-6 clearly confirms the twice greater level ratio values in autumn (mean I/O of 1.33) over summer (mean I/O of 0.706).

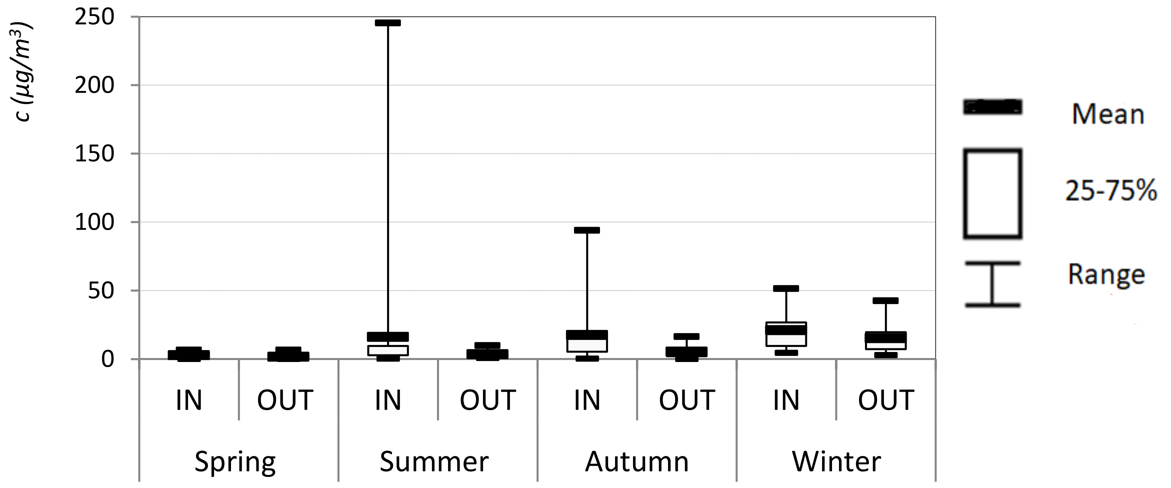

Figure 4-5 – Indoor and outdoor toluene levels during four seasons at 64 dwellings. Note: distribution and medians were statistically different across all seasons (p<0.001)

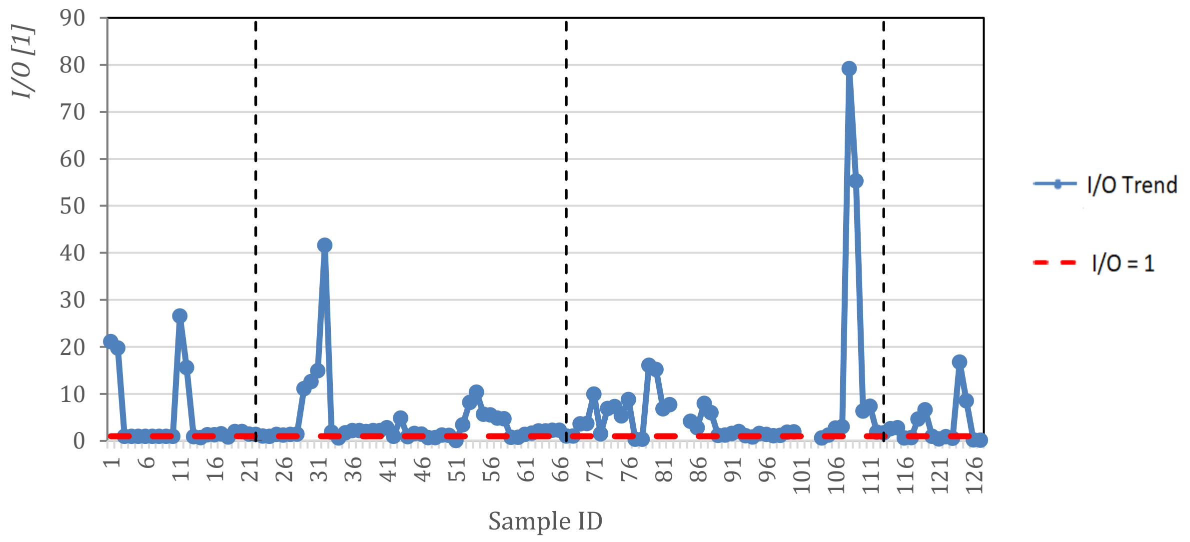

Figure 4-6 – Indoor to outdoor (I/O) ratio of toluene at 64 dwellings of the study. Note: vertical lines represent separation of calendar seasons

4.1.4.4 Trichloroethylene

Trichloroethylene concentrations, presented in Figure 4-7, were the highest during the summer season both for indoors and outdoors (mean of 24.9 and 21.3 μg/m^3, respectively). The lowest levels were registered in the spring (mean of 8.15 μg/m^3) indoors and during winter (mean of 7.18 μg/m^3) outdoors.

The I/O ratio levels for trichloroethylene, shown in Figure 4-8, were, for the most part, close to 1 throughout spring and summer. In autumn some spikes occurred and in winter the obtained ratios were approximately twice as high as in the other seasons, reaching I/O values up to 8.85.

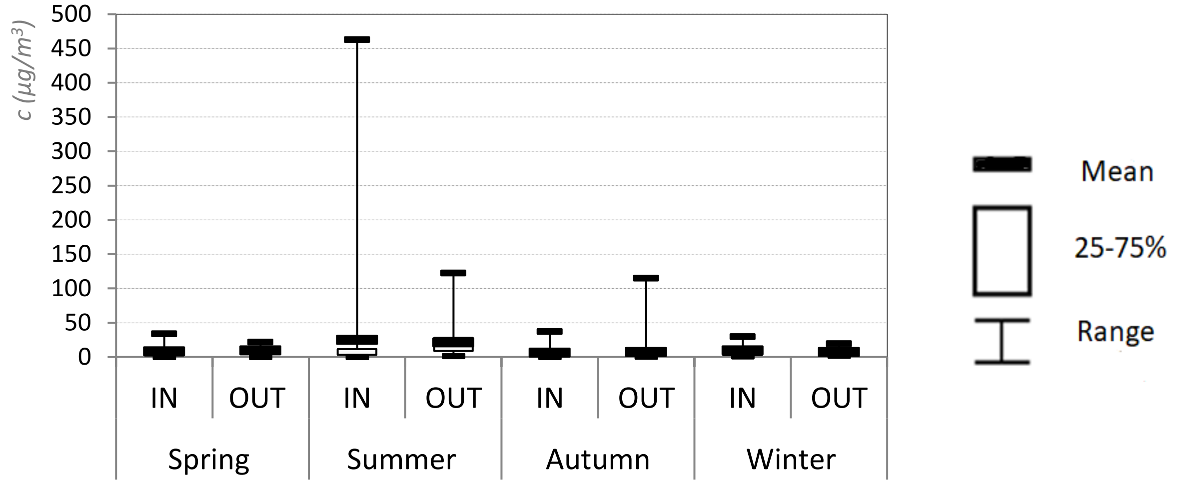

Figure 4-7 – Indoor and outdoor trichloroethylene levels during four seasons at 64 dwellings

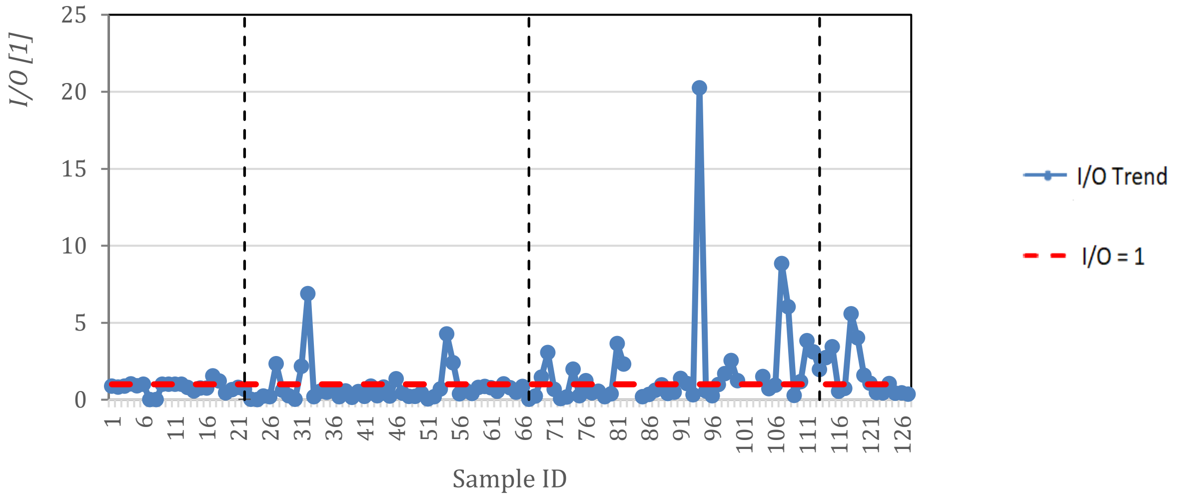

Figure 4-8 – Indoor to outdoor (I/O) ratio of trichloroethylene at 64 dwellings of the study. Note: vertical lines represent separation of calendar seasons

4.1.4.5 Tetrachloroethylene

The evaluation of tetrachloroethylene during the four seasons is shown in Figure 4-9. The results show that the highest levels were registered during the summer (mean of 4.66 µg/m^3) and in winter for outdoor air (mean of 5.07 µg/m^3).

While the I/O ratios exhibited in Figure 4-10 were close to 1 throughout the spring, high values were observed in summer (84), winter (60), and especially autumn (126), which are explained by high indoor concentrations and low corresponding outdoor concentrations in some households during those seasons.

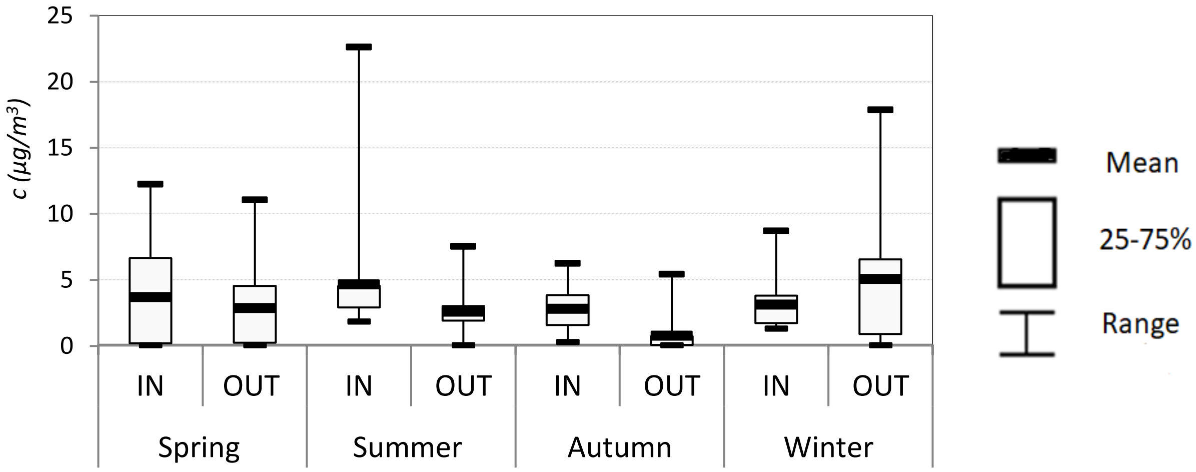

Figure 4-9 – Indoor and outdoor tetrachloroethylene levels during four seasons at 64 dwellings. Note: distribution was statistically different across all seasons ($p<0.009$)

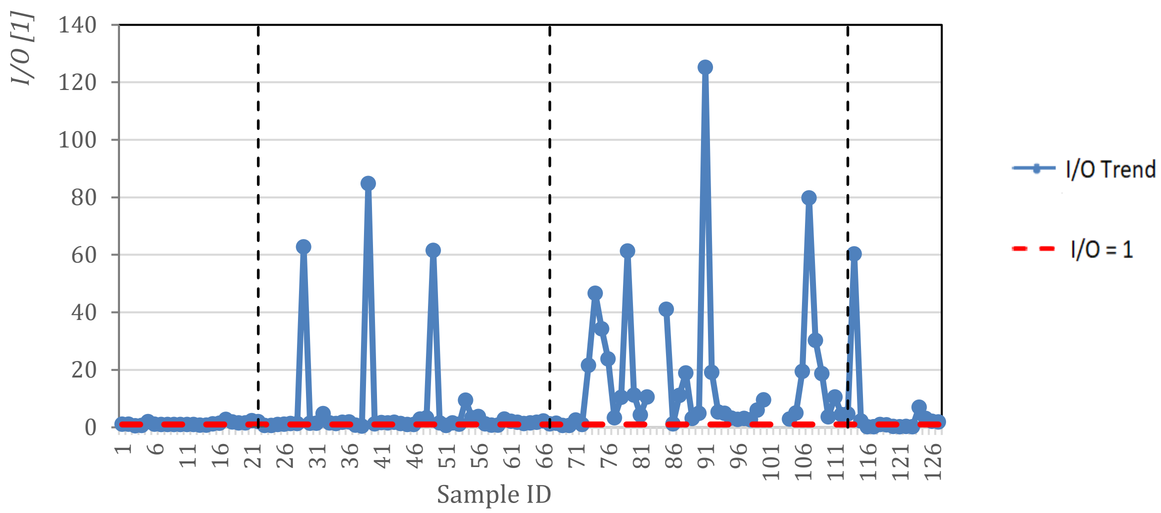

Figure 4-10 – Indoor to outdoor (I/O) ratio of tetrachloroethylene at 64 dwellings of the study. Note: vertical lines represent separation of calendar seasons

4.1.4.6 Pinene

The indoor levels of pinene were at least 5 times greater than the correspondent mean outdoor ones during all four seasons, as presented in Figure 4-11, with the highest mean values found in the summer for indoors (47.5 µg/m^3) and winter for outdoors (7.40 µg/m^3).

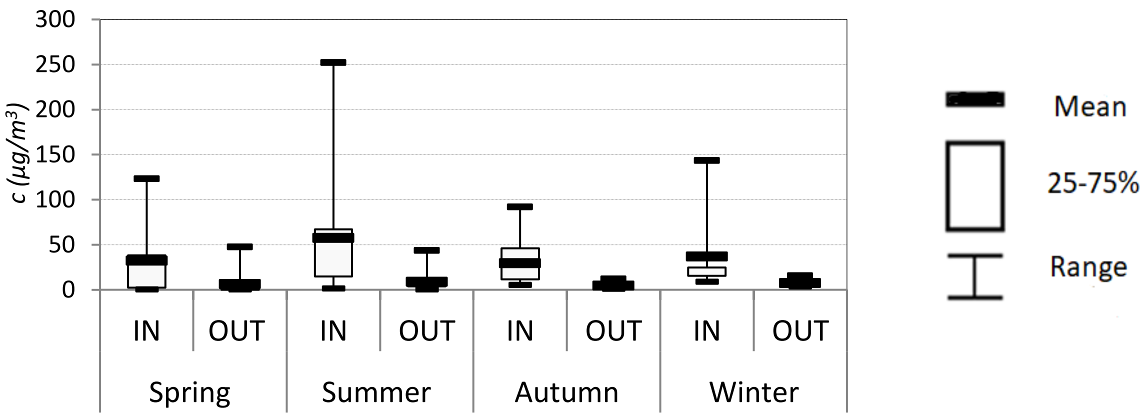

Figure 4-11 – Indoor and outdoor pinene levels during four seasons at 64 dwellings

Figure 4-12 shows extremely high indoor vs outdoor I/O values in spring and the beginning of summer, with maximum values of 550. The aromatic properties of α-pinene have led to its widespread use as fragrances (*Waidyanatha et al., 2021*) and the main human exposure occurs in a wide variety of personal care products (e.g., shampoos, body lotions, drugs, and natural health products), but also air fresheners, and household cleaners (*Nazaroff and Singer*, *2004*). In autumn and winter, the I/O ratio reached lower values, regularly being close to 1.

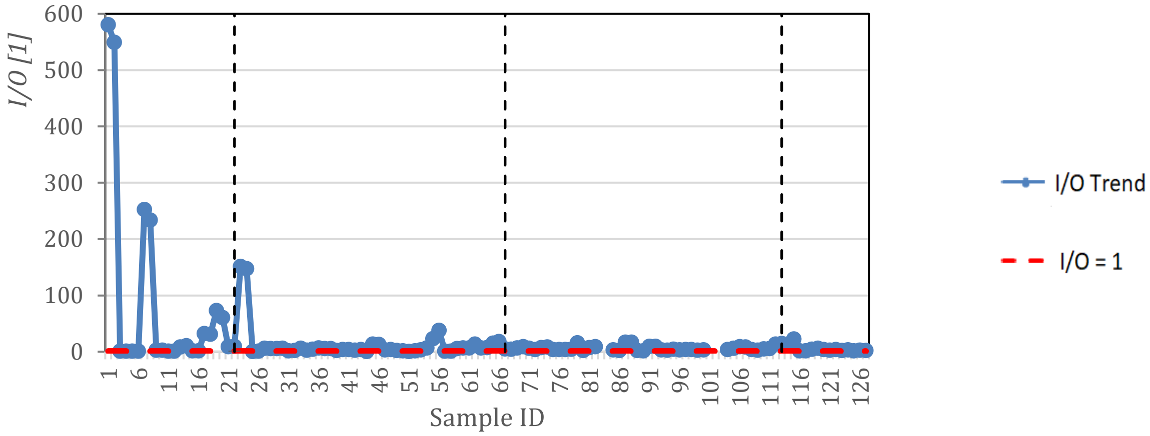

Figure 4-12 – Indoor to outdoor (I/O) ratio of pinene at 64 dwellings of the study. Note: vertical lines represent separation of calendar seasons

4.1.4.7 Limonene

The highest obtained indoor mean value of limonene (66.0 µg/m^3) was observed in spring, whereas the lowest one (14.1 µg/m^3) occurred in summer. In all seasons the indoor levels of limonene were at least 4 times higher than outdoors. Outdoor levels reached their maximum in spring (mean 14.3 µg/m^3) and the lowest in autumn (mean 2.59 µg/m^3). The values are represented in Figure 4-13.

The I/O ratio analysis, in Figure 4-14, showed high values during autumn and winter, ranging from 100 to over 1 800.

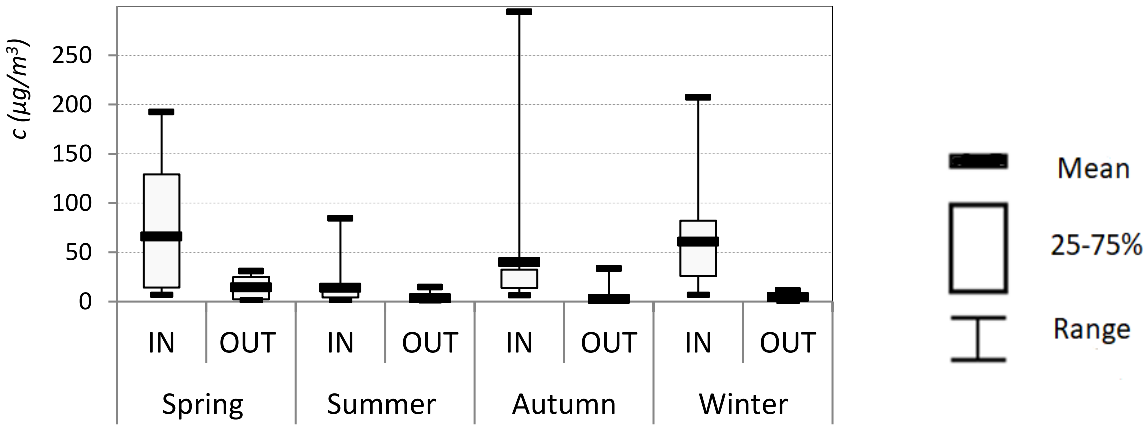

Figure 4-13 – Indoor and outdoor limonene levels during four seasons at 64 dwellings. Note: distribution and medians were statistically different across all seasons ($p<0.001$)

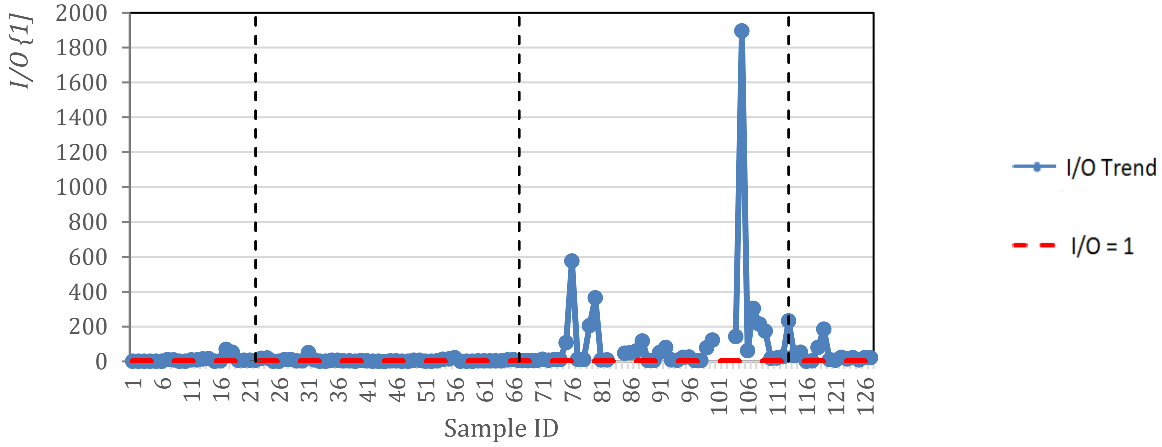

Figure 4-14 – Indoor to outdoor (I/O) ratio of limonene at 64 dwellings of the study. Note: vertical lines represent separation of calendar seasons

4.1.4.8 Xylenes

The indoor concentration of xylenes continuously increased throughout the year (Figure 4-15), with the highest mean registered indoors in winter (21.7 μg/m^3). The outdoor levels were also the highest in winter with mean concentration of 7.40 μg/m^3. Throughout the season, indoor mean levels ranged from twice to 4.5 times higher than the corresponding outdoor ones.

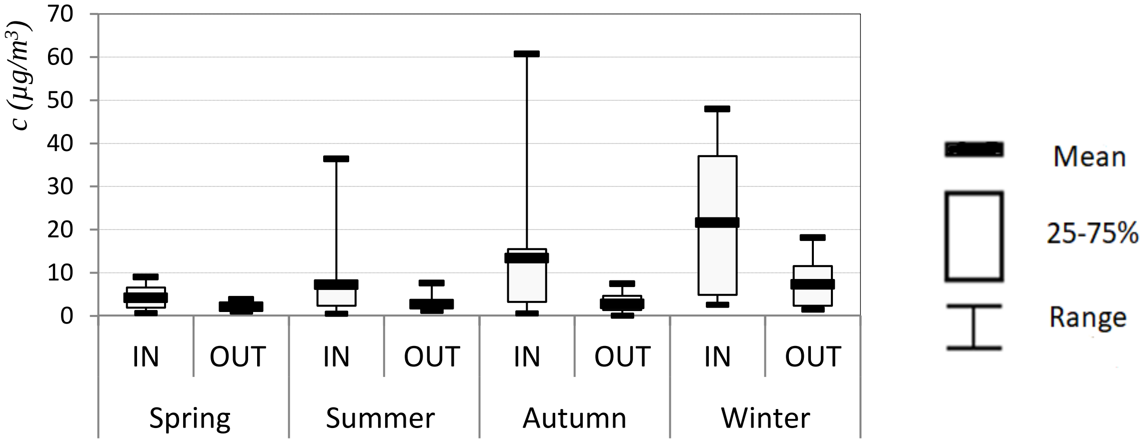

Figure 4-15 – Indoor and outdoor xylenes levels during four seasons at 64 dwellings. Note: distribution and medians were statistically different across all seasons (p<0.042)

The I/O ratio (Figure 4-16) throughout the year ranged from 2 to over 50, with one autumn maxima of 60 times higher indoor value than the corresponding outdoor concentration. Only in 13% of homes were I/O values lower than 1, with the majority coming in summer.

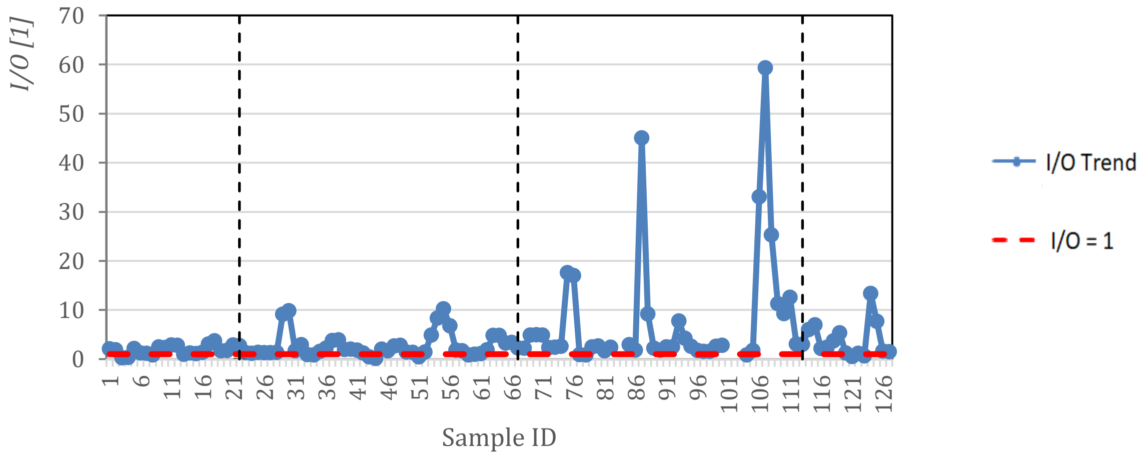

Figure 4-16 – Indoor to outdoor (I/O) ratio of xylenes at 64 dwellings of the study. Note: vertical lines represent separation of calendar seasons

4.1.4.9 VOC composition profiles

The contribution of total VOCs' content was determined using the seven target VOCs. The overall VOC composition was calculated excluding homes where the sum of the concentrations of all seven individual compounds was greater than the registered correspondent TVOCs concentration (which occurred due to the analytical methodology described in section 3.5 that calculates TVOCs concentrations and target VOCs concentrations differently). Consequently, the data set was reduced to 44 homes for indoor assessments (homes not included: 5 in spring, 15 in summer, and 2 in autumn) and 32 homes for outdoors (not considered: 7 in spring, 19 in summer, 5 in autumn, and 1 in winter). Table C-1 from Appendix C presents the summary of the indoor VOC profiles and the percentage of each VOC per season.

Figure 4-17 summarizes the TVOC profiles (in percentages), considering the seven individual compounds during four seasons in indoor air. The seven VOCs accounted for 55% (range 44-68% in winter and summer respectively) of TVOCs overall, thus 45% of TVOCs composition being not entirely characterized. This proportion accounts for other VOC species that were not identified. The seasonal trend demonstrated that limonene (17%) and pinene (16%) exhibited the biggest contribution to TVOC. Furthermore, pinene and limonene were the most abundant VOCs throughout all seasons, accounting, respectively, for 9.5% and 15% of TVOCs (in winter), and 23% (pinene in summer) and 26% (limonene in spring). Benzene had the lowest percentage (1.6–2.7% of TVOCs) in spring and summer, while tetrachloroethylene was the least abundant VOC in indoor air during colder seasons (1.1–1.6% in winter and autumn).

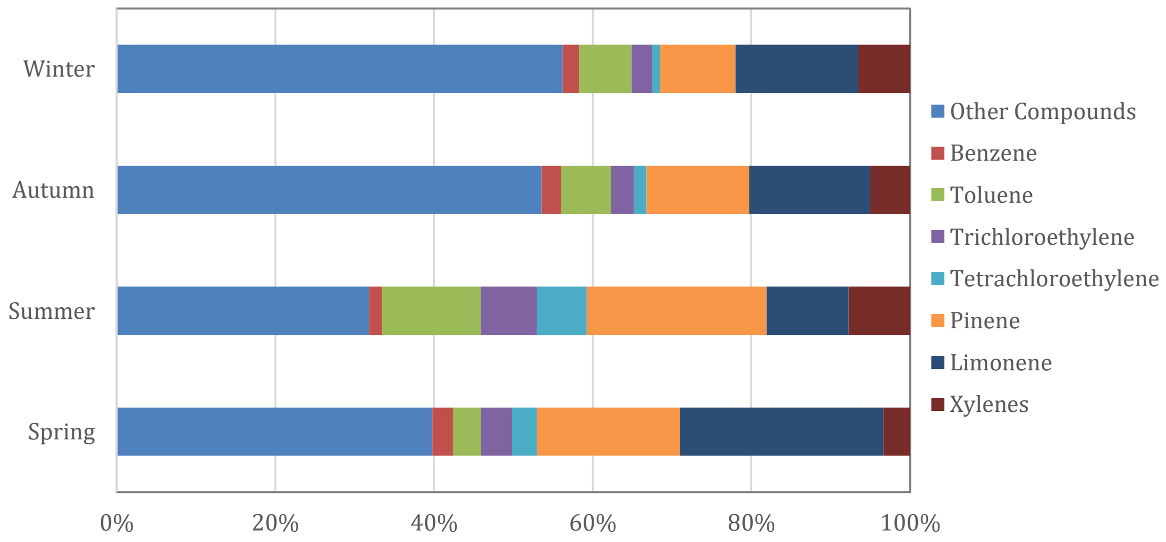

Figure 4-17 – TVOCs composition profiles in indoor air of homes during different seasons

The composition profile of outdoor air of the homes is presented in Figure 4-18. The obtained data shows that seven target VOCs contributed 65 % (range 55-72% throughout the year) of TVOCs. It is necessary to point out that the contribution of outdoor VOCs to outdoor TVOCs was higher than indoor VOCs to indoor TVOCS, the actual respective TVOCs concentration in outdoor air was much lower than indoors (5 times lower). Considering each season, trichloroethylene and pinene were the most abundant VOCs: 8.6–18 % and 8.8–16% in winter and summer, respectively. Similarly, for indoor air, benzene was the least abundant VOC in outdoor air during spring and summer (1.6–5.0%), with the lowest contribution in autumn and winter being observed for tetrachloroethylene, accounting for 1.6 and 5.7% of TVOCs, respectively. Finally, xylene showed a specific annual trend and was the only VOC whose abundance gradually increased throughout all seasons (5.4% in summer versus 8.7% in winter). However, it is necessary to point out that all the obtained results have to be carefully implied, as only seven individual VOCs were quantified. (Summary of the outdoor VOC profiles is detailed in Table C-2 from Appendix C).

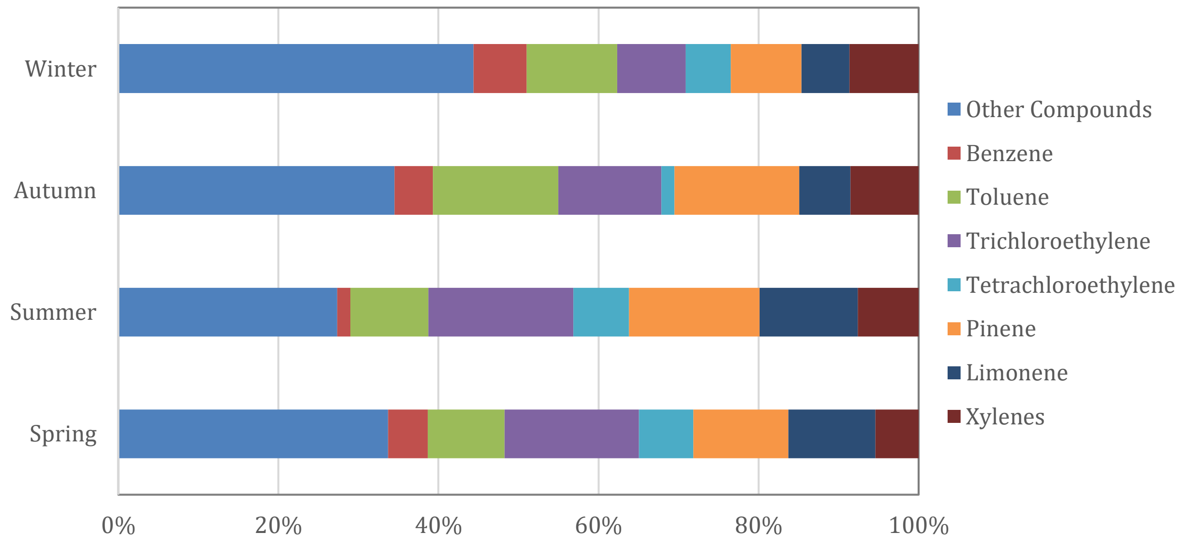

Figure 4-18 – TVOCs composition profiles in outdoor air of homes during different seasons

4.2 Health risk assessment

4.2.1 Carcinogenic risk

For readers' convenience the specific ECs (total and for each compound) throughout the study (based on equation (2)) are detailed in Table D-1 of Appendix D. (The detailed data of estimated cancer risks for VOCs in outdoor air is also presented in Tables D-2 and D-3 of Appendix D). The results obtained for the two other scenarios previously described (LOQ/2 and minimum concentration of a VOC) are also presented in Figures D-1 and D-2 of Appendix D.

Cancer risks (total and for each compound) in indoor air are summarised in Table 4-6. The risk assessment included two separate considerations. In the first step, CR was estimated only for the compounds (benzene, trichloroethylene, and tetrachloroethylene) for which IUR values are specifically reported by USEPA IRIS (*USEPA, 2022*). The second scenario also incorporated estimations for the other compounds, namely toluene, pinene, limonene, and xylenes, for which the required parameter was obtained via CTV Predictor. The USEPA sets a risk level of 10^{-6} for carcinogenic individual compounds and pathways with the understanding that it will generally cause negligible cancer risks. However, caution is recommended to ensure that cumulative cancer risks of all potential carcinogenic components do not have residual cancer risk exceeding the threshold established as 10^{-4} (*USEPA, 1989*). The obtained results, in represented by Figures 4-19a and 4-19b, showed that the CR of tetrachloroethylene was below the threshold of 10^{-6}, whereas benzene and trichloroethylene regularly exceeded (18 and 29 times, respectively) the threshold. Total CR (i.e., the sum of all the three compounds) was about 50 times higher than 10^{-6}, but well below the cumulative threshold of 10^{-4}. However, if other VOCs were incorporated into risk analysis (Figure 4-19b), the respective total CR increased, being 300 times higher than the protective threshold of the cumulative exposure. These results emphasize the importance of the risk assessment for the co-exposures to different compounds. It is noteworthy that based on the CTV Predictor scenario, cancer risks of toluene, pinene, limonene, and xylenes exceeded the established individual threshold in every single measurement, therefore indicating potential health effects for the respective occupants.

Considering all seven VOCs, the seasonal trends, represented in Figure 4-19 and Figure 4-20, demonstrated that total CR risks exceeded (220–370 times) the cumulative threshold of 10^{-4} during all four seasons. The lower total risk was observed in summer, most likely due to overall lower concentrations of the compounds, while colder months (winter and autumn) resulted in twice greater indoor total CR. Furthermore, it shall be clarified that among the seven target VOCs, the highest risks were due to exposure to limonene (the most abundant indoor VOC) in all seasons (range: $0.411–2.45\times10^{-2}$) except for summer, when the highest CR were observed for pinene ($CR=1.37\times10^{-2}$), resulting from both high indoor concentrations and high values of the IUR parameter.

4.2.2 Non carcinogenic risk

The non-cancer risk of VOCs in indoor air are summarized in Table 4-7, once again considering both the scenarios: with parameters from USEPA IRIS and evaluations of all seven compounds with missing parameters obtained by CTV predictor. HI was classified into three categories HI >1, 0.1<HI≤1, and HI≤0.1. The same classification was done for HQ. The results showed that trichloroethylene, pinene, and limonene exhibited mean values of HQ>1. Due to the high HQ of these compounds, total non-cancer risks (HI=ΣHQ) always exceeded the unity. When all seven compounds were considered, the estimated HI was 8.76 and the order of individual HQ was ranked: limonene > trichloroethylene > pinene > benzene > xylene > tetrachloroethylene > toluene.

The seasonal profiles of HQ in indoor air are presented in Figure 4-21. The highest HQ values originated during summer, spring and winter from trichloroethylene and in autumn from limonene. The lowest HQ value originated from toluene in every season. Though in general, outdoor VOCs were significantly lower than indoors, the main findings were similar (as shown in Figure D-1 of Appendix D). Firstly, the obtained results showed outdoor total HI>1 in both situations, indicating there may be concern for potential non-cancer effects. Secondly, when all seven VOCs were considered, the order of HQ was similar to indoor air risk analysis: trichloroethylene (HQ>1) > limonene > trichloroethylene > pinene > benzene > tetrachloroethylene > xylene > toluene. The detailed data of estimated non carcinogenic risk for VOCs in outdoor is presented in Table D-4 of Appendix D. The results obtained for the two other scenarios previously described (LOQ/2 and minimum concentration of a VOC) are presented in Figure D-3 of Appendix D

Table 4-6 - Cancer risk (CR) for each VOC and cumulative exposure risk in indoor air throughout the period of the study

	Benzene [a]	**Toluene [b]**	**Trichloro-ethylene [a]**	**Tetrachloro-ethylene [a]**	**Pinene [b]**	**Limonene [b]**	**Xylenes [b]**	**Total CR (USEPA IRIS)**	**Total CR (USEPA IRIS + CTV)**
Spring	1.88×10^{-5}	5.06×10^{-4}	1.90×10^{-5}	5.43×10^{-7}	7.66×10^{-3}	1.94×10^{-2}	8.44×10^{-4}	3.83×10^{-5}	2.84×10^{-2}
Summer	5.54×10^{-6}	2.89×10^{-3}	5.79×10^{-5}	6.87×10^{-7}	1.37×10^{-2}	4.14×10^{-3}	1.44×10^{-3}	6.41×10^{-5}	2.23×10^{-2}
Autumn	2.11×10^{-5}	3.15×10^{-3}	1.45×10^{-5}	4.15×10^{-7}	7.02×10^{-3}	2.45×10^{-2}	2.67×10^{-3}	3.61×10^{-5}	3.74×10^{-2}
Winter	2.74×10^{-5}	3.75×10^{-3}	2.26×10^{-5}	4.63×10^{-7}	8.80×10^{-3}	1.78×10^{-2}	4.28×10^{-3}	5.04×10^{-5}	3.47×10^{-2}
Total	1.82×10^{-5}	2.57×10^{-3}	2.85×10^{-5}	5.27×10^{-7}	9.30×10^{-3}	1.65×10^{-2}	2.31×10^{-3}	4.72×10^{-5}	3.07×10^{-2}

Note: a - estimates based on parameters from USEPA IRIS database; b - estimates based on parameters from CTV predictor

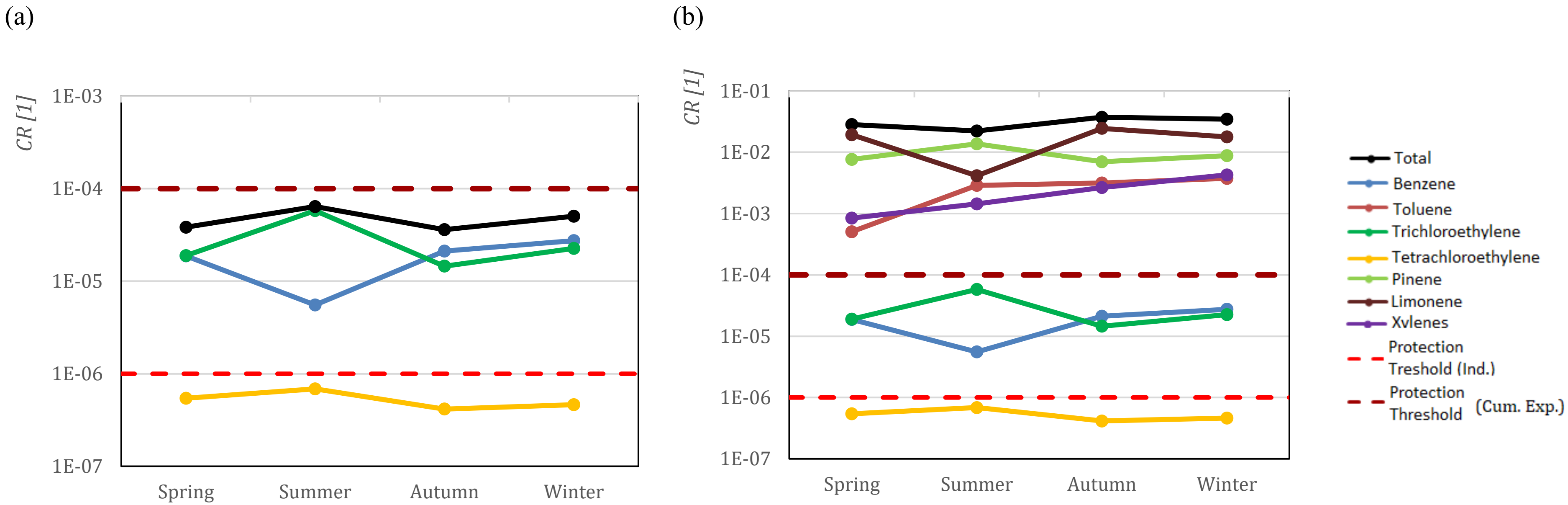

Figure 4-19 – Cancer risks (CR) for target VOCs in indoor air of 64 dwellings throughout four seasons; (a) estimation based on USEPA IRIS parameters; (b) estimation based on USEPA IRIS and CTV Predictor parameters

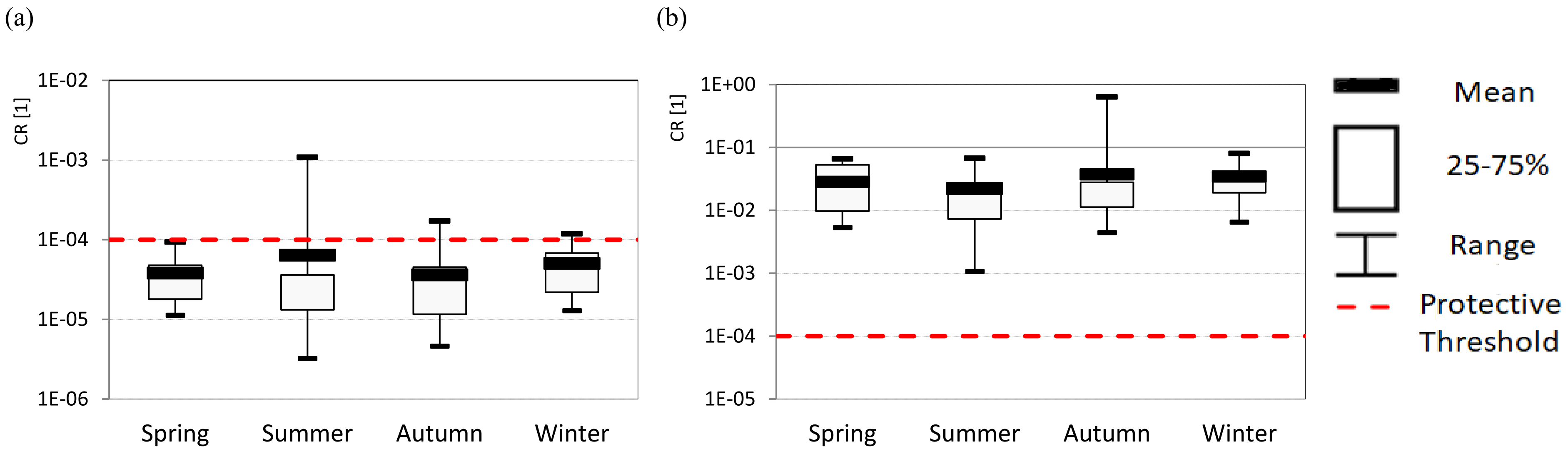

Figure 4-20 – Total cancer risk (total CR) in indoor air of 64 dwellings; (a) estimation based in USEPA IRIS parameters; (b) estimation based on USEPA IRS and CTV Predictor parameters

4.3 Toxicity ranking and prioritization

To further address the possible effects of the studied VOCs, the toxicological prioritization index (ToxPi) score was calculated for each analysed compound. The score calculations and results are relative to all included compounds and their parameter values, creating an overall hierarchy of toxicity, both over all parameters and for each parameter. Table 4-8 summarizes the respective ToxPi scores for the VOCs of the study. The hierarchy determined between the compounds is then presented in Figure 4-22, ranking VOCs in decreasing order of relative toxicity.

According to the prioritization scheme, tetrachloroethylene was characterized as the overall most toxic analysed chemical, being followed by benzene. These two compounds exhibit diverse toxicity profiles. Tetrachloroethylene exhibits large values for each toxicity parameter except for moderate values of RfC and CPV. The high BMD and BMDL values indicate that a low, individual dose of tetrachlorethylene may produce quicker response rates of adverse health effects. Benzene profile was dominated by CPV and NO(A)EL. Limonene, which ranked as the fourth most toxic compound, presented the biggest RfC and IUR, which suggests that continuous inhalation of relatively low amounts can lead to appreciable risks of adverse cancer impacts

Table 4-7 - Estimated non-cancer risk by hazard quotient (HQ) and hazard index (HI=ΣHQ) for VOCs in indoor air of 64 homes)

HQ	**Benzene [a]**	**Toluene [a]**	**Trichloro-ethylene [a]**	**Tetrachloro-ethylene [a]**	**Pinene [b]**	**Limonene [b]**	**Xylenes [a]**	**HI (USEPA IRIS)**	**HI (USEPA IRIS + CTV)**
Spring	8.04×10^{-2}	3.21×10^{-4}	2.31	5.22×10^{-2}	1.29	4.14	2.42×10^{-2}	2.47	7.90
Summer	2.37×10^{-2}	1.84×10^{-3}	7.06	6.60×10^{-2}	2.31	8.84×10^{-1}	4.15×10^{-2}	7.19	10.4
Autumn	9.03×10^{-2}	2.00×10^{-3}	1.77	3.99×10^{-2}	1.18	5.23	7.66×10^{-2}	1.98	8.39
Winter	1.17×10^{-1}	2.38×10^{-3}	2.75	4.45×10^{-2}	1.48	3.81	1.23×10^{-1}	3.04	8.33
Overall	7.79×10^{-2}	1.63×10^{-3}	3.47	5.07×10^{-2}	1.57	3.52	6.64×10^{-2}	3.67	8.76

Note: a - estimates based on parameters from USEPA IRIS database; b – estimates based on parameters from CTV predictor

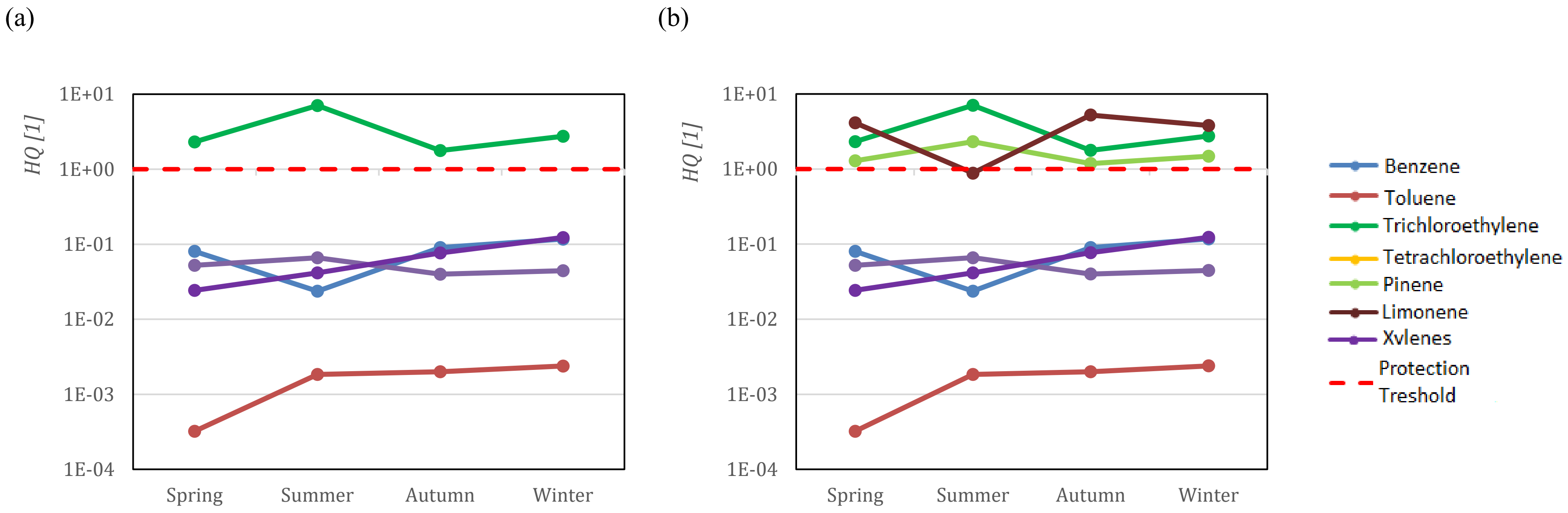

Figure 4-21 – Non cancer risk (HQ) in indoor air of 64 dwellings during four seasons; (a) estimation based on USEPA IRIS parameters; (b) estimation based on USEPA IRIS and CTV Predictor parameters

Table 4-8 – ToxPi values estimated for each parameter, considering each specific VOC

	ToxPi Score	Toxicity Ranking	RfC Score	IUR Score	CPV Score	NO(A)EL Score	BMD Score	BMDL Score
Tetrachloro-ethylene	0.638	1	0.440	0.000	0.453	0.935	1.00	1.00
Benzene	0.555	2	0.467	0.015	1.00	0.885	0.466	0.496
Trichloro-ethylene	0.527	3	0.714	0.007	0.000	1.00	0.594	0.848
Limonene	0.430	4	1.00	1.00	0.059	0.492	0.000	0.029
Pinene	0.430	5	0.960	0.813	0.148	0.505	0.086	0.066
m-Xylene	0.259	6	0.723	0.672	0.119	0.000	0.034	0.119
o-Xylene	0.212	7	0.357	0.691	0.132	0.044	0.050	0.000
Toluene	0.212	8	0.000	0.608	0.136	0.132	0.225	0.171
p-Xylene	0.192	9	0.357	0.641	0.110	0.006	0.032	0.004

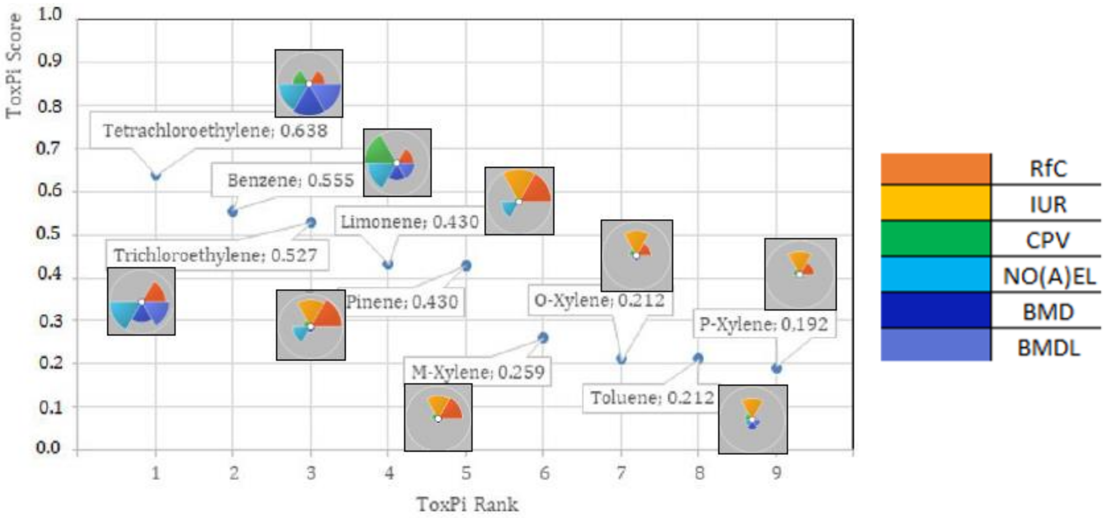

Figure 4-22 – Distribution dot plot of ToxPi scores for seven VOCs. Dots represent individual chemicals. Each compound was analysed using unweighted approach for the data from multiple databases, represented by: no observed adverse effect level (NO(A)EL); cancer potency value (CPV); RfD benchmark dose lower level (BMDL); RfD benchmark dose (BMD); inhalation unit risk (IUR); reference concentration (RfC)

4.4 References

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Zhang C., Luo S., Zhao W., Wang Y., Zhang Q., Qu C., Liu X., Wen X., 2021. Impacts of meteorological factors, VOCs emissions and inter-regional transport on summer ozone pollution in Yuncheng. Atmosphere, 12(12), 1661.

5. Conclusions

Overall, the results obtained in this work showed that across 64 homes indoor TVOCs ranged between 0.050 and 1 617 $\mu g/m^3$ (mean of 217 $\mu g/m^3$), being approximately 5 times higher than the respective levels outdoors. Out of these, 10% of the evaluated homes did not fulfil the Portuguese protective threshold (600 $\mu g/m^3$; set for indoor air quality in public buildings). The majority of the homes (97 %) exhibited I/O ratio higher than one, thus strongly suggesting predominant indoor origin of TVOCs. The large variability of the observed indoor levels was most likely caused by the differences and specificity of indoor emissions sources as well as the seasonal trends. To mitigate VOCs exposures, it is important to identify their major indoor (and outdoor) sources first.

The analysis of non-cancer risk showed a need for potential concerns in the homes, with the total (i.e., sum of 7 VOCs) exceeding the unity. Limonene, pinene, and trichloroethylene exhibited hazard quotient greater than one, with the following order of individual HQ being obtained among the VOCs: limonene > trichloroethylene > pinene > benzene > xylene > tetrachloroethylene > toluene. Regarding the cancer risk, among the target VOCs, trichloroethylene and benzene exceeded (29 and 18 times) the protective USEPA threshold of 10^{-6}. When all seven VOCs were incorporated into cancer risk analysis, the respective total cancer risk increased highly, being 300 times higher than the protective threshold of 10^{-4} for the cumulative exposure. These results showed that when evaluating the possible risks due to exposure to mixtures with many chemicals, which VOCs mixtures are, as many possible individual compounds should be considered.

Finally, among the VOCs compounds considered in this study tetrachloroethylene and benzene were ranked as the overall most toxic chemicals, though their toxicity profiles differed (*Holos et al., 2018*).

While the obtained results showed potential risks due to indoor air pollution in the studied homes, mitigation strategies are needed to help the occupants minimise the respective risks. The most effective way to reduce VOC levels at home is emissions source control (forms of paints, furnishings, selection, use and management of cleaning products, etc.), which requires further knowledge literacy of the occupants. Indoor pollution could be improved with enhanced household ventilation by ensuring cross-ventilation (via windows and doors), although recent evidence suggests that indoor VOCs are attenuated more by time duration than by ventilation (*Holos et al., 2018*). The use of devices, such as portable air cleaners or filters may, to some degree, improve the respective IAQ. Finally, interventions can be adapted to modify and presumably mitigate risks on a personal level, such as reducing obesity, promoting physical activity, smoking cessation and avoidance of second-hand smoke, and different choice of personal care products). Thus, to ensure a safe indoor environment, complex yet individual approaches are required, fully dependent on air pollution levels, the economic viability of the occupants, their knowledge literacy, as well health susceptibilities.

5.1 References

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APPENDIX

A. Checklist for characterization of the 64 homes

The following checklist was directly provided through NeoGene (FCT and FAPESP (FAPESP/19914/2014)).

NEOGENE

Home *Checklist*

I	D				-	C		

General Data Survey

Contacts

Name:

____

Telephone:____________________________E-mail:

____

Address

Street:

____

Postal code:___________________________

City: _______________________________

Responsible:____Date ________________________

I	D				-	C		

A. Building

A.1 Location and Neighbourhood

1. Location

□ Urban □ Suburban □ Rural

Notes: ______________________________

____

2. Nearby air pollution sources (up to 100 m)

□ None	□ Agriculture	□ Landfill, waste disposal
□ Traffic related	□ Animal husbandry	□ Cooling Towers, HVAC
□ Industrial	□ Forested areas	□ Chimneys. Smokestacks
□ Commercial	□ Gas stations	□ Construction works
□ Car parking	□ Garages	□ Others

Notes: ______________________________

____

A.2 Building Type and Construction

3. Typology

□ Single-family house
□ Row housing
□ Apartment block
□ Other: ____

4. Date of original construction:__________________(year)

5. Originally built as a residential building?

□ yes
□ no

6. Has there ever been any refurbishment or retrofitting?

□ yes: **6.1. Date**: ________________________________
6.2. Action: ____

□ no

Notes: ______________________________

B. Dwelling

B.1 General Information

7. Position in building (only in row housing and apartment block)

7.1 Options:

□ A – in contact with unheated attics, flat roof
□ B – surrounded other apartments top/bellow/sides(s)
□ C - in contact with unheated cellars, garages, soil

7.2 Floor identification: □ ground-floor □ 1st floor
□ 2nd floor □ 3rd floor □ other: ________________

8. Did the mother live in the current home during the pregnancy?

□ yes
□ no

8.1 if yes, during how much time:_________________________(years, months)

8.2 Proximity to a garage or car parking

□ none □ next to (within a 10 m radius)
□ above □ under

B.2 Dwelling Construction & Pathologies

9. Has there ever been any refurbishment or retrofitting?

□ yes
□ no

9.1 If yes. When (date): ____

9.2. Where:

□ ceiling facing □ ceiling finish
□ floor facing □ floor finish
□ wall facing □ wall finish
□ false walls/ceilings
□ window frame finish
□ other. ____

10. Is there any observation of biological /biochemical pathology (e.g. mold, fungi, mildew, rot)?

□ yes
□ no

10.1. if yes.: Where: ____

11. Are there any physical pathologies (e.g. cracks, fissures, staining, bubbling, peeling)?

□ yes
□ no

11.1. if yes.: Where: ____

B.3 Dwelling Ventilation and Heating

12. General ventilation
- □ natural
- □ mechanical (if, regularly used)

13. Extraction location
- □ Kitchen
- □ Bathroom, toilet
- □ other

14. Space heating
- □ none
- □ portable appliances
- □ space radiators
- □ radiant floor
- □ air conditioning
- □ other:_______________________________

15. Combustion devices in the home

15.1 Type
- □ fireplace
  - □ open
  - □ close
- □ salamander
- □ portable heater
- □ stove, furnace
- □ other: _________________________________
- □ none

15.2. Location of device
- □ living room
- □ kitchen
- □ other: ____

16. Is the heating system currently used?
- □ yes
- □ no

B.4 Dwelling Use and Occupation

17. Regular number of occupants:______________(adults);__________(children, <18 years)

18. Humidity control and others

- □ none
- □ air cleaners
- □ humidifiers
- □ dehumidifiers
- □ other

19. Is allowed to smoke indoors?

- □ yes
- □ no

19.1- if yes, approx.- number of smokers: ____________________

19.2. Average number of cigarettes/day: _____________________

19.3 Where is "allowed": □ all rooms □ kitchen □ living room □ bedroom □ other: ___________________________

20. Are pets/animals indoors?

- □ yes
- □ no

20.1 if yes:

□ dogs(s) □ cat(s) □ bird(s) □ other: ____________________

20.2. Free roaming or caged?

- □ free roaming
- □ caged

21. Generally, are "air fresheners" used?

□ yes □ no

If yes,

21.1. With combustion: □ candles □ incense □ other

21.2. Without combustion: □ air fresheners

□ passive □ electric plugged

□ sprays

22. Presence of indoor plants?

- □ none
- □ living room 22.1. if yes: number: ________________________
- □ bedroom 22.2. if yes: number: ________________________
- □ other 22.3. if yes: number: ________________________

C. Room

C.1 General Room Information

Floorplan

---

23. Floor area (m^2): ____________________
24. Ceiling height (m): __________________

C.2 Room Construction and Systems Characteristics

25. Ceiling material: ____
26. Wall material: ____
27. Floor material: ____

28. During the past 12 months, has the interior of the room been remodelled, renovated or painted?

- ▯ yes
- ▯ no

28.1. If yes:

When was it remodelled, renovated or painted (the last time): __________________

28.2 What was remodelled, renovated or painted?

- ▯ ceiling
- ▯ walls
- ▯ floors
- ▯ metals pipes / radiators
- ▯ others

28.3. What kind of refurbishment /renovation or painting material was used?

- ▯ wall paper
- ▯ water-soluble paint ▯ water-resistant (synthetic) paint
- ▯ varnish
- ▯ wood panels
- ▯ others: ____

29. During the past 3 months, has the interior of the room been remodelled, renovated or painted?

- ▯ yes
- ▯ no

29.1. If yes:

When was it remodelled, renovated or painted (the last time): __________________

29.2 What was remodelled, renovated or painted?

- □ ceiling
- □ walls
- □ floors
- □ metals pipes / radiators
- □ others

29.3. What kind of refurbishment /renovation or painting material was used?

- □ wall paper
- □ water-soluble paint   □ water-resistant (synthetic) paint
- □ varnish
- □ wood panels
- □ others: ____

30. During the past 12 months, has new furniture (e.g. cough, sofa, bed, baby crib, rugs, ..) been installed in the room?

- □ yes
- □ no

30.1. The new furniture is made of:

- □ wood natural /painted / varnished
- □ particle boards natural /painted / varnished
- □ other

31. Room fenestration

31.1. area (m^2): ____________________

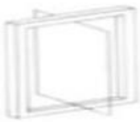
31.2 orientation: ____________________

32. Type of window and opening frequency

□ fixed   □ single-hung   □ double-hung   □ concertina   □ sliding

Frequency	fixed	single-hung	double-hung	concertina	Sliding
Never	□	□	□	□	□
Rarely	□	□	□	□	□
Occasionally	□	□	□	□	□
Regularly	□	□	□	□	□
Constantly	□	□	□	□	□

□ pivot □ tilting □ awning □ hopper □ casement





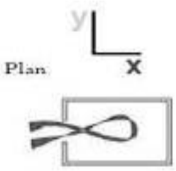
Frequency	pivot	Tilting	awning	hopper	Casement
Never	□	□	□	□	□
Rarely	□	□	□	□	□
Occasionally	□	□	□	□	□
Regularly	□	□	□	□	□
Constantly	□	□	□	□	□

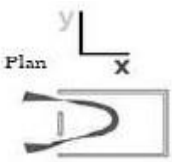
33. Windows characteristics

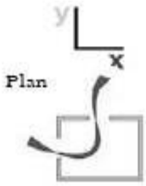
	Framing	**Type of glass**
Exterior window	□ wood □ aluminium □ other	□ single □ double
Interior window	□ wood □ aluminium □ other	□ single □ double.

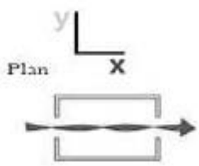
34. Air circulation typologies

□ single window □ single-sided □ adjacent walls □ cross-ventilation









35. Heating appliance type: ____________________________

35.1. Heating appliance on/off:

- □ on
- □ off
- □ intermittent

C.3 Room Construction Pathologies

36. Is there any observation of biological/biochemical pathology (e.g. fungi, mold, mildew, rot)?
- yes
- no

36.1. if yes, where is it present?
- walls
- ceiling
- other: ____________________________________

37. Are there any physical pathologies (e.g. cracks, fissures, staining, bubbling, peeling)?
- yes
- no

37.1. if yes, where is it present?
- walls
- ceiling
- other: ____________________________________

C.4 Room Use and Occupation

38. Regular number of occupants: ______________________

39. Textiles in the room
- none
- stuffed toys
- rugs, carpets
- cushions
- curtains
- other, ____

40. Equipments
- TV
- computer
- printer
- radio
- humidifier
- dehumidifier
- other: __________________________
- none

C.5 Cleaning Operations/Agents

41. Are the windows open during the cleaning of the rooms?

□ yes
□ no

42. Type of cleaning products used:

□ bleach or detergent with bleach
□ detergent with ammonia
□ detergent without bleach
□ detergent without ammonia
□ water
□ other

43. Cleaning activities

		Morning	Afternoon	Frequency						Date of last cleaning
				Daily	2-3 times per week	Once a week	2-3 times a month	Once a month	< than once a month	
Floors/carpets	Swept	□	□	□	□	□	□	□	□	
	Vacuumed	□	□	□	□	□	□	□	□	
Smooth floors	Washed	□	□	□	□	□	□	□	□	
	Waxed	□	□	□	□	□	□	□	□	
	Polished	□	□	□	□	□	□	□	□	
Surfaces	Dusted	□	□	□	□	□	□	□	□	
	Polished	□	□	□	□	□	□	□	□	
	Cleaned	□	□	□	□	□	□	□	□	
Curtains washed		□	□	□	□	□	□	□	□	
Windows washed		□	□	□	□	□	□	□	□	
Others		□	□	□	□	□	□	□	□	

**********************END OF CHECKLIST****************

Table A-1 – Characteristics of the studied households (N=64)

Building characteristics	**N**	**%**
Construction (years)		
Mean ± SD (min-max)	27 ± 20 (1-84)	
Building location		
Urban area	58	91
Rural area	6	9
Near of source of outdoor air pollution		
Busy road (car/parking/highway)	44	69
Industry	7	11
Forested areas	11	17
Construction works	2	3
Type of building		
Single-family home	17	27
Row housing	8	12
Apartment	39	61
Ground-floor	5	13
1st floor	8	20
2nd floor	9	23
3rd floor	10	26
>4th floor	7	18
Dwelling characteristics	**N**	**(%)**
Number of occupants		
Mean ± SD (min-max)	4 ± 1 (3-6)	
1-4	29	45
4-6	35	55
Renovation/decoration		
No	25	38
Yes	39	57
>12 months	22	56
12-3 months	10	26
<3 months	4	10
Unknown	3	8
Heating system		
No	58	91
Yes	6	9
Smokers	37	58
Non-Smokers	27	42
Presence of humidifier		
No	53	83
Yes	11	17
Use of air fresheners (frequently/often)		
No	21	33
Yes	43	67
With combustion	11	26
Without combustion	18	42
Both (with/without combustion)	14	32
Domestic pets (with fur)		
No	37	58
Yes	27	42

SD: standard deviation; Min: minimum; Max: maximum

Table A-1 – Characteristics of the studied households (N=64) (continued)

Room characteristics	**N**	**%**
Living room	47	73
Bedroom	16	25
Kitchen	1	2
Volume (m^3)		
Mean ± SD (min-max)	60 ± 36 (20-175)	
0-50	22	34
51-100	20	31
101-150	1	2
151-200	3	5
Unknown	18	28
Floor area (m^2)		
Mean ± SD (min-max)	22 ± 14 (7-68)	
0-15	23	36
16-30	22	34
31-45	7	11
46-60	3	5
61-75	2	3
Unknown	7	11
Type of floor material		
Parquet	20	31
Wood/cork	19	30
Other	25	39
Type of window		
Sliding	52	81
Casement	7	11
Hopper	2	3
Other	3	5
Window framing		
Wood	7	11
Aluminium	50	78
Other	7	11
Type of glass		
Single	31	48
Double	33	52
Window opening frequency		
Rarely	4	6
Occasionally	10	16
Regularly	31	48
Constantly	19	30
Presence of stuffed toys		
No	42	66
Yes	22	34
Presence of rugs, carpets		
No	14	22
Yes	50	78
Presence of curtains		
No	12	19
Yes	52	81

SD: standard deviation; Min: minimum; Max: maximum

Table A-1 – Characteristics of the studied households (N=64) (continued)

Room characteristics	**N**	**%**
Cleaning procedures		
Sweeping	3	5
Vacuuming	8	12
Vacuuming + washed	44	69
Sweeping + washed	9	14

B. Detailed information of VOC concentrations in the 64 homes

Table B-1 – VOC concentrations (μg/m³) in indoor and outdoor air of 64 homes sampled in this study

Sampling date	Location	TVOCs	Benzene	Toluene	Trichloro-ethylene	Tetrachloro-ethylene	Pinene	Limonene	Xylenes
14/05/2018	Indoors	143	8.40	3.17	11.2	6.74	87.1	29.9	5.00
	Indoors	118	8.14	2.97	10.7	5.85	82.4	28.6	4.69
	Outdoors	22.7	3.23	-2.71	12.9	5.67	0.00	17.8	2.40
	Outdoors	20.7	3.21	-2.71	13.1	4.9	0.00	17.9	2.50
19/05/2018	Indoors	-8.97	3.80	-4.54	11.5	6.24	0.00	17.4	0.664
	Indoors	-18.3	4.02	-4.58	11.5	7.11	0.00	17.6	0.923
	Outdoors	154	5.23	-2.00	13.0	11.1	0.00	25.8	2.61
	Outdoors	185	5.26	-2.03	11.2	10.5	0.00	27.7	2.81
23/05/2018	Indoors	214	5.04	-1.49	11.1	12.2	0.00	42.5	5.01
	Indoors	106	4.03	-2.19	11.3	7.26	0.00	40.4	2.83
	Outdoors	53.0	3.45	-3.10	12.2	5.86	0.00	30.5	2.37
	Outdoors	51.7	3.36	-3.36	11.2	6.02	0.00	29.1	2.36
28/05/2018	Indoors	165	3.09	-4.13	0.00	0.00	37.9	192	1.84
	Indoors	155	3.31	-4.67	0.00	0.00	35.0	183	1.41
	Outdoors	23.9	3.24	-4.71	12.6	0.00	0.00	20.0	1.61
	Outdoors	30.2	3.41	-4.22	12.0	0.00	0.00	20.6	1.70
02/06/2018	Indoors	290	4.59	-1.06	10.6	0.00	123	55.8	9.07
	Indoors	320	4.51	-1.10	10.7	0.00	123	64.1	8.91
	Outdoors	92.2	3.39	-3.64	10.5	0.00	46.9	28.6	3.67
	Outdoors	150	3.40	-3.49	10.8	0.00	47.6	30.8	3.85
04/06/2018	Indoors	291	13.3	4.00	0.00	0.00	0.00	187	7.36
	Indoors	271	10.9	2.34	0.00	0.00	0.00	178	5.94
	Outdoors	26.6	4.02	-2.18	0.00	0.00	0.00	22.7	2.58
	Outdoors	26.9	3.64	-3.24	0.00	0.00	0.00	22.5	2.11
06/06/2018	Indoors	48.8	1.37	2.20	15.4	0.716	10.5	18.0	1.09
	Indoors	58.3	1.44	1.97	8.92	0.709	13.2	20.1	1.28
	Outdoors	17.6	1.39	2.29	19.2	0.915	1.23	1.35	1.10
	Outdoors	17.4	1.40	2.57	15.8	0.856	1.21	1.21	1.03
09/06/2018	Indoors	80.6	1.65	5.49	3.14	1.86	31.6	6.78	2.14
	Indoors	90.4	1.65	5.67	2.66	1.95	32.6	7.01	2.68
	Outdoors	49.2	1.53	4.12	4.16	1.45	17.6	3.15	1.99
	Outdoors	52.0	1.51	4.10	3.57	1.33	18.0	3.05	1.95
11/06/2018	Indoors	205	3.18	6.14	33.8	6.35	40.5	163	6.87
	Indoors	186	2.23	5.77	11.2	4.29	38.4	151	8.37
	Outdoors	28.6	1.84	3.88	22.0	2.21	1.25	2.34	2.23

	Outdoors	30.8	1.83	6.71	9.29	2.19	1.23	2.88	2.27
16/06/2018	Indoors	55.1	1.39	4.67	2.01	2.63	10.9	12.4	2.51
	Indoors	54.1	1.36	4.53	2.47	2.78	9.13	11.7	2.38
	Outdoors	17.4	1.22	2.28	4.65	1.68	0.00	1.70	1.48
	Outdoors	14.6	1.21	2.22	3.82	1.72	0.00	1.68	1.35
25/06/2018	Indoors	122	3.17	6.64	5.13	7.15	14.63	12.7	6.51
	Indoors	137	3.12	6.42	5.45	6.93	15.40	13.3	6.60
	Outdoors	28.8	2.16	4.39	6.52	2.98	1.64	2.13	2.29
	Outdoors	32.2	2.13	4.51	8.17	3.40	1.62	1.99	2.43
02/07/2018	Indoors	69.8	2.34	2.96	0.00	1.95	22.7	41.2	1.91
	Indoors	67.9	2.30	2.86	0.00	1.94	22.1	40.2	1.87
	Outdoors	16.4	2.01	2.80	4.96	2.73	0.00	2.44	1.47
	Outdoors	16.6	1.88	2.79	13.4	2.62	0.00	2.15	1.66
16/07/2018	Indoors	35.1	1.35	6.04	0.998	2.58	3.49	1.99	3.66
	Indoors	33.7	1.44	5.49	0.965	2.52	4.65	1.94	3.37
	Outdoors	25.1	1.18	4.34	4.41	2.49	5.38	1.76	2.72
	Outdoors	15.8	1.10	4.25	5.07	2.17	4.52	1.70	2.66
18/07/2018	Indoors	37.2	0.595	1.29	6.86	2.63	16.2	19.5	1.51
	Indoors	36.7	0.591	1.30	5.89	2.65	15.5	19.1	1.59
	Outdoors	4.54	0.661	0.89	2.93	1.92	2.76	1.74	1.15
	Outdoors	7.80	0.665	0.86	9.89	1.95	2.95	1.70	1.18
23/07/2018	Indoors	93.8	1.26	21.5	0.849	3.14	20.73	3.88	16.9
	Indoors	87.9	1.44	22.0	0.850	3.58	20.8	3.83	16.5
	Outdoors	8.9	0.61	1.93	3.34	0.00	3.88	1.67	1.86
	Outdoors	17.0	0.607	1.74	28.5	2.32	3.53	1.66	1.68
25/07/2018	Indoors	384	0.746	140	265	2.22	2.71	84.5	2.70
	Indoors	711	0.992	245	463	3.87	4.04	8.57	3.43
	Outdoors	73.9	0.390	9.34	123	1.49	2.14	1.68	1.60
	Outdoors	43.0	0.237	5.89	67.3	0.799	1.69	0.983	1.19
26/07/2018	Indoors	42.06	0.667	6.45	1.68	4.08	15.8	3.10	2.41
	Indoors	32.4	0.657	2.36	8.01	3.46	13.2	2.71	2.27
	Outdoors	17.3	0.718	3.35	8.83	2.47	2.51	1.71	2.62
	Outdoors	20.4	0.691	3.57	14.5	2.5	4.76	1.75	2.75
28/07/2018	Indoors	48.0	0.346	2.69	6.10	4.47	17.1	12.1	2.14
	Indoors	56.4	0.351	3.31	5.87	4.73	19.9	11.2	3.01
	Outdoors	12.5	0.203	1.53	12.5	2.47	4.10	1.85	1.39
	Outdoors	12.7	0.204	1.48	8.90	2.38	2.89	1.83	1.37
01/08/2018	Indoors	113	0.456	6.69	9.914	2.62	240	9.33	7.57
	Indoors	115	0.363	6.03	31.8	2.78	252	9.20	6.98
	Outdoors	44.5	0.285	2.98	54.8	3.31	42.7	3.65	2.02
	Outdoors	45.0	0.293	3.02	57.4	6.21	43.6	3.36	1.78
06/08/2018	Indoors	86.2	0.334	7.32	4.61	4.24	29.3	3.62	5.23
	Indoors	86.0	0.279	7.02	22.85	4.06	48.8	20.7	5.05

	Outdoors	39.1	0.355	3.22	31.5	0.00	12.3	4.75	2.69
	Outdoors	39.2	0.341	3.15	44.0	3.32	12.8	4.92	2.56
11/08/2018	Indoors	38.1	0.398	4.83	9.04	3.91	18.3	5.54	2.33
	Indoors	33.4	0.331	2.43	34.5	3.71	16.1	5.09	2.08
	Outdoors	21.4	0.238	1.71	42.6	2.24	5.08	2.19	1.29
	Outdoors	21.4	0.247	2.47	39.3	2.33	6.06	2.40	1.70
21/08/2018	Indoors	95.4	0.388	33.3	0.696	2.97	15.9	11.0	2.17
	Indoors	16.4	0.178	5.74	8.60	1.88	2.40	1.49	0.54
	Outdoors	72.6	0.356	6.77	2.80	1.61	4.09	14.6	4.88
	Outdoors	56.9	0.241	6.25	10.6	1.40	4.52	11.4	4.51
28/08/2018	Indoors	84.5	0.404	4.28	6.14	3.38	66.3	8.59	4.91
	Indoors	90.7	0.385	4.20	20.2	3.36	66.0	8.81	4.43
	Outdoors	20.4	0.355	2.59	26.2	3.07	5.00	2.40	2.43
	Outdoors	18.2	0.364	2.79	15.0	3.33	5.02	2.48	2.61
01/09/2018	Indoors	46.1	1.90	2.14	8.06	5.36	19.3	4.08	4.63
	Indoors	56.0	2.37	2.14	2.38	6.11	20.1	4.47	5.07
	Outdoors	17.6	0.206	2.81	19.7	1.82	5.57	2.10	1.75
	Outdoors	16.7	0.206	2.86	11.4	1.80	5.59	2.08	1.80
05/09/2018	Indoors	41.8	0.338	2.30	6.00	3.08	7.24	10.6	3.19
	Indoors	44.9	0.350	2.23	7.81	3.00	6.10	10.5	3.18
	Outdoors	20.4	2.41	1.84	27.8	0.00	3.69	1.71	2.30
	Outdoors	19.1	0.390	1.85	18.9	1.87	3.99	1.70	2.37
10/09/2018	Indoors	0.218	0.210	0.307	0.863	1.86	1.31	1.81	0.777
	Indoors	43.1	0.290	7.70	1.51	4.09	8.82	3.61	2.54
	Outdoors	18.2	0.266	2.27	17.5	2.56	6.60	1.85	1.85
	Outdoors	15.1	0.272	2.22	8.18	2.47	6.10	1.84	1.82
19/09/2018	Indoors	90.7	1.91	15.3	11.9	3.42	15.3	6.49	11.2
	Indoors	120	3.98	18.6	31.2	22.6	28.4	24.3	17.2
	Outdoors	19.0	0.458	1.87	17.5	3.01	4.56	2.10	2.30
	Outdoors	12.2	0.554	1.79	7.31	2.38	4.31	2.03	2.07
22/09/2018	Indoors	1196	0.992	10.7	3.36	7.86	125	46.7	19.9
	Indoors	1315	2.00	10.9	4.02	8.46	186	50.9	20.7
	Outdoors	20.8	0.312	1.85	1.41	2.32	5.45	3.23	1.95
	Outdoors	16.3	0.333	1.97	10.5	2.22	4.89	2.43	3.07
22/09/2018	Indoors	95.5	1.38	13.7	9.29	5.81	12.7	9.61	5.01
	Indoors	91.2	1.14	13.4	12.0	4.32	16.8	8.19	5.38
	Outdoors	66.7	0.615	2.82	15.1	4.49	14.2	9.09	2.78
	Outdoors	80.8	0.496	2.83	30.8	5.28	14.8	10.9	3.21
12/09/2018	Indoors	83.6	1.71	7.72	13.3	6.38	61.3	5.22	6.27
	Indoors	118	1.68	7.58	11.2	16.8	90.0	13.0	7.11
	Outdoors	71.7	1.39	9.89	16.9	7.56	10.6	3.44	7.29
	Outdoors	94.5	2.19	9.79	13.0	5.71	14.0	3.50	7.28
17/09/2018	Indoors	74.6	2.22	8.71	9.98	4.19	69.6	6.59	4.47

	Indoors	79.5	2.30	9.03	8.90	4.24	80.0	7.28	5.34
	Outdoors	34.1	2.04	6.27	13.1	1.91	10.1	2.81	4.09
	Outdoors	22.7	1.86	5.25	16.6	2.26	5.90	2.42	2.82
26/09/2018	Indoors	206	1.77	8.25	6.24	4.41	230	11.6	36.4
	Indoors	208	2.39	8.11	7.48	4.23	231	11.5	36.0
	Outdoors	56.4	0.78	3.86	6.15	3.16	35.2	3.46	7.63
	Outdoors	49.6	0.75	3.79	9.70	2.71	32.9	3.05	7.47
08/09/2018	Indoors	192	3.87	9.26	14.1	5.45	186	23.2	11.8
	Indoors	191	3.75	8.95	11.5	6.53	182	23.3	11.5
	Outdoors	38.1	0.73	4.05	29.3	3.06	12.1	2.91	3.65
	Outdoors	25.9	0.594	3.92	13.5	2.83	10.2	2.41	3.41
01/10/2018	Indoors	211	1.22	8.57	3.33	4.19	43.6	14.6	12.9
	Indoors	213	1.17	8.47	10.9	4.26	44.2	13.9	12.8
	Outdoors	42.5	1.51	7.97	115	3.38	9.28	2.53	5.68
	Outdoors	39.6	1.48	8.01	47.7	2.85	10.2	2.44	5.86
08/10/2018	Indoors	101	2.51	26.7	15.2	3.85	77.8	12.8	32.5
	Indoors	101	1.65	27.0	13.8	3.90	71.7	14.5	33.0
	Outdoors	88.9	0.91	7.24	10.5	5.45	12.0	2.67	6.70
	Outdoors	64.0	0.93	7.20	4.50	5.13	8.01	2.92	6.66
10/10/2018	Indoors	200	1.40	1.50	0.439	3.05	51.6	23.3	6.93
	Indoors	123	1.04	0.234	0.480	1.75	31.5	14.1	4.00
	Outdoors	120	0.86	-0.276	0.663	1.15	8.32	1.92	1.43
	Outdoors	43.4	0.95	-0.191	8.43	1.66	8.55	1.95	1.70
15/10/2018	Indoors	142	5.65	15.4	0.470	2.86	30.4	26.8	5.34
	Indoors	150	5.80	15.4	8.62	3.38	32.5	27.4	5.45
	Outdoors	20.5	1.05	2.23	2.74	0.13	4.13	2.66	2.29
	Outdoors	21.0	1.03	2.11	4.34	0.072	4.00	2.61	2.11
17/10/2018	Indoors	189	37.5	2.23	2.55	1.72	11.1	29.0	19.7
	Indoors	184	34.8	3.61	3.82	1.20	9.96	28.8	19.8
	Outdoors	13.7	1.00	0.415	10.38	0.00	2.76	0.269	1.12
	Outdoors	10.1	1.02	0.409	3.09	0.041	2.67	-0.062	1.17
19/10/2018	Indoors	63.6	1.12	1.34	2.09	2.93	14.8	25.5	2.46
	Indoors	68.7	1.13	1.29	2.52	3.44	17.0	25.7	2.46
	Outdoors	31.1	0.801	3.29	4.83	0.87	3.97	2.14	2.73
	Outdoors	25.2	1.53	3.03	4.67	0.33	3.89	2.68	2.86
29/10/2018	Indoors	143	1.76	5.93	0.127	5.06	47.7	17.6	3.01
	Indoors	14.0	1.86	6.03	0.624	5.29	6.13	18.28	3.17
	Outdoors	12.0	0.876	0.367	0.814	0.083	3.03	0.086	1.23
	Outdoors	10.0	0.895	0.396	1.62	0.471	3.10	-0.201	1.19
03/11/2018	Indoors	706	6.11	92.9	7.26	3.18	60.1	29’	3.72
	Indoors	737	5.99	94.1	7.15	3.16	64.4	294	5.08
	Outdoors	67.8	1.84	13.6	2.00	0.72	8.60	33.5	2.20
	Outdoors	59.9	2.16	12.1	3.09	0.30	7.23	31.4	2.09

06/11/2018	Indoors	384	4.68	44.2	15.5	3.18	18.1	153	38.4
	Indoors	417	10.5	53.1	18.2	3.44	23.2	2081	38.6
12/11/2018	Indoors	184	5.53	15.8	0.00	4.65	10.9	37.3	4.22
	Indoors	111	3.41	10.9	0.436	1.37	7.48	23.1	2.64
	Outdoors	11.2	1.03	3.77	0.805	0.113	3.45	0.776	1.46
	Outdoors	10.5	1.03	3.79	1.32	1.05	3.43	0.456	1.45
14/11/2018	Indoors	354	3.70	23.4	3.42	1.69	64.5	31.8	60.8
	Indoors	376	3.76	23.6	4.62	1.64	64.8	32.7	14.5
	Outdoors	16.6	1.41	2.91	5.59	0.151	3.86	0.534	1.35
	Outdoors	15.6	1.44	3.88	4.77	0.086	3.83	0.281	1.58
17/11/2018	Indoors	103	1.48	6.37	1.23	1.35	6.62	14.0	3.37
	Indoors	105	1.49	6.42	2.16	1.34	6.64	14.8	2.85
	Outdoors	22.5	1.20	5.16	3.14	0.423	3.44	2.78	1.54
	Outdoors	22.0	1.18	5.10	4.43	0.273	4.21	2.61	1.59
19/11/2018	Indoors	261	8.36	8.35	2.51	6.26	49.4	39.4	9.24
	Indoors	256	8.55	10.6	5.23	5.54	51.5	39.0	9.22
	Outdoors	20.6	1.52	5.18	1.83	0.00	5.24	0.782	3.80
	Outdoors	26.9	1.56	5.16	5.05	0.29	5.41	0.482	3.75
21/11/2018	Indoors	176	5.49	9.04	1.25	1.97	17.7	9.83	16.4
	Indoors	119	3.84	6.87	37.1	1.53	12.6	7.17	9.27
	Outdoors	23.9	2.05	7.77	4.04	0.36	5.07	1.13	2.12
	Outdoors	21.8	2.07	7.94	1.83	0.31	4.98	1.09	2.21
21/11/2018	Indoors	105	1.91	4.79	-0.079	2.30	19.22	17.2	2.60
	Indoors	82.3	1.62	3.95	0.592	1.54	12.9	14.0	1.78
	Outdoors	15.9	0.916	2.96	0.264	0.712	4.26	0.735	1.00
	Outdoors	10.8	0.883	2.85	2.32	0.536	4.10	0.570	1.02
26/11/2018	Indoors	23.0	2.68	12.9	5.11	1.88	23.5	6.23	9.46
	Indoors	182	2.72	12.7	9.32	2.18	23.0	6.53	9.18
	Outdoors	52.2	3.53	10.9	5.24	0.594	6.29	1.52	6.19
	Outdoors	47.2	3.48	10.7	5.51	0.812	6.14	1.38	5.99
28/11/2018	Indoors	154	2.48	11.0	2.53	0.302	10.4	36.9	5.90
	Indoors	153	2.53	10.8	2.62	0.480	10.4	37.5	5.90
	Outdoors	23.9	1.91	5.73	0.994	0.00	3.79	0.470	2.28
	Outdoors	22.5	1.84	5.55	2.14	0.00	3.46	0.308	2.10
02/12/2018	Indoors	177	2.18	12.7	4.85	5.25	23.8	12.6	5.07
	Indoors	139	2.15	10.7	3.63	3.82	15.5	8.74	3.51
05/12/2018	Indoors	1617	8.03	19.6	10.0	1.32	92.1	147	50.9
10/12/2018	Indoors	357	0.862	10.8	4.21	2.14	13.0	74.2	6.16
	Indoors	506	1.14	21.1	6.0	2.22	18.4	94.7	12.5
	Outdoors	75.3	1.01	16.4	2.81	0.724	3.54	0.523	7.48
	Outdoors	67.3	1.01	16.4	8.47	0.434	2.91	-0.089	7.23
12/12/2018	Indoors	122	1.256	4.709	1.708	0.975	12.406	13.869	2.468
	Indoors	135	1.357	5.187	3.229	3.995	9.524	15.211	2.966

	Outdoors	24.8	0.214	1.710	1.818	-0.428	1.354	0.221	0.075
	Outdoors	18.8	0.279	1.717	0.365	-0.325	1.140	-0.016	0.012
15/12/2018	Indoors	131.6	1.07	4.14	1.70	1.52	7.96	10.72	1.27
	Indoors	80.2	0.576	2.77	0.822	0.938	5.30	8.66	0.563
	Outdoors	13.7	-0.625	0.052	0.281	-0.181	2.03	-0.479	-0.235
	Outdoors	9.99	-0.592	0.026	3.03	-1.06	1.93	-0.787	-0.256
17/12/2018	Indoors	218	5.35	58.5	8.40	2.68	16.8	17.2	49.2
	Indoors	313	5.58	59.9	13.6	3.12	15.8	11.0	50.2
	Outdoors	47.7	1.93	9.20	7.23	0.717	3.52	1.00	5.31
	Outdoors	31.5	2.24	8.05	3.55	0.293	2.99	0.567	4.00
19/12/2018	Indoors	256	5.57	18.4	25.0	4.97	60.1	14.8	19.3
	Indoors	196	4.21	13.9	19.0	3.55	43.3	11.6	14.6
	Outdoors	52.0	1.82	9.58	8.05	1.10	4.41	0.532	6.27
	Outdoors	40.0	1.51	7.99	9.70	0.747	2.96	0.046	4.88
05/01/2019	Indoors	1052	11.1	26.7	29.9	3.02	143	82.7	31.5
	Indoors	1097	10.2	26.9	29.8	3.15	143	87.2	32.7
	Outdoors	89.2	4.34	10.2	11.0	0.00	10.4	2.61	5.27
	Outdoors	65.5	4.27	9.50	8.65	1.37	6.42	1.65	4.69
07/01/2019	Indoors	217	10.1	14.9	10.6	4.18	21.9	23.8	38.5
	Indoors	284	10.9	15.8	11.3	4.30	23.5	25.4	40.6
	Outdoors	194	16.3	22.1	19.7	17.9	15.4	11.0	18.2
	Outdoors	156	16.7	20.6	15.4	16.5	12.8	10.0	16.8
09/01/2019	Indoors	310	4.94	38.2	10.6	3.90	20.2	53.6	46.1
	Indoors	318	5.53	40.0	10.6	3.56	21.0	58.0	48.0
	Outdoors	79.9	3.39	8.18	1.91	3.71	4.67	0.669	12.5
	Outdoors	52.5	2.44	6.03	2.64	3.75	3.35	0.313	9.04
11/01/2019	Indoors	209	5.44	16.7	10.4	2.34	34.9	47.2	12.4
	Indoors	123	3.21	8.60	5.16	1.32	21.7	28.4	6.10
	Outdoors	108	7.43	17.0	6.60	5.40	8.91	4.91	10.4
	Outdoors	112	7.63	17.2	4.90	5.03	8.92	4.63	11.9
16/01/2019	Indoors	303	4.78	6.92	3.52	2.64	25.3	81.2	4.49
	Indoors	180	2.66	4.40	2.27	1.51	14.1	45.1	2.56
	Outdoors	66.2	7.28	7.41	7.78	6.93	7.11	3.36	3.88
	Outdoors	64.1	7.32	7.48	5.19	6.97	6.76	3.09	4.03
23/01/2019	Indoors	1319	9.44	51.5	8.04	8.73	20.3	207	24.0
	Indoors	635	3.66	24.5	1.70	2.37	8.82	96.3	11.2
	Outdoors	61.0	1.29	3.06	7.68	1.24	5.93	10.0	1.79
	Outdoors	60.2	1.22	2.86	4.16	0.750	5.35	10.8	1.47
16/02/2019	Indoors	85.3	2.49	9.67	1.16	1.45	9.17	6.92	2.93
	Indoors	86.0	2.41	9.62	0.81	1.51	8.72	7.09	2.82
	Outdoors	30.0	1.74	38.2	2.66	0.661	3.62	0.323	1.79
	Outdoors	27.1	1.71	42.6	2.26	0.800	3.81	0.342	1.90

C. Individual VOC abundance

Table C-1 – VOC content (%) in indoor air throughout the period of the study

	Benzene (%)	Toluene (%)	Trichloro-ethylene (%)	Tetrachloro-ethylene (%)	Pinene (%)	Limonene (%)	Xylenes (%)	VOCs (%)
Spring	2.63	3.53	3.86	3.16	18.0	25.7	3.37	60.2
Summer	1.60	12.4	7.07	6.30	22.7	10.3	7.76	68.2
Autumn	2.44	6.33	2.84	1.61	13.0	15.3	5.00	46.5
Winter	2.08	6.59	2.57	1.06	9.47	15.4	6.58	43.8
Overall	2.19	7.22	4.09	3.03	15.8	16.7	5.68	54.7

Note: Percentage is expressed in relation to total of all VOCs (TVOCs)

Table C-2 - VOC content (%) in outdoor air throughout the period of the study

	Benzene (%)	Toluene (%)	Trichloro-ethylene (%)	Tetrachloro-ethylene (%)	Pinene (%)	Limonene (%)	Xylenes (%)	VOCs (%)
Spring	4.98	9.57	16.8	6.78	11.9	10.9	5.42	66.3
Summer	1.61	9.79	18.1	6.95	16.3	12.3	7.61	72.6
Autumn	4.79	15.7	12.9	1.62	15.6	6.41	8.52	65.5
Winter	6.63	11.3	8.56	5.65	8.83	5.98	8.65	55.6
Overall	4.50	11.6	14.1	5.25	13.2	8.88	7.55	65.0

Note: Percentage is expressed in relation to total of all VOCs (TVOCs)

D. Health risk assessment

Table D-1 – Exposure concentrations (EC) (µg/m³) estimated for each specific VOC in indoor air of 64 homes for each season

	Benzene	Toluene	Trichloroethylene	Tetrachloroethylene	Pinene	Limonene	Xylenes
Spring	2.41	1.61	4.62	2.09	18.2	37.4	2.42
Summer	0.71	9.18	1.41	2.64	32.6	79.9	4.15
Autumn	2.71	9.99	3.54	1.60	16.7	47.3	7.66
Winter	3.52	11.9	5.50	1.78	20.9	34.4	12.3
Overall	2.34	8.17	3.77	2.03	22.1	49.75	6.63

Table D-2 – Exposure concentrations (EC) (µg/m³) estimated for each specific VOC in outdoor air of 64 homes for each season

	Benzene	Toluene	Trichloro-ethylene	Tetrachloro-ethylene	Pinene	Limonene	Xylenes
Spring	0.75	0.46	2.66	0.77	1.72	3.87	0.60
Summer	0.19	0.94	5.74	0.70	2.41	0.87	0.75
Autumn	0.36	1.47	2.05	0.21	1.27	0.70	0.78
Winter	1.60	4.10	1.94	1.37	2.00	1.23	2.00
Overall	0.73	1.74	3.10	0.76	1.85	1.67	1.03

Table D-3 - Cancer risk (CR) for each VOC and cumulative exposure risk in outdoor air throughout the period of the study

	Benzene[a]	**Toluene[b]**	**Trichloro-ethylene[a]**	**Tetrachloro-ethylen[a]**	**Pinene[b]**	**Limonene[b]**	**Xylenes[b]**	**Total CR (USEPA IRIS)**	**Total CR (USEPA IRIS + CTV)**
Spring	5.85×10^{-6}	1.46×10^{-4}	1.09×10^{-5}	2.01×10^{-7}	7.24×10^{-4}	1.63×10^{-3}	2.08×10^{-4}	1.70×10^{-5}	2.72×10^{-3}
Summer	1.49×10^{-6}	2.97×10^{-4}	2.35×10^{-5}	1.83×10^{-7}	1.02×10^{-3}	3.66×10^{-4}	2.62×10^{-4}	2.52×10^{-5}	1.97×10^{-3}
Autumn	2.81×10^{-6}	4.64×10^{-4}	8.41×10^{-6}	5.47×10^{-8}	5.34×10^{-4}	2.95×10^{-4}	2.73×10^{-4}	1.13×10^{-5}	1.58×10^{-3}
Winter	1.25×10^{-5}	1.29×10^{-3}	7.95×10^{-6}	3.56×10^{-7}	8.41×10^{-4}	5.10×10^{-4}	6.95×10^{-4}	2.08×10^{-5}	3.36×10^{-3}
Total	5.66×10^{-6}	5.49×10^{-4}	1.27×10^{-5}	1.99×10^{-7}	7.79×10^{-4}	7.02×10^{-4}	3.59×10^{-4}	1.86×10^{-5}	2.41×10^{-3}

Note: a - estimates based on parameters from USEPA IRIS database; b - estimates based on parameters from CTV predictor

Table D-4 – Non cancer risk by hazard quotient (HQ) and hazard index (HI=ΣHQ) for each specific VOC in outdoor air throughout the period of the study

HQ	Benzene[(a)]	Toluene[(a)]	Trichloro-ethylene[(a)]	Tetrachloro-ethylene[(a)]	Pinene[(b)]	Limonene[(b)]	Xylenes[(a)]	HI (USEPA IRIS)	HI (USEPA IRIS + CTV)
Spring	2.50×10^{-2}	9.25×10^{-5}	1.33	1.93×10^{-2}	1.22×10^{-1}	4.28×10^{-1}	5.98×10^{-3}	1.38	1.93
Summer	6.36×10^{-3}	1.88×10^{-4}	2.87	1.76×10^{-2}	1.71×10^{-1}	9.62×10^{-1}	7.53×10^{-3}	2.90	4.03
Autumn	1.20×10^{-2}	2.94×10^{-4}	1.03	5.26×10^{-3}	9.00×10^{-2}	7.75×10^{-1}	7.83×10^{-3}	1.06	1.92
Winter	5.34×10^{-2}	8.19×10^{-4}	9.69×10^{-1}	3.42×10^{-2}	1.42×10^{-1}	1.36×10^{-1}	2.00×10^{-2}	1.08	1.36
Total	2.42×10^{-2}	3.49×10^{-4}	1.55	1.91×10^{-2}	1.31×10^{-1}	1.84×10^{-1}	1.03×10^{-2}	1.60	1.92

Note: a - estimates based on parameters from USEPA IRIS database; b - estimates based on parameters from CTV predictor

(a) (b)

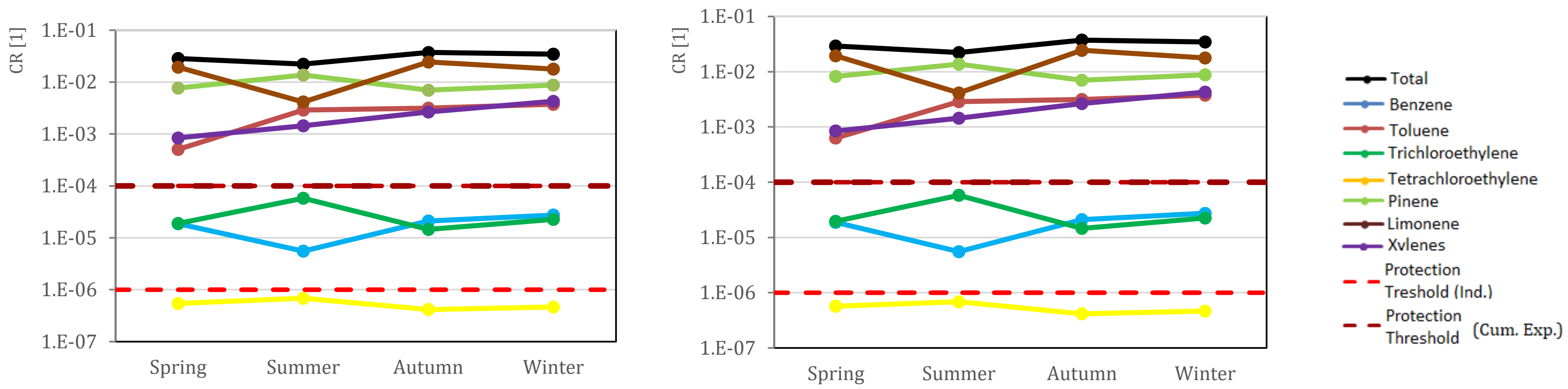


Figure D-1 – Cancer risks (CR) for target VOCs in indoor air of 64 dwellings during four seasons; (a) when below LOQ substituted with equal LOQ/2; (b) when below LOQ substituted with equivalent minimum concentrations observed in the same season

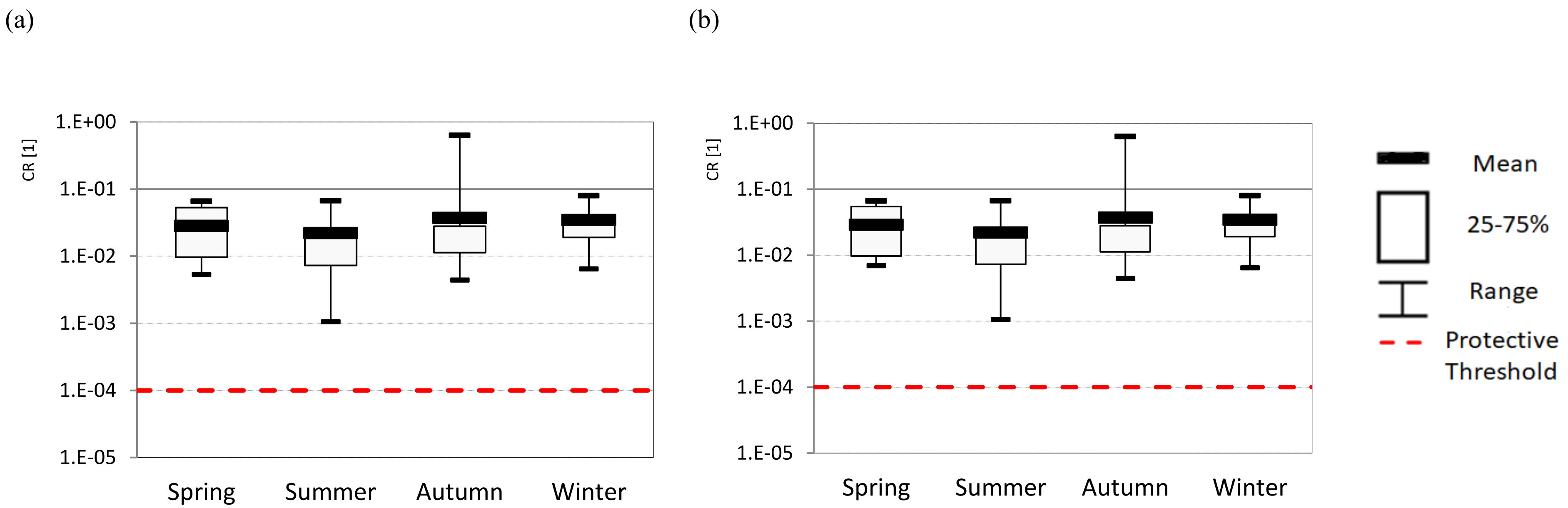


Figure D-2 – Total cancer risk (total CR) in indoor air of 64 dwellings; (a) when below LOQ substituted with equal LOQ/2; (b) when below LOQ substituted with equivalent minimum concentrations observed in the same season

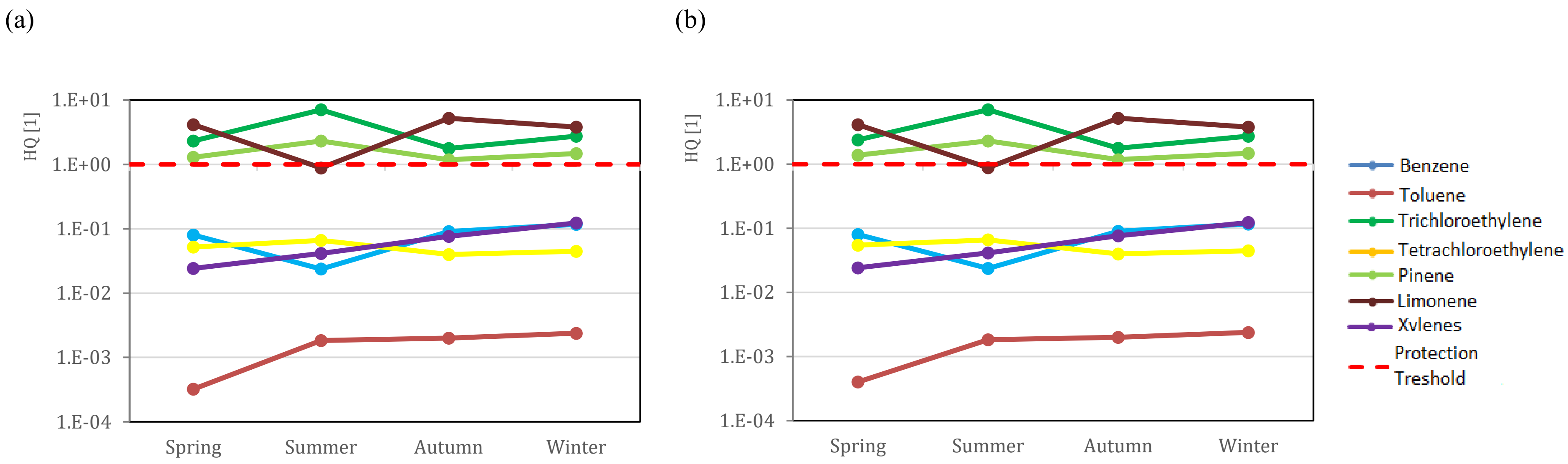


Figure D-3 – Non cancer risk (HQ) in indoor air of 64 dwellings during four seasons; (a) when below LOQ substituted with equal LOQ/2; (b) when below LOQ substituted with equivalent minimum concentrations observed in the same season