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Tese apresentada à Universidade de Aveiro para cumprimento dos requisitos necessários à obtenção do grau de Doutor em Ciências e Engenharia do Ambiente, realizada sob a orientação científica da Doutora Célia dos Anjos Alves, Investigadora Principal com Habilitação do Centro de Estudos do Ambiente e do Mar da Universidade de Aveiro e co-orientação da Doutora Susana Marta Almeida, Investigadora Auxiliar no Centro de Ciências e Tecnologias Nucleares do Instituto Superior Técnico, e Doutora Teresa Pinheiro, Investigadora Auxiliar no Centro de Ciências e Tecnologias Nucleares do Instituto Superior Técnico.

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palavras-chave

Biomassa, combustão doméstica, material particulado, caraterização química, dose, toxicidade.

resumo

A combustão de biomassa para aquecimento residencial é reconhecida como uma fonte importante de material particulado não apenas no ar ambiente, mas também no interior das habitações. A exposição a partículas resultantes da queima de biomassa tem sido associada a um vasto leque de efeitos adversos na saúde. Sabe-se que as propriedades físicas e químicas das partículas inaladas afetam acentuadamente as respostas biológicas. Ao longo dos anos, muitos estudos tiveram como foco os perfis de emissão da combustão residencial de biomassa. No entanto, com o aparecimento e a crescente quota de mercado de novos equipamentos de pequena escala alimentados automaticamente com biocombustíveis prensados, a investigação deve ser direcionada para a caracterização das emissões desses sistemas de combustão alimentados quer com novos pellets disponíveis no mercado, quer com pellets produzidos a partir de novas matérias primas potencialmente relevantes. Apesar da abundância de publicações dedicadas às emissões e composição das partículas da queima residencial de biomassa, o impacto desta fonte na qualidade do ar interior tem sido pouco estudado, sobretudo no que diz respeito às características químicas e toxicológicas do material particulado. Os dois objetivos principais desta tese foram: i) obter os perfis químicos e toxicológicos para sistemas alimentados a pellets, e ii) avaliar o impacto de equipamentos tradicionais na qualidade do ar interior, propriedades do material particulado, dose depositada no trato respiratório e respostas biológicas. Para atingir o primeiro objetivo, foram selecionados quatro tipos de pellets (duas marcas de pellets com certificação ENplus A1, uma marca de pellets sem certificação e pellets de acácia produzidos em laboratório) para realizar experiências numa instalação laboratorial de combustão e determinar fatores de emissão de gases e material particulado (PM_{10}). Para atingir o segundo objetivo, realizaram-se amostragens de partículas em duas habitações com equipamentos de combustão distintos (lareira aberta e recuperador de calor), na ausência de outras fontes interiores. A dose de partículas inaladas no interior das habitações e depositadas no trato respiratório humano foi estimada utilizando um modelo de exposição/dose (ExDoM2). A composição química das PM_{10} resultantes quer dos ensaios laboratoriais, quer dos microambientes residenciais, foi analisada em termos de iões inorgânicos solúveis em água, carbono orgânico e elementar e especiação orgânica detalhada. Adicionalmente, nas amostras de partículas colhidas no interior das habitações, foram também determinados elementos maioritários e traço. Foi utilizada uma bateria de ensaios *in vitro* para avaliar a ecotoxicidade, citotoxicidade e mutagenicidade das amostras de PM_{10}.

resumo

Os resultados obtidos nos ensaios laboratoriais indicaram que o material lenhoso alternativo selecionado para a peletização contribuiu para um aumento dramático das emissões de partículas, as quais apresentaram propriedades químicas distintas e um potencial toxicológico elevado. Observou-se que mesmo o material certificado nem sempre cumpre os requisitos de emissão estabelecidos pela diretiva Ecodesign. As partículas emitidas pela combustão de pellets apresentaram na sua composição maioritariamente iões inorgânicos solúveis em água. O carbono elementar dominou a fração de material carbonáceo nas partículas dos pellets comerciais, ao passo que o carbono orgânico constitui a componente mais abundante nas amostras resultantes da queima de pellets de acácia. Os resultados mostraram que as partículas dos pellets de acácia foram as mais ecotóxicas e citotóxicas, enquanto não foi detetada mutagenicidade para nenhum biocombustível. Na campanha de amostragem realizada em microambientes residenciais durante a utilização de diferentes equipamentos de combustão, observou-se uma exposição mais elevada, dose depositada no trato respiratório humano mais alta e uma toxidade superior para as partículas colhidas durante a operação da lareira aberta, refletindo a menor eficiência de combustão deste equipamento. Durante a sua utilização, foi registado um aumento superior nos níveis de material particulado (mais de 12 vezes relativamente às concentrações de fundo) em comparação com o observado para o recuperador de calor (aumento de 2 vezes). O material carbonáceo representou cerca de 44% da massa de PM_{10} nas amostras colhidas durante a operação da lareira, enquanto a operação do recuperador de calor reduziu quase pela metade o conteúdo total de carbono nas partículas. Os iões solúveis em água e os elementos apresentaram contribuições variáveis para a massa das partículas no interior das habitações, sendo geralmente superiores durante a operação do recuperador de calor. Em ambos os microambientes residenciais foram detetados vários traçadores químicos de combustão de biomassa, assinalando a contribuição desta fonte para as partículas interiores. A avaliação da biorreatividade revelou que as partículas emitidas pela lareira foram as mais ecotóxicas e citotóxicas, enquanto que não foi detetada mutagenicidade em quaisquer das amostras testadas. Vários constituintes detetados nas partículas internas, como os hidrocarbonetos aromáticos policíclicos, apresentaram correlações significativas com o aumento da toxicidade. Considerando os resultados obtidos, os proprietários devem ser encorajados a atualizar a tecnologia de combustão, a fim de reduzir os produtos de combustão incompleta dentro das suas habitações.

keywords

Biomass, residential combustion, particulate matter, chemical characterisation, dose, toxicity

abstract

Biomass combustion for residential heating is recognised as an important source of particulate matter, not only in the ambient air, but also inside the dwellings. Exposure to biomass burning particles has been linked to a vast array of adverse health effects. The physical and chemical properties of inhaled particles are thought to greatly affect the biological responses. Over the years, many studies have focused on emission source profiles of residential biomass combustion. However, with the advent and growing market share of new small-scale appliances automatically fed with compressed biofuels, research efforts need to be devoted to the characterisation of emissions from these appliances either from new commercially available pellets or from pellets made from potentially relevant raw materials. Despite the wealth of publications on emissions and composition of particles from residential biomass combustion, the impact of this source on the indoor air quality has been scarcely studied, especially with regard to the chemical and toxicological characteristics of the particles. The two main objectives of this thesis were: i) to obtain chemical and toxicological profiles for pellet-fuelled heating systems, and ii) to evaluate the impact of traditional appliances on indoor air quality, properties of particulate matter, deposited dose in the respiratory tract and biological responses. For the fulfilment of the first objective, four types of pellets were selected (two brands of ENplus A1 certified pellets, one brand of non-certified pellets, and laboratory-produced acacia pellets) to carry out experiments in a laboratory combustion facility to determine emission factors of gaseous compounds and particulate matter (PM_{10}). To achieve the second objective, particulate samples were collected in two households equipped with distinct combustion appliances (open fireplace and woodstove) in the absence of other indoor sources. The dose of inhaled indoor particles deposited in the human respiratory tract was estimated using an exposure dose model (ExDoM2). The chemical composition of PM_{10} from both laboratory experiments and residential microenvironments was analysed for water soluble inorganic ions, organic and elemental carbon and detailed organic speciation. Additionally, in samples collected indoors, major and trace elements were also determined. A battery of *in vitro* assays was used to assess the ecotoxicity, cytotoxicity and mutagenicity of the PM_{10} samples. The results obtained from the laboratory measurements indicated that the alternative woody raw material selected for pelletising contributed to a dramatic increase in particulate emissions, with distinctive chemical properties and increased toxicological potential. It was observed that even certified material does not always meet emission requirements set by the Ecodesign directive. Particles from pellet combustion were mainly composed of water soluble inorganic constituents.

abstract

The carbonaceous fraction of particulate samples from commercial pellets was dominated by elemental carbon, while organic carbon was the most abundant constituent in samples from the combustion of acacia pellets. The results showed that particles from acacia pellets were the most ecotoxic and cytotoxic, while mutagenicity was not detected for any biofuel. In the sampling campaign carried out in residential microenvironments while using different combustion devices, higher exposures, higher doses in the human respiratory tract and higher toxicity of the particles collected during the operation of the open fireplace were observed, as a result of the lower combustion efficiency. When using this combustion equipment, a higher increase in particulate matter levels (over 12 times compared to background concentrations) was registered compared to that measured with the woodstove (2-fold increase). The carbonaceous material accounted for a PM_{10} mass fraction of about 44% in samples from the room equipped with fireplace, while the woodstove operation almost halved the total particulate carbon content. Water soluble ions and trace elements showed variable contributions to the mass of the indoor particles and were generally higher during the operation of the woodstove. Several chemical markers of biomass combustion were detected in both residential microenvironments, highlighting the input of this source to indoor particles. The bioreactivity assessment showed that particles emitted by the fireplace were the most ecotoxic and cytotoxic, while mutagenicity was not detected in any of the tested samples. Combustion-related organic compounds in indoor particles, such as polycyclic aromatic hydrocarbons, displayed significant correlations with the increase in toxicity. In view of the results obtained, homeowners should be encouraged to upgrade the wood burning technology in order to reduce the products of incomplete combustion inside their dwellings.

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Acronyms and Chemical Formulas

ANOVA	Analysis of Variance
AI	Alveolar Interstitial
aqSOA	Aqueous Secondary Organic Aerosol
ASHRAE	American Society of Heating, Refrigerating and Air-Conditioning Engineers
BaP	Benzo[a]pyrene
$B[a]P_{eq}$	Benzo[a]pyrene equivalents
BC	Black Carbon
BSTFA	N,O-bis(trimethylsilyl)-trifluoroacetamide
CESAM	Centre for Environmental and Marine Studies
CH_2O	Formaldehyde
CH_4	Methane
CMB	Chemical Mass Balance
CO	Carbon Monoxide
CO_2	Carbon Dioxide
COPD	Chronic Obstructive Pulmonary Disease
CPI	Carbon Preference Index
C_XH_Y	Total Hydrocarbons
C_2H_6	Ethane
C_3H_8	Propane
C^2TN	Centre for Nuclear Sciences and Technologies
DF	Deposition Fraction
DMSO	Dimethyl Sulfoxide
DNA	Deoxyribonucleic Acid
EC	Elemental Carbon
EDTA	Ethylenediaminetetraacetic acid
EEA	European Environment Agency
EF	Emission Factor
EMEP	European Monitoring and Evaluation Programme
ET	Extrathoracic

EU	European Union
ExDoM2	Exposure Dose Model
FBS	Fetal Bovine Serum
FCT	Portuguese Foundation for Science and Technology
FTIR	Fourier Transform Infrared Spectrometer
GC-MS	Gas Chromatography–Mass Spectrometry
GI	Gastrointestinal
HCl	Hydrogen Chloride
$HClO_4$	Perchloric Acid
HF	Hydrogen Fluoride
HNO_3	Nitric Acid
HPAEC	High-Performance Anion Exchange Chromatography
HPLC	High-Performance Liquid Chromatography
HQ	Hazard Quotient
HRT	Human Respiratory Tract
IARC	International Agency for Research on Cancer
ICRP	International Commission on Radiological Protection
IRIS	Integration Risk Information System
IUR	Inhalation Unit Risk
KCl	Potassium Chloride
KOH	Potassium Hydroxide
K_2CO_3	Potassium Carbonate
K_2SO_4	Potassium Sulphate
LDH	Lactate Dehydrogenase
MA	Monosaccharide Anhydrides
MMAD	Mass Median Aerodynamic Diameter
MMD	Mass Median Diameter
MR	Mutagenicity Ratio
MTT	3-[4,5-Dimethylthiazole-2-yl]-2,5-Diphenyltetrazolium Bromide
NDIR	Non-Dispersive Infrared
NH_3	Ammonia
NO	Nitrogen Oxide

NO_x	Nitrogen Oxides
NO_2	Nitrogen Dioxide
N_2O	Nitrous Oxide
OA	Organic Aerosol
OC	Organic Carbon
OECD	Organisation for Economic Co-operation and Development
OGC	Organic Gaseous Compounds
O_2	Oxygen
OM	Organic Matter
PAH	Polycyclic Aromatic Hydrocarbon
PAM	Potential Aerosol Mass
PBS	Phosphate Buffered Saline
PE	Percentage Error
PET	Poly (ethylene terephthalate)
PI	Propidium Iodide
PM	Particulate Matter
PMF	Positive Matrix Factorisation
PM_1	Particulate matter less than or equal to 1 μm in aerodynamic diameter
$PM_{2.5}$	Particulate matter less than or equal to 2.5 μm in aerodynamic diameter
PM_4	Particulate matter less than or equal to 4 μm in aerodynamic diameter
PM_{10}	Particulate matter less than or equal to 10 μm in aerodynamic diameter
R_fC	Reference Concentration
R_fD	Reference Dose
RNS	Reactive Nitrogen Species
ROS	Reactive Oxygen Species
RT	Respiratory Tract
SMPS	Scanning Mobility Particle Sizer
SOA	Secondary Organic Aerosol
SO_2	Sulphur Dioxide
S9	Rat Liver Microsomal
TB	Tracheobronchial
TC	Total Carbon

TEF	Toxic Equivalent Factor
TMCS	Trimethylchlorosilane
TOC	Total Organic Carbon
TOE	Total Organic Extract
TSP	Total Suspended Particles
TU	Toxicity Units
UPLC	Ultraperformance Liquid Chromatography
US	United States
USA	United States of America
USEPA	United States Environmental Protection Agency
WHO	World Health Organisation
WST-8	Water Soluble Tetrazolium
2-NAP	2-Naphthol
1-OHP	1-Hydroxypyrene

CHAPTER 1

Chapter 1. General Introduction

Air pollution consistently ranks among the top risk factors for mortality worldwide (Health Effects Institute, 2020). According to the most recent report from the Health Effects Institute, in 2019, air pollution was responsible for 6.67 million deaths worldwide. According to the same report, 26% of global deaths from stroke were attributable to total air pollution while the percentage reached 30% for lower respiratory infections and 40% for chronic obstructive pulmonary disease (COPD) (Health Effects Institute, 2020). Among the pollutants present in ambient air, particulate matter (PM) is regarded as one of the most harmful since it has been classified by the International Agency for Research on Cancer (IARC) as a carcinogen to humans (group 1) (Loomis et al., 2013). PM is generally classified by size into PM_{10}, $PM_{2.5}$ and PM_1, which are defined as the fraction of particles with equivalent aerodynamic diameters less than or equal to 10 µm, 2.5 µm and 1 µm, respectively.

Residential biomass combustion is a major source of atmospheric PM worldwide (Olsen et al., 2020; Vicente and Alves, 2018). Furthermore, the impact of this source on indoor PM levels is also noticeable (e.g. Bartington et al., 2017; Castro et al., 2018; de Gennaro et al., 2015; Guo et al., 2008; McNamara et al., 2013; Parajuli et al., 2016; Salthammer et al., 2014; Saraga et al., 2015). In developing countries, solid fuel combustion is an important source of household air pollution. Indoor exposure can occur at concentrations orders of magnitude greater than those observed in the developed world (Balmes, 2019; Clark et al., 2013; Naeher et al., 2007). Indoor emissions from household combustion of biomass fuel (primarily wood) were categorised as probably carcinogenic to humans (group 2A) by IARC (2010). In industrialised countries, residential biomass combustion for heating purposes is still a common practice that contributes to significant exposures indoors and outdoors, mostly in winter (Amann et al., 2018; Naeher et al., 2007; Sigsgaard et al., 2015). In the European Union (EU), from 1990 to 2015, the use of biomass as a fuel for household heating doubled. In Portugal, more than 40% of primary energy supply for residential heating in 2015 was based on biomass (Bertelsen and Mathiesen, 2020). By 2030, the use of biomass in the residential sector is projected to increase in the EU by 36% (Amann et al., 2018). In fact, in the scope of the updated European energy policy (Clean energy for all Europeans package), the EU has set a target of 32% for renewable energy sources in the energy mix by 2030 (Directive 2018/2001/EU), which might increase the share of biomass of overall renewable energy production.

According to a recent report (Amann et al., 2018), in 2005, biomass combustion in the residential sector was responsible for 46% and for more than 30% of total primary emissions of $PM_{2.5}$ in the EU and in Portugal, respectively. The widespread use of traditional small combustion units, operated manually in batch mode, is a major problem since such combustion appliances generate higher PM emissions than modern, automatically fed combustion appliances (Olsen et al., 2020; Vicente and Alves, 2018). In Portugal, even though a trend towards the replacement of conventional stoves by more modern technologies (e.g. pellet stoves and boilers) is observed, traditional appliances are still predominant since, even in recent years, conventional stoves and boilers, as well as open fireplaces, represent about 80% of the consumption of wood (Pereira et al., 2020).

To tackle pollutant emissions from solid fuel combustion in small combustion installations the EU legislation includes the Commission Regulation 2015/1185 (implementing Directive 2009/125/EC - Ecodesign requirements for energy-related products), which establishes a framework for setting ecodesign requirements for solid fuel local space heaters, including emission requirements for several pollutants (PM, CO, NO_x, and organic gaseous compounds – OGC) to be met by 2022. Additionally, the Regulation 2017/1369 sets the energy labelling framework for energy-related products (Commission Delegated Regulation (EU) 2015/1186 and (EU) 2015/1187 for energy labelling of local space heaters and solid fuel boilers, respectively) in order to specify a mandatory energy label. This regulation also intends to inform consumers about the energy efficiency and to encourage the purchase of more energy efficient products. Moreover, although the use of biomass in the residential sector is expected to increase, the Energy Efficiency Directive (2018/2002/EU) and Energy Performance of Buildings Directive (2018/844/EU) might indirectly contribute to the reduction of emissions by decreasing energy consumption in the European Union (Amann et al., 2018).

1.1. Biomass combustion: Principles and particle formation

Combustion is an exothermic reaction that needs three main ingredients to occur: oxygen, heat and fuel. The combustion process can be divided into different stages (Fig. 1.1): heating-up, drying, devolatilisation (or thermal pyrolysis), combustion of the volatiles and combustion of the char (Williams et al., 2012). The first stage uses energy to evaporate the fuel moisture and dry the fuel. If the moisture content is too high, the heating value of the wood and the combustion efficiency decrease, since a considerable amount of energy is necessary to vaporise the water (Simoneit, 2002). Usually the temperature at which the pyrolysis starts is around 160 – 250 °C (Williams et al., 2012). At this stage, biomass large structures (e.g. cellulose, hemicellulose and lignin) are decomposed by heat together with the vaporisation of water and extractives (Rogge et al., 1998; Simoneit, 2002). In this step, a large part of the biomass (about 80%) is converted to volatile products (Williams et al., 2012). The compounds released are completely or partially combusted in the flame and char formation proceeds until the release of combustible volatile substances drops below the minimum level required for the flame propagation (Rogge et al., 1998; Simoneit, 2002). Although char represents about 10-30% wt. of the total biomass, it can still contain up to a third of the energy content of the biomass (Williams et al., 2012). The combustion process can be either continuous or batch mode, which means that the combustion stages can overlap or take place separately, respectively (Berndes et al., 2008; Nussbaumer, 2003).

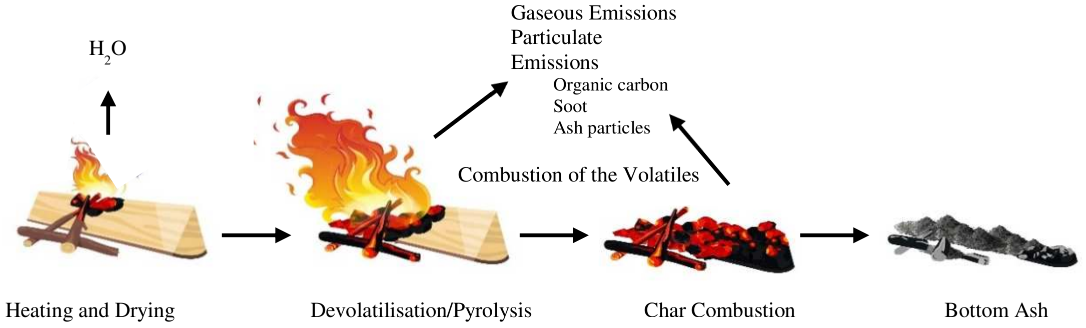

Figure 1.1. Description of the biomass combustion stages.

The quality of the combustion is driven by the temperature achieved during the process, availability of oxygen, sufficient residence time and enough turbulence to promote the mixture between the combustion air and the fuel (Berndes et al., 2008; Nussbaumer, 2003). In addition to CO_2 and water vapour, biomass combustion releases a wide range of different products, including gaseous (e.g. CO, C_XH_Y, NO_x, NH_3, N_2O) and particulate compounds (Nussbaumer, 2003).

The physicochemical characteristics of the particles emitted from biomass combustion devices is largely dependent on the equipment, operating conditions and fuel burned (Olsen et al., 2020; Vicente and Alves, 2018). Particulate matter from small scale biomass combustion has been characterised by a unimodal size distribution (Bari et al., 2011; Lamberg et al., 2013; Tissari et al., 2008) and by mass median diameters (MMD), from both batch mode fed and automatically fed combustion appliances, below 1 µm in size (Boman et al., 2004, 2011; Lamberg et al., 2011a, 2013; Pettersson et al., 2011; Tissari et al., 2008). Nevertheless, MMD have been reported to be higher during log wood combustion in batch mode operated appliances (179 to 658 nm) (Lamberg et al., 2011a; Pettersson et al., 2011) compared to the combustion of wood pellets (101 to 336 nm) (Boman et al., 2011; Lamberg et al., 2011b, 2011a; Tissari et al., 2008).

Regarding the chemical composition of the particles generated from biomass combustion, they can be categorised into three main classes: organic carbon, soot and inorganic particles (Bølling et al., 2009; Obaidullah et al., 2012).

Under incomplete combustion conditions, at low temperatures (300-500°C), the thermal degradation of the wood constituents (cellulose, hemicellulose and lignin) releases organic carbon (Bølling et al., 2009). At higher temperatures (~800-1000°C), and lack of oxygen, soot can be formed from organic precursors inside the fuel rich area of the flame (Bølling et al., 2009; Nussbaumer, 2010). Soot particles contain a mixture of elemental carbon and organic carbon (Bølling et al., 2009; Obaidullah et al., 2012). The mechanism of soot formation involves the release of hydrocarbons from the fuel during the devolatilisation, formation of polycyclic aromatic hydrocarbons (PAHs) and particle growth by surface reactions, coagulation and agglomeration (Nussbaumer, 2010; Obaidullah et al., 2012).

Under favourable combustion conditions (high temperatures, good oxygen supply and turbulence), achieved in modern combustion technologies, PM emissions are dominated by inorganic ash particles (Bølling et al., 2009; Nussbaumer, 2010). These particles are mainly composed of potassium compounds, such as potassium sulphate (K_2SO_4), potassium chloride (KCl), potassium hydroxide (KOH) and potassium carbonate (K_2CO_3) (Boman et al., 2011, 2004; Johansson et al., 2003; Pettersson et al., 2011; Sippula et al., 2007). The formation of inorganic particles is initiated by the vaporisation of easily volatilised ash forming elements (e.g. S, Cl, Na, K and Zn) from the biomass (Wiinikka and Gebart, 2005). Particles are formed by nucleation and subsequent growth by condensation and coagulation (Sippula et al., 2007; Wiinikka and Gebart, 2005). The release of ash-forming species during the combustion of biomass depends on both the fuel composition and combustion temperature (Knudsen et al., 2004; Van Lith et al., 2006). For example, the study by Knudsen et al. (2004) showed that the fuel content of Cl and Si largely affected the K release in distinct ways: while Cl favoured the release of K to the gas phase, Si promoted the retention of K in bottom ash.

The fuel composition plays a major role in PM emissions from combustion in modern appliances. Although wood and woody fuels are mainly composed of carbon (48.7 – 57.0% dry, ash free basis), oxygen (32.0 – 45.3% dry, ash free basis) and hydrogen (5.4 – 10.2% dry, ash free basis) (Vassilev et al., 2010), they also present minor amounts of other inorganic compounds, such as nitrogen (N), calcium (Ca), potassium (K), magnesium (Mg), manganese (Mn), sulphur (S), chlorine (Cl), iron (Fe), aluminium (Al), zinc (Zn), among others (Obernberger et al., 2006). Considering that PM emissions are closely related to the fuel content of specific elements, fuel indexes were developed and have been used to predict PM emissions from biomass combustion under favourable combustion conditions (Feldmeier et al., 2019; Jeguirim et al., 2017; Sippula et al., 2017).

Whereas more efficient combustion conditions, achieved in automatically fired combustion appliances, yield low organic emissions and favour formation of inorganic particles, the opposite is observed for the operation of batch mode fired appliances (Olsen et al., 2020; Vicente and Alves, 2018). In addition to the combustion appliance, the fuel and combustion conditions also play a key role on the organic emissions from residential combustion (e.g. Czech et al., 2018; Gonçalves et al., 2011; Orasche et al., 2013; Schmidl et al., 2011). Organic emissions from biomass combustion are composed of a wide range of compounds, including anhydrosugars, PAHs, phenolic compounds and resin acids. Among these, levoglucosan has been one of the most analysed constituents. It is biomass combustion tracer widely used to apportion the contribution of this source to the atmospheric levels (Vicente and Alves, 2018). Levoglucosan emissions from traditional wood burning appliances have been reported to vary throughout the combustion cycle, being enhanced during the start-up phase and decreasing during flaming combustion (Calvo et al., 2015). During the operation of automatically fired combustion appliances, Schimdl et al. (2011) only detected levoglucosan during the start-up phase, while Alves et al. (2017) reported that, on average, the anhydrosugar particle mass fractions obtained for the combustion of seven biofuels in a pellet stove were 30 to 70 times lower than the values found for manually fired systems. The later researchers also observed differences in emissions depending on the biofuel burned, including between combustion of diverse wood pellets. Considering the decrease in organic emissions with the increase in combustion efficiency reported in numerous researches (Olsen et al., 2020; Vicente and Alves, 2018), an update of the chemical tracers might be needed if the trend towards the replacement of batch mode operated stoves by automatically fed appliances continues.

1.2. PM-related health effects

An extensive research effort has been invested in examining the relationship between long- and short-term exposure to ambient PM and the resulting health effects (Anderson et al., 2012; Darquenne et al., 2020; Kim et al., 2015; Pope, 2000). PM-related health effects include both acute (e.g. pulmonary inflammation, systemic acute phase response, exacerbation of chronic diseases, such as asthma, change in blood pressure, heart rate variability) and chronic effects (e.g. lung cancer, pneumonia, decreased lung function, decreased lung growth, cardiovascular mortality, myocardial infarction, hypertension, premature death, stroke). The physical and chemical properties of inhaled particles are thought to greatly affect the biological responses. Research work targeting PM characteristics of concern have pointed out several possible properties, including particle size and specific inorganic and organic chemical constituents, such as metals and PAHs (Kelly and Fussell, 2012; Kim et al., 2015).

Wood smoke exposure, in particular, has been linked to a vast array of adverse health effects (Naeher et al., 2007; Sigsgaard et al., 2015; Zelikoff et al., 2002). Several studies compiled in the review conducted by Naeher et al. (2007) showed epidemiological evidence of respiratory symptoms (e.g. wheeze, cough, nocturnal awakening, congestion, lung function decrement, bronchiolitis or pneumonia) in children associated with the presence of woodstoves. Several respiratory symptoms (cough, sore throat, chest tightness, and phlegm) in women living in non-smoking households were also related to the use of fireplaces (Naeher et al., 2007). In Spain, a strong association between indoor air pollution exposure, from wood or charcoal burning, and COPD in women was reported by Orozco-Levi et al. (2006). Additionally, the PM levels in areas greatly impacted by wood smoke in winter were associated with increased asthma emergency room visits, increased daily mortality, and hospital admissions of cardiac and respiratory patients (Naeher et al., 2007). Sigsgaard et al. (2015) reviewed epidemiological observations in areas of the developed world where biomass combustion was a known source of ambient air pollution. Associations between PM and respiratory symptoms (chest congestion and wheeze) in young children, low birth weight, otitis media, infant bronchiolitis, cardiovascular mortality, increased medication use, decreased lung function, increased respiratory and cardiovascular (excluding ischaemic heart disease) hospital admissions, emergency room visits for asthma and hospitalisations were among the positive correlations found in the reviewed studies. Studies of health impacts following wood stove intervention strategies in USA, Canada and Australia have been also reviewed by Sigsgaard et al. (2015). In the USA, after a community wood stove exchange in Libby, Montana, the symptoms (wheeze, watery eyes, cold, bronchitis and throat infection) among school children were significantly reduced. In Launceston (Australia), the proportion of households burning wood was reduced from 66% to 30%, due to a government-coordinated fuel switching intervention, which translated in male mortality significant reductions (18% from cardiovascular and 28% from respiratory causes).

Exposure to household air pollution from solid fuel combustion is a major health hazard, affecting strongly the population in developing countries (Health Effects Institute, 2020). In 2017, 3.6 billion people (47% of the global population) were exposed to smoke from solid fuel combustion, accounting for about 1.6 million deaths worldwide (Health Effects Institute, 2019). The health outcomes arising from exposure to biomass burning smoke in developing countries have been extensively reviewed and comprise an increase in the incidence of respiratory illness, including pneumonia, tuberculosis, asthma, and COPD, as well as non-respiratory illness, such as low birth weight, cataracts and cardiovascular events (Fullerton et al., 2008; Kim et al., 2011; Laumbach and Kipen, 2012). Wylie et al. (2014) analysed the data from two cross-sectional cohorts of pregnant women, with identical case report forms and study procedures, to evaluate effects of exposure to biomass smoke on birth weight, preterm birth and stillbirth. Although the authors found insignificant associations between wood fuel use and reduced birth weight, a persistent adverse impact on preterm delivery was recorded.

In developing countries, air pollution from biomass fuel combustion is a major health concern affecting mainly women and children owing to the considerable amount of time spent in the proximity to combustion sources (Balmes, 2019; Sood, 2012; WHO, 2016). In 2012, women and children accounted for over 60% of all premature deaths from household air pollution. In low- and middle-income countries household air pollution causes over half of all pneumonia deaths in children aged under 5 years. Additionally, household air pollution is the leading cause of diseases like stroke, COPD, lung cancer and heart disease for women (WHO, 2016). Pathak et al. (2020) conducted a meta-analysis aiming to investigate the association between indoor air pollution and risk of COPD and chronic bronchitis. The pooled analysis showed that exposure to indoor air pollution arising from solid biomass fuel combustion increased the risks of COPD and chronic bronchitis by 2.65 and 2.89 times, respectively, compared to non-biomass fuels. Similarly, in a systematic review, Kurmi et al. (2010) found positive associations between the use of solid fuels and COPD and chronic bronchitis. Pooled estimates for different types of fuel revealed that exposure to wood smoke while performing domestic work presents a greater risk of development COPD and chronic bronchitis than other fuels. According to the WHO global household energy database, in low- and middle-income countries, more than 50% of residents use biomass as primary cooking fuel (WHO, 2016).

In developing countries, solid fuels are usually burned in simple and highly inefficient stoves (e.g. pit in the ground, three rocks/stones, or U-shaped hole in a block of clay), without flues or chimneys to vent the smoke outside, leading to extremely high pollutant concentrations in the vicinity of the stove (ASHRAE, 2016; Balmes, 2019). Exposure is frequently aggravated by the unproper space ventilation (Balmes, 2019). The use of cleaner fuels, such as electricity, would be the most effective measure to reduce the exposure to solid fuel combustion smoke. However, taking into consideration the unfeasibility of this option, other interventions have been targeted. Interventions to reduce adverse respiratory outcomes from solid fuel smoke exposure in developing countries included outdoor relocation of cooking with solid fuels, partitioning of kitchen from living space, window in kitchen and improved cookstoves (Sood, 2012). Given the importance of the combustion efficiency in the emission of contaminants, controlled trials have been conducted to assess the health impact of reducing indoor air pollution through the improvement of the combustion technology and/or fuel (Jack et al., 2015; Mortimer et al., 2017; Romieu et al., 2009; Smith et al., 2011). Mortimer et al. (2017) hypothesised that replacing open fires with cleaner biomass cookstoves would reduce pneumonia incidence in children. The researchers found no evidence that the intervention contributed to a decrease in the risk of pneumonia in young Malawian children but observed a reduction in burns. Smith et al. (2011) investigated the effects of a stove intervention on pneumonia in rural Guatemalan children where, traditionally, cooking is performed using wood fuels in open fires. Findings from the trial have shown that, although a significant reduction in severe pneumonia was recorded, the chimney stove did not significantly reduce physician-diagnosed pneumonia in children. The researchers hypothesised that the reasons for no effect being detected could be mainly attributable to insufficient exposure reduction. Parajuli et al. (2016) conducted a study in Nepalese rural settlements in order to evaluate the indoor air quality in households with traditional and improved cookstoves. Although the study reported remarkable lower particle concentrations in the households with improved stoves than in the households with traditional cookstoves, the $PM_{2.5}$ average concentration was still very high (825 ± 731 µg m^{-3}), largely exceeding the WHO indoor air quality guidelines ($PM_{2.5}$: 25 µg m^{-3} 24-h mean). Onyeneke et al. (2019) utilised cross-sectional data from Cross River State to analyse the impacts of improved cook stoves on the environmental and health outcomes of rural women. This study found no evidence of the reduction of indoor air pollution linked diseases associated with stove design and users' behaviour. The researchers pointed the need to rethink the stove design and to consider the behaviour of the user while cooking. Although several studies found no statistically significant effects on primary health outcomes, in the other cases, the improvement of stoves has proven to be an effective measure in reducing morbidity in developing countries (Laumbach and Kipen, 2012; McCracken et al., 2007; Romieu et al., 2009).

1.2.1. Deposition of particles in the respiratory tract

Upon inhalation, particles may deposit in the respiratory tract (RT) or be exhaled. Regarding deposition of PM, the human RT can be divided into three main anatomical regions: i) extrathoracic or nasopharyngeal region, ii) tracheobronchial region and iii) pulmonary or alveolar region (Fig. 1.2). These regions are very distinct in terms of their structure, airflow patterns, function, retention time and sensitivity to deposited particles (Hinds, 1999; Kulkarni et al., 2011; Lippmann et al., 1980).

The deposition of particles in the RT is governed by mechanisms of impaction, settling, diffusion, and by some minor mechanisms, namely interception and electrostatic deposition (Asgharian et al., 2018; Hinds, 1999; Hofmann, 2011; Lippmann et al., 1980). The deposition of inhaled particles in regions of the RT is driven by the physicochemical properties of the particles (e.g. size, hygroscopicity, shape, density) and the characteristics of individuals (e.g. age, gender, health status, breathing pattern, anatomy of the airways, etc.) (Hinds, 1999; Lippmann et al., 1980).

The adverse response to inhaled particles depends on the time of interaction between the lung tissue and the particles. For this reason, the retention of particles within the RT plays a major role on the health outcomes (Kulkarni et al., 2011). After inhalation, particles can be cleared from the RT by natural defence mechanisms that operate in different regions of the lung to eliminate foreign material. In the extrathoracic region, mechanical clearance (e.g. sneezing, coughing or swallowing of the deposited material) is the main protective mechanism. In the tracheobronchial region, mucociliary clearance (e.g. secretion of mucus loaded with particles) is the mechanism to remove deposited particles. At the alveolar surface, macrophages (white blood cells produced by the differentiation of monocytes in tissues) help to engulf and relocate foreign material through their phagocytic activity. Another clearance mechanism is translocation in which the material absorbed from the RT (tracheobronchial or alveolar region) is transferred to other tissues in the body. Finally, particles can be dissociated into material that can be absorbed into the blood (Hussain et al., 2011; Kulkarni et al., 2011).

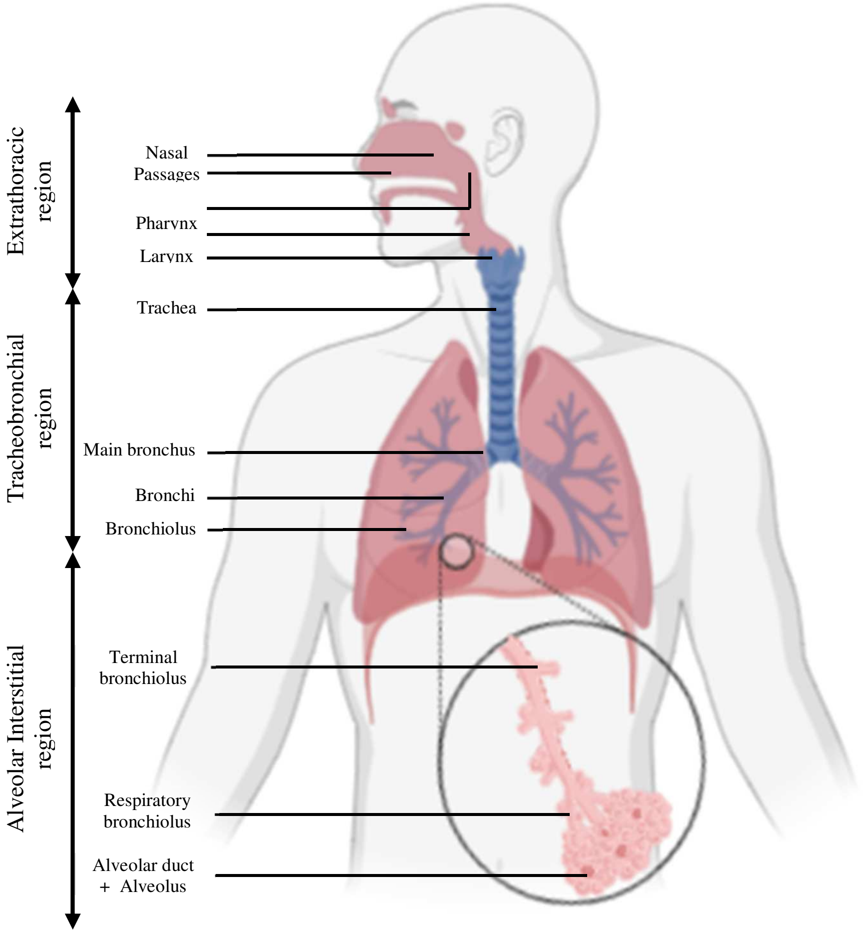

Figure 1.2. Anatomical regions of the human respiratory tract. Adapted from ICPR (1994).

The estimation of the deposition of inhaled particles is of great importance to understand dose-response relationships and to assess the inhalation risks associated with PM. For this reason, research effort has been devoted to quantify the deposition of particles in the RT through a vast array of different techniques. The total lung deposition can be measured directly *in vivo* by monitoring the concentrations of inhaled and exhaled particles (Kim, 2009; Löndahl et al., 2014, 2008; Muala et al., 2015). The regional deposition can be estimated indirectly *in vivo*, for example, by means of radioaerosol inhalation (Kim, 2009). Experimental determination of aerosol deposition patterns has been also carried out using models and replica casts of human airways (e.g. Kim et al., 1994; Oldham et al., 2000; Schlesinger et al., 1977; Zhou and Cheng, 2005). Additionally, numerous mathematical models have been developed to predict the total and regional particle deposition in the human RT (e.g. Aleksandropoulou and Lazaridis, 2013; Hofmann, 2011; Hussain et al., 2011; ICRP, 1994). The comparisons between experimentally obtained and modelled total deposition fractions have shown reasonable correlations (Hofmann, 2011; Lazaridis et al., 2001; Löndahl et al., 2008).

1.2.2. Biological mechanisms

Several mechanisms have been proposed to explain the associations between exposure to PM and adverse health effects found in epidemiological studies. The proposed mechanisms involved in the physiopathology of disease include oxidative stress, inflammation, genotoxicity and cytotoxicity.

Reactive oxygen species (ROS) are produced under normal cellular metabolism and are involved in physiological reactions, which are beneficial against infection (Mazzoli-Rocha et al., 2010). However, the imbalance between the production of ROS and the anti-oxidant defence can trigger oxidative stress (Gurjar et al., 2010; Li et al., 2003; Mazzoli-Rocha et al., 2010). Oxidative stress mediated by PM can arise from the direct generation of ROS (surface of particles or adsorbed compounds) or upon particle-cell interactions (Knaapen et al., 2004; Mazzoli-Rocha et al., 2010; Peixoto et al., 2017; Risom et al., 2005). At low levels of oxidative stress, several antioxidant and detoxification enzymes are induced, and PM exposure does not lead to adverse biological outcomes. When the antioxidant response fails or is inadequate to deal with increasing ROS production, intermediate levels of oxidative stress can induce a pro-inflammatory response. At high levels of oxidative stress, the antioxidant defences are overwhelmed, resulting in cytotoxic effects (Li et al., 2003; Valavanidis et al., 2008). Cell death, under overpowering levels of ROS, may be the underlying mechanism of the development or exacerbation of respiratory diseases, such as emphysema and COPD (Peixoto et al., 2017). Oxidative stress and inflammation are closely related processes that can be induced by each other (Traboulsi et al., 2017).

Inflammation is regarded as an important mechanism involved in PM-induced health effects (Anderson et al., 2012; Schwarze et al., 2006). This process comprises cells of the immune system and the production and release of signalling molecules, such as cytokines and chemokines, that mediate both immune cell recruitment and intracellular signalling control mechanisms (King, 2007; Turner et al., 2014). Alveolar macrophages and epithelial cells play an important role in the onset of inflammatory responses upon PM exposure (Corsini et al., 2019). The activity of the immune cells stimulates the release of inflammatory mediators and ROS, which accumulate in the damaged area and may lead to cell death. The vicious cycle that increases and/or prolongs the inflammatory reactions can overwhelm the defence mechanisms and possibly progress to chronic inflammation (Duan et al., 2020; Schwarze et al., 2006). The local lung inflammation stimulated by PM can leak into systemic circulation and lead to cardiovascular system and reproductive adverse effects, including low birth weight (Corsini et al., 2019).

There are three main pathways linking PM to adverse cardiovascular effects (Fig. 1.3). The first one reflects the ability of small sized particles or particle constituents to translocate into the systemic circulation, therefore, gaining access to different extra pulmonary sites. Through this pathway, particles can have a direct effect on the cardiovascular system (Du et al., 2016; Fiordelisi et al., 2017). Additionally, particles can affect the cardiovascular system by two indirect pathways. One is mediated by pulmonary oxidative stress and inflammatory response and the other is related to the ability of particles to impact the autonomic nervous system (Du et al., 2016; Fiordelisi et al., 2017; Nemmar et al., 2013; Schwarze et al., 2006). PM exposure can lead to changes in autonomic nervous system balance leading to changes in the pattern of breathing, and heart rate variability. Heart rate variability can be associated with the higher risk of cardiac arrhythmias (Schwarze et al., 2006). Additionally, PM may induce changes in blood coagulation, which can lead to the development of myocardial infarction (Schwarze et al., 2006).

Particle-induced genotoxicity can result from primary (absence of pulmonary inflammation) and secondary genotoxicity (particle-elicited inflammation). Primary genotoxicity can be induced by distinct mechanisms, such as ROS generation (e.g. from particle surfaces), or DNA-adduct formation by reactive metabolites of particle-bound organic compounds (e.g. PAHs). Secondary genotoxicity involves a pathway of genetic damage resulting from the oxidative DNA attack by ROS/reactive nitrogen species (RNS) generated during particle-elicited inflammation (Gurjar et al., 2010; Schins and Knaapen, 2007). DNA attack by oxidants can lead to DNA structural alterations (e.g. base pair mutations, deletions or insertions). Additionally, ROS and RNS can also interact with lipids and proteins abundantly present in biomembranes, resulting in oxidised molecules. These, upon reaction, can produce several products that are known to damage DNA and are associated with mutagenesis (Knaapen et al., 2004). Cells have their own protective mechanisms (e.g. DNA repair, apoptosis, cell cycle arrest) to maintain DNA integrity and prevent cell dysfunction and uncontrolled growth and proliferation. However, erroneous DNA repair and apoptosis failure may eventually culminate in malignant lung disease (Gurjar et al., 2010; Knaapen et al., 2004; Peixoto et al., 2017).

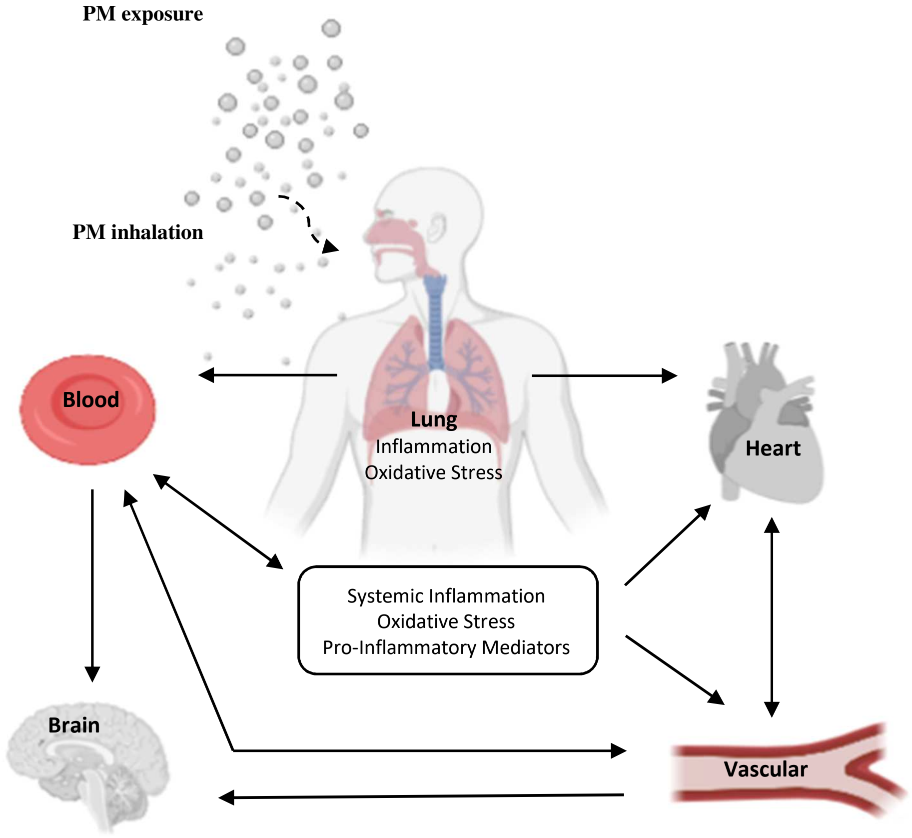

Figure 1.3. Potential pathways linking PM exposure with cardiopulmonary morbidity and mortality. Adapted from Pope and Dockery (2006).

As described above, PM can trigger cell death by distinct pathways, including inflammation, oxidative stress, and DNA damage. There are three main cell death mechanisms: apoptosis, necrosis and autophagy (Peixoto et al., 2017; Traboulsi et al., 2017). Apoptosis is a programmed cell death characterised by cellular fragmentation, membrane blebbing and cell shrinkage. Necrosis is an uncontrolled death pathway characterised by the loss of cell membrane integrity and cell swelling. Autophagy is a form of programmed cell death. It is morphologically characterised by the vacuolisation, degradation of cytoplasmic contents, and slight chromatin condensation (Fink and Cookson, 2005; Peixoto et al., 2017; Traboulsi et al., 2017). The intensity of oxidative stress appears to have a key role in the cell death pathway. Under tolerable levels of ROS, cells undergo apoptosis in order to protect other cells from inflammation and avoid the proliferation of damaged cells. At increasing levels of ROS, oxidised proteins trigger autophagosome formation and prevent further oxidative stress to protect other cells. In the case of intense exposure to high PM levels, the inflammation and exacerbation of oxidative stress may result in so much damage that mitochondrial dysfunction and destabilisation of the cellular mechanisms leads to necrotic cell death (Peixoto et al., 2017).

1.2.3. PM toxicity *in vivo*

While the evidence of PM-induced health effects has been highlighted in epidemiological studies, toxicological studies can shed light into the biological mechanisms involved in the recorded associations. *In vivo* studies, both in humans and animals, have been conducted in order to assess the effect of wood smoke on lung function and on specific biomarkers (e.g. measured in body fluids such as urine and blood, tissue samples, exhaled breath) related to disease (Bølling et al., 2009; Lewtas, 2007; McCracken et al., 2012).

An overview of outcomes after exposure of animals to wood smoke were presented in the reviews by Naeher et al. (2007) and Zelikoff et al. (2002). Overall, these reviews gather evidence that wood smoke can compromise pulmonary immune defence mechanisms, which are vital for resistance against pulmonary infections. Regarding acute exposures, Naeher et al. (2007) reviewed the outcomes of *in vivo* wood smoke inhalation studies, using rabbits as test subjects, which included epithelial cell injury, mucociliary escalator dysfunction, and inflammatory response. In short-term experiments with rats and mice, loss of epithelium, lipid peroxidation and inflammatory response were observed, because of wood smoke inhalation. The ability of short-term repeated exposure to wood smoke to exacerbate allergic airway responses in already sensitised mice was investigated by Barrett et al. (2006). The researchers reported that although the effects of wood smoke on allergic airway parameters were relatively mild, they were comparable to those observed with other pollutant mixtures, such as diesel exhaust. More recently, two studies examined the toxicological properties of particles from different small-scale combustion appliances, representing old and modern technologies, after exposure of healthy C57BL/6J mice by intratracheal aspiration (Happo et al., 2013; Uski et al., 2012). In the aforementioned studies, particles from modern technologies evoked greater inflammation compared to those from old technology appliances and increased inflammatory activity was associated with ash components of the PM emissions. Moreover, Happo et al. (2013) also found the highest cytotoxic and genotoxic activities for PM emissions from modern technology appliances after evaluation of lung tissue damage. The effects of exposure to wood smoke particles by intragastric or intratracheal instillation of Fischer 344 rats was investigated by Danielsen et al. (2010). The researchers evaluated wood smoke particles collected under high and low oxygen supply in order to produce particles with different physicochemical characteristics. Findings from this study demonstrated that exposure to wood smoke can induce oxidative stress and inflammation in both liver and lung by the pulmonary and oral exposure routes.

Over the past years, several controlled human inhalation studies have investigated the toxicity of wood smoke-derived PM to complement epidemiological observations. Unosson et al. (2013) reported arterial stiffness and reduction in heart rate variability in subjects exposed to diluted wood smoke (PM_1 = 314 ± 38 µg m^{-3}, 3-h exposure) from a common Nordic woodstove. In a controlled inhalation study with healthy humans, diluted smoke ($PM_{2.5}$ = 240 - 280 µg m^{-3}, 4-h exposure, 2 sessions 1 week apart) from wood combustion in a woodstove caused an inflammatory response, and signs of increased oxidative stress, lipid peroxidation and altered coagulation factor levels in blood (Barregard et al., 2008, 2006). However, Sehlstedt et al. (2010) found no acute airway inflammatory responses after exposure of healthy subjects to diluted wood smoke ($PM_{2.5}$ = 224 ± 22 µg m^{-3}, 3-h exposure) from a wood pellet boiler operating under incomplete combustion conditions with PM emissions dominated by organic matter. Similarly, Stockfelt et al. (2013) reported that markers of systemic inflammation did not increase after exposure of healthy adults to wood smoke from the start-up and burn-out phases of the wood-burning cycle ($PM_{2.5}$ = 295 µg m^{-3} and 146 µg m^{-3}). Moreover, the researchers found that the effects on biomarkers of coagulation and lipid peroxidation did not indicate an increased risk of cardiovascular diseases in healthy adults by short-term exposure to wood smoke. Furthermore, Forchhammer et al. (2012) investigated the level of oxidatively damaged DNA and biomarkers related to inflammation, oxidative stress and DNA repair after exposure (3-h) of non-smoking atopic subjects to 14, 220, or 354 µg m^{-3} of particles from a modern wood stove. The researchers concluded that wood smoke had no apparent effect on the studied endpoints.

1.2.4. PM toxicity *in vitro*

In vitro assays are very useful to study the pathways activated by PM at cellular level using simplified models. Despite their limitations, *in vitro* tests are less expensive and less time consuming than *in vivo* experiments, which also have associated ethical issues. For this reason, the toxicity of PM emissions from biomass burning has been assessed by several *in vitro* tests focused on different endpoints (e.g. cytotoxicity, inflammation, oxidative stress, genotoxicity), which are selected according to the mechanisms involved in the PM-related health effects.

Biomass burning particles have been reported to induce cytotoxicity and genotoxicity in human and murine cell lines (e.g. Danielsen et al., 2009; Jalava et al., 2012; Kasurinen et al., 2016, 2017; Marabini et al., 2017; Tapanainen et al., 2011; Uski et al., 2014). It appears that particles derived from different combustion appliances induce differential cytotoxicity and genotoxicity. The distinct responses have been associated with the chemical composition of the particles that is highly variable under different combustion conditions in conventional or modern combustion appliances. In fact, the physical and chemical properties of biomass burning particles, as well as the magnitude of their emissions, can differ considerably for equipment with different combustion efficiency. While studies using mouse RAW264.7 macrophages reported that particles emitted from automatically fed appliances and efficient combustion conditions are more cytotoxic than the ones arising from traditional wood combustion appliances and intermediate and smouldering combustion conditions (Leskinen et al., 2014; Tapanainen et al., 2011; Uski et al., 2014), the opposite result was reported for the potency of the particles in inducing DNA damage (Jalava et al., 2012; Tapanainen et al., 2011; Uski et al., 2014). Marabini et al. (2017) also observed higher DNA damage in A549 cells from particles collected during log wood combustion than from those arising from pellet combustion. The researchers attributed this result to the differences in the particulate PAH fraction. In addition to the combustion appliance selected, the fuel burned also appears to play a key role on the bioreactivity of the released particles (Kasurinen et al., 2017, 2016; Marchetti et al., 2019). For example, in the study by Kasurinen et al. (2017), PM_1 samples collected from a modern soapstone masonry heater fuelled with birch, spruce or beech logs were tested in a human lung epithelial cell line. The results indicated that PM_1 samples from the combustion of beech logs reduced drastically the cellular metabolic activity, whist the PM_1 from the combustion of spruce logs had the highest DNA damaging potential. In an earlier study, Kasurinen et al. (2016) tested standard softwood pellets and three alternative pellets (poplar, miscanthus, and wheat straw) and also found clear differences in the chemical composition of the PM emissions, which was reflected in their toxicological effects.

The most widely employed methods to assess the cytotoxicity of biomass burning particles are the 3-[4,5-dimethylthiazole-2-yl]-2,5-diphenyltetrazolium bromide (MTT) and lactate dehydrogenase (LDH) assays. The MTT assay evaluates the metabolic activity of cells by measuring the amount of formazan generated by active mitochondria that cleave the MTT salt, whereas the LDH assay assesses the cell membrane integrity through the measurement of the cytoplasmatic enzyme lactate dehydrogenase that leaks into the extracellular space (culture medium). While studies employing the MTT test have reported that biomass combustion derived particles are cytotoxic (Jalava et al., 2012; Kasurinen et al., 2017; Marabini et al., 2017; Tapanainen et al., 2011; Uski et al., 2014), most research using the LDH test has observed no cytotoxic effects (Corsini et al., 2013, 2017; Dilger et al., 2016; Kasurinen et al., 2017; Kocbach et al., 2008b). The discrepancy between LDH release data and the reduction in viability detected by MTT suggests that the impairment of viability may be due to the induction of the apoptotic cell death pathway in which the integrity of the plasma membrane is maintained (Peixoto et al., 2017).

Contrasting results have been reported for the generation of ROS after cell exposure to particles derived from biomass combustion. In the study carried out by Uski et al. (2014), particles from efficient combustion caused concentration-dependent increase in the ROS production in murine macrophages, while such effect was not detected with particles derived from less efficient combustion. On the other hand, Corsini et al. (2013) reported only a slight increase, not statistically significant, in ROS following exposure of lung epithelial cells to particles from the combustion of both fir and beech pellets in a pellet stove. ROS formation was reported by Dilger et al. (2016) after exposure of lung epithelial cells to particles collected from incomplete combustion of mixed fuels in a tiled stove. Marabini et al. (2017) tested fir and beech biomass in two combustion appliances, namely a pellet stove and a wood stove. The production of ROS, assessed after 24-h exposure of A549 cells, was only significant for particles emitted by beech wood combustion.

The inflammatory potential of biomass burning derived particles has been described by several studies using diverse cellular models, such as human blood monocytes (Corsini et al., 2013, 2017; Kocbach et al., 2008b), human lung epithelial cells (Corsini et al., 2017, 2013; Kasurinen et al., 2017; Marchetti et al., 2019), human epidermal keratinocytes (Ke et al., 2018), human first trimester trophoblast cell line (Erlandsson et al., 2020) and murine macrophages (Jalava et al., 2012, 2010; Kasurinen et al., 2016; Uski et al., 2014). These studies highlighted that PM-mediated inflammation depends on the chemical composition of particles, which is mainly related to the combustion technology and combustion conditions, and that different cells have distinct responses. In addition to different cell types, distinct pro-inflammatory mediators have been selected to evaluate the PM potential to trigger inflammation. Different mediators can also lead to divergent interpretations of the results. For example, Tapanainen et al. (2011) compared particles emitted from two different combustion appliances, a pellet boiler and a conventional masonry heater, reporting no statistically significant differences in mouse macrophages inflammatory responses between the two PM samples. The influence of combustion conditions (smouldering, intermediate and efficient) on the inflammatory response was investigated by Uski et al. (2014). The results suggested that samples from the intermediate condition were more potent inducing inflammation in mouse macrophages than those from efficient and smouldering combustion. The effect of the fuel selected on the pro-inflammatory effects of particles in THP-1 (Corsini et al., 2017), A549 (Corsini et al., 2017) and RAW264.7 (Kasurinen et al., 2016) cells has also been reported.

In addition to cultures of eukaryotic cells, bacterial bioassays have been developed to provide a cost effective, rapid and easy to perform tool to assess environmental pollution. Many of these tests have been applied to investigate the genotoxicity of particles from residential biomass combustion (Schulze et al., 2019; Shen, 2017, and references therein). Among bacterial assays, the Ames test has been widely used. Developed by Bruce Ames and his colleagues in the 1970s, the Ames test is a short-term bioassay that allows the detection of potential mutagenic compounds. The detailed assay guidelines can be obtained in the Organisation for Economic Co-operation and Development (OECD) test guideline 471 (OECD, 1997). The Ames test can be carried out using different tester strains of *Salmonella typhimurium* and/or *Escherichia coli* in order to detect point mutations, which involve substitution, addition or deletion of one or a few DNA base pairs (OECD, 1997). The mutagenic activity of the particulate extractable organic matter, and particularly the PAH extracts, from residential combustion of solid fuels has been assessed over the years using the Ames test (Canha et al., 2016; Shen, 2017 and references therein; Vu et al., 2012; Yang et al., 2010). The literature review performed by Shen et al. (2017) indicates that T98 and TA100 strains are the two most widely used and that the emissions from solid fuel combustion comprise not only compounds requiring mammalian activation, but also compounds that are direct acting mutagens. Additionally, the authors pointed out that the mutagenic potential of particles from biomass combustion appears to depend on the combustion technology. Additionally, the combustion stage (flaming versus smouldering) also plays a major role regarding the mutagenic potency of particles from biomass burning, as described by Kim et al. (2018). The researchers found that, on a mass basis, flaming samples were more active than smouldering samples. More recently, Champion et al. (2020) burned two types of pellets in three cookstoves and evaluated the mutagenicity of the extractable organic matter from the filter-bound PM. The mutagenicity emission factors obtained by the researchers spanned 3 orders of magnitude and correlated with PAHs.

Toxicity assays using luminescent bacteria have been widely applied, including in the investigation of environmental samples, such as particulate matter (Abbas et al., 2018; Girotti et al., 2008; Kováts and Horváth, 2016; Ma et al., 2014). According to Tositti et al. (2018), although the light emission inhibition assays lack of specificity, they allow assessing the overall toxic potential of any sample, providing a simple and efficient methodology useful as a screening tool. One of the most commonly used bioluminescence inhibition assays is based on the *Vibrio fischeri* bacterium. There are several commercial test kits using this strain (e.g. Microtox, LUMIStox and ToxAlert). The bioassay has been widely applied to characterise the toxicity of ambient aerosols (Aammi et al., 2017; Evagelopoulos et al., 2009; Kováts et al., 2012; Pintér et al., 2017; Roig et al., 2013; Romano et al., 2020; Turóczi et al., 2012), particulate exhaust emissions (Ács et al., 2013; Corrêa et al., 2017; Kováts et al., 2013; Turóczi et al., 2012; Vouitsis et al., 2009), particles from solid fuel in fluidised bed reactors (Barbosa et al., 2013, 2009; Skodras et al., 2009) and, to a lesser extent, residential biomass combustion-derived particles (Turóczi et al., 2012). Turóczi et al. (2012) collected biomass smoke samples downwind from softwood and hardwood burning in an open fireplace. The *Vibrio fischeri* bioluminescence inhibition bioassay was employed to assess the overall ecotoxicity of PM. The ecotoxicity of urban aerosol, diesel PM, resuspended road dust, particles from cigarette smoking and biomass burning particles was compared revealing that wood smoke was more ecotoxic than particulates emitted from modern diesel engines.

1.3. Objectives

The mounting evidence on the importance of the contribution of residential biomass combustion to the aerosol burden, led to carry out several studies focused on the characterisation of emissions from this source, taking into account fuel and appliance specificities at country level (Olsen et al., 2020; Vicente and Alves, 2018). In Portugal, within the nationally funded research project BIOEMI (PTDC/AMB/65706/2006), characteristic emission profiles have been developed for the prevalent Portuguese biofuels burned in representative traditional appliances (fireplace and woodstove) in use in the country. In the framework of the AIRUSE-LIFE project, the influence of operational practices on emissions from Portuguese batch fired combustion appliances was evaluated. Moreover, several biofuels, including agro-fuels, were tested for their environmental impact in an automatically fed pellet stove purchased in Portugal. The databases produced by both projects included emission factors of both gaseous and particulate matter, as well as the detailed chemical characterisation of PM (water soluble ions, trace elements, organic carbon, elemental carbon, and several organic compounds). Despite the development of novel emission databases, for the first time, with country-specific chemical signatures for residential biomass combustion in the framework of these projects, there are still many gaps in knowledge. In fact, considering that modern combustion appliances, such as pellet stoves, are gaining prominence among homeowners, and taking into account the search for new raw materials for pellet production, as well as the introduction of certified pelletised fuels in the market, research efforts need to be devoted into the characterisation of emissions from these appliances fuelled either with new commercially available pellets or with pellets made with new, potentially relevant, raw materials. Despite the wealth of publications on emissions and composition of particles from residential biomass combustion (Olsen et al., 2020; Vicente and Alves, 2018), the impact of this source on the indoor air quality of Portuguese households has been far less studied (Canha et al., 2018), especially with regard to the chemical characteristics and bioreactivity of the emitted particles.

Knowledge of PM-related biological effects is crucial for assessing human risk of inhalation. *In vitro* toxicological studies have demonstrated that different toxic mechanisms are activated by biomass burning particles, depending on the combustion appliances and fuels (studies described in section 1.2.4). Although several studies encompassed toxicological and physicochemical characterisation of PM from small combustion appliances, it is noteworthy that current data is based mostly on combustion appliances and fuels commonly used in Nordic countries (Danielsen et al., 2009; Erlandsson et al., 2020; Jalava et al., 2012, 2010; Kocbach et al., 2008a, 2008b; Leskinen et al., 2014; Tapanainen et al., 2011; Uski et al., 2014). Regarding indoor PM arising from the operation of combustion appliances, there is still a paucity of toxicological data and physicochemical profiles of the emitted particles. So far, only two studies have focused on the assessment of the *in vitro* bioreactivity of the indoor PM produced by biomass combustion (Ke et al., 2018; Marchetti et al., 2019). In spite of the scarce research on the subject, there is evidence that indoor combustion particles from different biomass sources may impact on lung cells and keratinocytes according to different pathways (Ke et al., 2018; Marchetti et al., 2019).

The main objective of this thesis was to assess the chemical composition and toxicity of particles from residential biomass combustion, including different biofuels, small-scale wood or pellet-fuelled heating systems. The investigation was based on laboratory and field measurements, encompassing a comprehensive characterisation of particulate species.

In order to fulfil this general objective, the following specific aims were defined:

- to perform an extensive and critical bibliographic compilation of particulate emission factors from residential biomass combustion obtained worldwide and to identify knowledge gaps and research opportunities (Paper I);
- to characterise the particulate and gaseous emissions from the combustion of pelletised commercial fuels under different operating conditions (Paper II);
- to determine the effect of an alternative pelletised raw material on particulate and gaseous emissions from a residential pellet stove (Paper III);
- to evaluate the role of the type of pellet burned in the toxic potential of the PM emitted by using a battery of approaches (Paper IV);
- to clarify how the operation of Portuguese wood burning appliances can affect the indoor levels and chemical properties of PM (Paper V);
- to estimate the dose in the respiratory tract based on PM exposure during the operation of wood combustion appliances, indoors and outdoors (Paper VI);
- to determine the role of distinct wood burning appliances in the biological effects associated with the PM emitted and to explore links between the toxicological outcomes and the chemical properties of particles (Paper VII).

1.4. List of publications and author's contribution

The research presented in this document was mostly held in the Department of Environment and Planning, Department of Biology and Centre for Environmental and Marine Studies (CESAM) of the University of Aveiro. An internship at the Centre of Environmental Sciences of the University of Pannonia in Veszprém, Hungary, was also carried out. This thesis is based on the following seven scientific research articles:

Paper I. Vicente, E.D., Alves, C.A., 2018. An overview of particulate emissions from residential biomass combustion. Atmos. Res. 199, 159–185. http://dx.doi.org/10.1016/j.atmosres.2017.08.027

Paper II. Vicente, E.D., Vicente, A.M., Evtyugina, M., Tarelho, L.A.C., Almeida, S.M., Alves, C., 2020. Emissions from residential combustion of certified and uncertified pellets. Renew. Energy 161, 1059–1071. https://doi.org/10.1016/j.renene.2020.07.118

Paper III. Vicente, E.D., Vicente, A.M., Evtyugina, M., Carvalho, R., Tarelho, L.A.C., Paniagua, S., Nunes, T., Otero, M., Calvo, L.F., Alves, C., 2019. Emissions from residential pellet combustion of an invasive acacia species. Renew. Energy 140, 319–329. https://doi.org/10.1016/j.renene.2019.03.057

Paper IV. Vicente, E.D., Figueiredo, D., Gonçalves, C., Lopes, I., Kováts, N., Oliveira, H., Alves, C.A. (to be submitted). *In vitro* toxicity of PM_{10} emissions from residential pellet combustion. Environmental Research.

Paper V. Vicente, E.D., Vicente, A.M., Evtyugina, M., Oduber, F.I., Amato, F., Querol, X., Alves, C., 2020. Impact of wood combustion on indoor air quality. Sci. Total Environ. 705, 135769. https://doi.org/10.1016/j.scitotenv.2019.135769

Paper VI. Vicente, E.D., Alves, C.A., Martins, V., Almeida, S.M. Lazaridis, M. (submitted). Lung-deposited dose of particulate matter from residential exposure to smoke from wood burning. Environmental Science and Pollution Research.

Paper VII. Vicente, E.D., Figueiredo, D., Gonçalves, C., Oliveira, H., Lopes, I., Kováts, N., Pinheiro, T., Alves, C.A (submitted). *In vitro* toxicity of indoor and outdoor PM_{10} from residential wood combustion. Science of the Total Environment.

Paper I integrates a literature review on particulate emissions from residential biomass combustion. It was written jointly by the author and C.A. Alves.

Paper II presents pellet stove emissions for different commercial pellet fuels (certified and non-certified) under distinct operating conditions. The laboratory experiments were designed by C. Alves, L.A.C. Tarelho and the author. The author was responsible for conducting the experiments, including sampling, with the assistance of L.A.C. Tarelho. The author carried out the ion and carbon analyses and prepared the PM_{10} samples for the organic speciation by gas chromatography–mass spectrometry (GC-MS). A.M. Vicente and M. Evtyugina were responsible for this latter analytical determination. The author analysed and interpreted the data and wrote the manuscript under the supervision of C. Alves and S.M. Almeida.

Pellets made of wood from an invasive acacia species were tested in a pellet stove. Combustion emissions are analysed in Paper III. These pellets were manufactured by L.A.C. Tarelho. The experiments, comprising sampling, were conducted by the author with the assistance of R. Carvalho and S. Paniagua. The author performed the carbon and ion analyses under the supervision of T. Nunes. The preparation and clean-up of PM_{10} samples for the analysis of organic constituents were also carried out by the author. A.M. Vicente and M. Evtyugina were responsible for the detailed organic speciation. The author analysed and interpreted the data and contributed the most to writing the manuscript. C. Alves, M. Otero and L.F. Calvo made a critical review.

Paper IV includes the evaluation of the ecotoxic, cytotoxic and mutagenic potential of PM_{10} emitted from the combustion of four different pellets types (two brands of certified pellets, one commercial brand of non-certified pellets and laboratory made pellets from an invasive species). The conceptualisation of the work was made by the author and C. Alves. The evaluation of the ecotoxicity of the samples was performed by the author under the supervision of N. Kováts. The cytotoxicity assays were carried out by the author with the assistance of D. Figueiredo under the supervision of H. Oliveira. The mutagenic potential of the samples was evaluated by the author and C. Gonçalves with the supervision of I. Lopes. The author performed the interpretation of results, statistical analysis and writing of the paper, which was reviewed by the co-authors before submission.

Paper V involves the study of the impact of wood burning on indoor air quality. The field measurements were conceptualised by the author and C. Alves. The author was responsible for carrying out the field measurements. The analysis of metals was performed by F. Amato and X. Querol, while the detailed organic characterisation of the PM_{10} samples was conducted by A.M. Vicente and M. Evtyugina after the preparation of the samples by the author and F. Oduber. The author was in charge of carbon and ion analysis, interpretation of results and writing of the paper, which was reviewed in detail by C. Alves before submission.

The lung-deposited dose of particulate matter from residential exposure to smoke from wood burning was assessed in paper VI. The work was conceptualised by the author and C. Alves. The author applied the ExDoM2 model with the support of V. Martins. M. Lazaridis validated the results.

The author was responsible for the interpretation of results and writing of the paper, which was reviewed in detail by all co-authors before submission.

Paper VI comprises the toxicity evaluation of indoor and outdoor PM_{10} from residential wood combustion using a battery of *in vitro* tests (*Vibrio Fischeri* bioluminescence inhibition assay, cytotoxicity assays and Ames test). The work was planned by the author and C. Alves. The author carried out the ecotoxicity assessment using the *Vibrio Fischeri* bacteria. The cytotoxicity of the particulate samples was evaluated by the author and D. Figueiredo, whilst the mutagenicity evaluation was performed by the author and C. Gonçalves. The ecotoxicity, cytotoxicity and mutagenicity assays were supervised by N. Kováts, H. Oliveira and I. Lopes, respectively. Data interpretation, statistical analysis and writing of the manuscript were performed by the author. All co-authors reviewed the manuscript before submission.

References

Aammi, S., Karaca, F., Petek, M., 2017. A toxicological and genotoxicological indexing study of ambient aerosols ($PM_{2.5-10}$) using *in vitro* bioassays. Chemosphere 174, 490–498. https://doi.org/10.1016/j.chemosphere.2017.01.141

Abbas, M., Adil, M., Ehtisham-ul-Haque, S., Munir, B., Yameen, M., Ghaffar, A., Shar, G.A., Asif Tahir, M., Iqbal, M., 2018. *Vibrio fischeri* bioluminescence inhibition assay for ecotoxicity assessment: a review. Sci. Total Environ. 626, 1295–1309. https://doi.org/10.1016/j.scitotenv.2018.01.066

Ács, A., Ferincz, Á., Kovács, A., Jancsek-Turóczi, B., Gelencsér, A., Kiss, G., Kováts, N., 2013. Ecotoxicological characterisation of exhaust particulates from diesel-powered light-duty vehicles. Cent. Eur. J. Chem. 11, 1954–1958. https://doi.org/10.2478/s11532-013-0326-0

Aleksandropoulou, V., Lazaridis, M., 2013. Development and application of a model (ExDoM) for calculating the respiratory tract dose and retention of particles under variable exposure conditions. Air Qual. Atmos. Health 6, 13–26. https://doi.org/10.1007/s11869-010-0126-z

Alves, C.A., Vicente, E.D., Rocha, S., Vicente, A.M., 2017. Organic tracers in aerosols from the residential combustion of pellets and agro-fuels. Air Qual. Atmos. Health 10, 37–45. https://doi.org/10.1007/s11869-016-0406-3

Amann, M., Cofala, J., Klimont, Z., Nagl, C., Schieder, W., 2018. Measures to address air pollution from small combustion sources. Amann M. (Ed.). International Institute for Applied Systems Analysis (IIASA) and Environment Agency, Austria

Anderson, J.O., Thundiyil, J.G., Stolbach, A., 2012. Clearing the air: a review of the effects of particulate matter air pollution on human health. J. Med. Toxicol. https://doi.org/10.1007/s13181-011-0203-1

Asgharian, B., Owen, T.P., Kuempel, E.D., Jarabek, A.M., 2018. Dosimetry of inhaled elongate mineral particles in the respiratory tract: the impact of shape factor. Toxicol. Appl. Pharmacol. 361, 27–35. https://doi.org/10.1016/j.taap.2018.05.001

ASHRAE, 2016. ASHRAE Position Document on Combustion of solid fuels and indoor air quality in primarily developing countries. American Society of Heating, Refrigerating and Air-Conditioning Engineers. Georgia, USA.

Balmes, J.R., 2019. Household air pollution from domestic combustion of solid fuels and health. J. Allergy Clin. Immunol. https://doi.org/10.1016/j.jaci.2019.04.016

Barbosa, R., Dias, D., Lapa, N., Lopes, H., Mendes, B., 2013. Chemical and ecotoxicological properties of size fractionated biomass ashes. Fuel Process. Technol. 109, 124–132. https://doi.org/10.1016/j.fuproc.2012.09.048

Barbosa, R., Lapa, N., Boavida, D., Lopes, H., Gulyurtlu, I., Mendes, B., 2009. Co-combustion of coal and sewage sludge: Chemical and ecotoxicological properties of ashes. J. Hazard. Mater. 170, 902–909. https://doi.org/10.1016/j.jhazmat.2009.05.053

Bari, M.A., Baumbach, G., Brodbeck, J., Struschka, M., Kuch, B., Dreher, W., Scheffknecht, G., 2011. Characterisation of particulates and carcinogenic polycyclic aromatic hydrocarbons in wintertime wood-fired heating in residential areas. Atmos. Environ. 45, 7627–7634. https://doi.org/10.1016/j.atmosenv.2010.11.053

Barregard, L., Sällsten, G., Andersson, L., Almstrand, A.C., Gustafson, P., Andersson, M., Olin, A.C., 2008. Experimental exposure to wood smoke: effects on airway inflammation and oxidative stress. Occup. Environ. Med. 65, 319–324. https://doi.org/10.1136/oem.2006.032458

Barregard, L., Sällsten, G., Gustafson, P., Andersson, L., Johansson, L., Basu, S., Stigendal, L., 2006. Experimental exposure to wood-smoke particles in healthy humans: effects on markers of inflammation, coagulation, and lipid peroxidation. Inhal. Toxicol. 18, 845–853. https://doi.org/10.1080/08958370600685798

Barrett, E.G., Henson, R.D., Seilkop, S.K., McDonald, J.D., Reed, M.D., 2006. Effects of hardwood smoke exposure on allergic airway inflammation in mice. Inhal. Toxicol. 18, 33–43. https://doi.org/10.1080/08958370500282340

Bartington, S.E., Bakolis, I., Devakumar, D., Kurmi, O.P., Gulliver, J., Chaube, G., Manandhar, D.S., Saville, N.M., Costello, A., Osrin, D., Hansell, A.L., Ayres, J.G., 2017. Patterns of domestic exposure to carbon monoxide and particulate matter in households using biomass fuel in Janakpur, Nepal. Environ. Pollut. 220, 38–45. https://doi.org/10.1016/j.envpol.2016.08.074

Berndes, G., Baxter, L., Coombes, P., Delcarte, J., Evald, A., Hartmann, H., Jansen, M., Koppejan, J., Livingston, W., Loo, S. van, Madrali, S., Moghtaderi, B., Nägele, E., Nussbaumer, T., Obernberger, I., Oravainen, H., Preto, F., Skreiberg, Ø., Tullin, C., Thek, G., 2008. The Handbook of Biomass Combustion and Co-firing. Earthscan, London, UK.

Bertelsen, N., Mathiesen, B.V., 2020. EU-28 residential heat supply and consumption: historical development and status. Energies 13. https://doi.org/10.3390/en13081894

Bølling, A.K., Pagels, J., Yttri, K.E., Barregard, L., Sallsten, G., Schwarze, P.E., Boman, C., 2009. Health effects of residential wood smoke particles: the importance of combustion conditions and physicochemical particle properties. Part. Fibre Toxicol. 6, 29. https://doi.org/10.1186/1743-8977-6-29

Boman, C., Nordin, A., Bostrom, D., Ohman, M., 2004. Characterization of inorganic particulate matter from residential combustion of pelletized biomass fuels. Energ. Fuel. 18, 338–348.

Boman, C., Pettersson, E., Westerholm, R., Boström, D., Nordin, A., 2011. Stove Performance and emission characteristics in residential wood log and pellet combustion, part 1: pellet stoves. Energ. Fuel. 25, 307–314. https://doi.org/10.1021/ef100774x

Calvo, A.I., Martins, V., Nunes, T., Duarte, M., Hillamo, R., Teinila, K., Pont, V., Castro, A., Fraile, R., Tarelho, L., Alves, C., 2015. Residential wood combustion in two domestic devices: Relationship of different parameters throughout the combustion cycle. Atmos. Environ. 116, 72–82. https://doi.org/10.1016/j.atmosenv.2015.06.012

Canha, N., Lage, J., Galinha, C., Coentro, S., Alves, C., Almeida, S.M., 2018. Impact of biomass home heating, cooking styles, and bread toasting on the indoor air quality at Portuguese dwellings: A case study. Atmosphere (Basel) 9. https://doi.org/10.3390/atmos9060214

Canha, N., Lopes, I., Vicente, E.D., Vicente, A.M., Bandowe, B.A.M., Almeida, S.M., Alves, C.A., 2016. Mutagenicity assessment of aerosols in emissions from domestic combustion processes. Environ. Sci. Pollut. Res. 23. https://doi.org/10.1007/s11356-016-6292-2

Castro, A., Calvo, A.I., Blanco-Alegre, C., Oduber, F., Alves, C., Coz, E., Amato, F., Querol, X., Fraile, R., 2018. Impact of the wood combustion in an open fireplace on the air quality of a living room: Estimation of the respirable fraction. Sci. Total Environ. 628–629, 169–176. https://doi.org/10.1016/j.scitotenv.2018.02.001

Champion, W.M., Warren, S.H., Kooter, I.M., Preston, W., Krantz, Q.T., DeMarini, D.M., Jetter, J.J., 2020. Mutagenicity- and pollutant-emission factors of pellet-fueled gasifier cookstoves: Comparison with other combustion sources. Sci. Total Environ. 739, 139488. https://doi.org/10.1016/j.scitotenv.2020.139488

Clark, M.L., Peel, J.L., Balakrishnan, K., Breysse, P.N., Chillrud, S.N., Naeher, L.P., Rodes, C.E., Vette, A.F., Balbus, J.M., 2013. Health and household air pollution from solid fuel use: the need for improved exposure assessment. Environ. Health Perspect. 121, 1120–1128. https://doi.org/10.1289/ehp.1206429

Corrêa, A.X.R., Testolin, R.C., Torres, M.M., Cotelle, S., Schwartz, J.J., Millet, M., Radetski, C.M., 2017. Ecotoxicity assessment of particulate matter emitted from heavy-duty diesel-powered vehicles: influence of leaching conditions. Environ. Sci. Pollut. Res. 24, 9399–9406. https://doi.org/10.1007/s11356-017-8521-8

Corsini, E., Budello, S., Marabini, L., Galbiati, V., Piazzalunga, A., Barbieri, P., Cozzutto, S., Marinovich, M., Pitea, D., Galli, C.L., 2013. Comparison of wood smoke $PM_{2.5}$ obtained from the combustion of FIR and beech pellets on inflammation and DNA damage in A549 and THP-1 human cell lines. Arch. Toxicol. 87, 2187–2199. https://doi.org/10.1007/s00204-013-1071-z

Corsini, E., Marinovich, M., Vecchi, R., 2019. Ultrafine particles from residential biomass combustion: A review on experimental data and toxicological response. Int. J. Mol. Sci. 20. https://doi.org/10.3390/ijms20204992

Corsini, E., Ozgen, S., Papale, A., Galbiati, V., Lonati, G., Fermo, P., Corbella, L., Valli, G., Bernardoni, V., Dell'Acqua, M., Becagli, S., Caruso, D., Vecchi, R., Galli, C.L., Marinovich, M., 2017. Insights on wood combustion generated proinflammatory ultrafine particles (UFP). Toxicol. Lett. 266, 74–84. https://doi.org/10.1016/j.toxlet.2016.12.005

Czech, H., Miersch, T., Orasche, J., Abbaszade, G., Sippula, O., Tissari, J., Michalke, B., Schnelle-Kreis, J., Streibel, T., Jokiniemi, J., Zimmermann, R., 2018. Chemical composition and speciation of particulate organic matter from modern residential small-scale wood combustion appliances. Sci. Total Environ. 612, 636–648. https://doi.org/10.1016/j.scitotenv.2017.08.263

Danielsen, P.H., Loft, S., Jacobsen, N.R., Jensen, K.A., Autrup, H., Ravanat, J.L., Wallin, H., Møller, P., 2010. Oxidative stress, inflammation, and DNA damage in rats after intratracheal instillation or oral exposure to ambient air and wood smoke particulate matter. Toxicol. Sci. 118, 574–585. https://doi.org/10.1093/toxsci/kfq290

Danielsen, P.H., Loft, S., Kocbach, A., Schwarze, P.E., Møller, P., 2009. Oxidative damage to DNA and repair induced by Norwegian wood smoke particles in human A549 and THP-1 cell lines. Mutat. Res. - Genet. Toxicol. Environ. Mutagen. 674, 116–122. https://doi.org/10.1016/j.mrgentox.2008.10.014

Darquenne, C., Schmid, O., Prisk, G.K., 2020. Aerosols and the human lung: an introduction. World Scientific, Singapore.

de Gennaro, G., Dambruoso, P.R., Di Gilio, A., di Palma, V., Marzocca, A., Tutino, M., 2015. Discontinuous and continuous indoor air quality monitoring in homes with fireplaces or wood stoves as heating system. Int. J. Environ. Res. Public Health 13, 1–9. https://doi.org/10.3390/ijerph13010078

Dilger, M., Orasche, J., Zimmermann, R., Paur, H.R., Diabaté, S., Weiss, C., 2016. Toxicity of wood smoke particles in human A549 lung epithelial cells: the role of PAHs, soot and zinc. Arch. Toxicol. 90, 3029–3044. https://doi.org/10.1007/s00204-016-1659-1

Du, Y., Xu, X., Chu, M., Guo, Y., Wang, J., 2016. Air particulate matter and cardiovascular disease: the epidemiological, biomedical and clinical evidence. J. Thorac. Dis. 8, 8–19. https://doi.org/10.3978/j.issn.2072-1439.2015.11.37

Duan, R.-R., Hao, K., Yang, T., 2020. Air pollution and chronic obstructive pulmonary disease. Chronic Dis. Transl. Med. https://doi.org/10.1016/j.cdtm.2020.05.004

Erlandsson, L., Lindgren, R., Nääv, Å., Krais, A.M., Strandberg, B., Lundh, T., Boman, C., Isaxon, C., Hansson, S.R., Malmqvist, E., 2020. Exposure to wood smoke particles leads to inflammation, disrupted proliferation and damage to cellular structures in a human first trimester trophoblast cell line. Environ. Pollut. 264, 114790. https://doi.org/10.1016/j.envpol.2020.114790

Evagelopoulos, V., Zoras, S., Samaras, P., Triantafyllou, A., Albanis, T., Kassomenos, P., 2009. Toxicity of fine and coarse atmospheric particles using *Vibrio fischeri*, in: Kungolos, A., Aravossis, K., Karagiannidis, A., Samaras, P. (Eds.), 2nd International Conference on Environmental Management, Engineering, Planning and Economics (CEMEPE 2009) & SECOTOX Conference. Thessaloniki, Greece.

Feldmeier, S., Wopienka, E., Schwarz, M., Schön, C., Pfeifer, C., 2019. Applicability of fuel indexes for small-scale biomass combustion technologies, part 2: TSP and NOx emissions. Energ. Fuel. 33, 11724–11730. https://doi.org/10.1021/acs.energyfuels.9b02589

Fink, S.L., Cookson, B.T., 2005. Apoptosis, pyroptosis, and necrosis: Mechanistic description of dead and dying eukaryotic cells. Infect. Immun. https://doi.org/10.1128/IAI.73.4.1907-1916.2005

Fiordelisi, A., Piscitelli, P., Trimarco, B., Coscioni, E., Iaccarino, G., Sorriento, D., 2017. The mechanisms of air pollution and particulate matter in cardiovascular diseases. Hear. Fail Rev 22, 337–347. https://doi.org/10.1007/s10741-017-9606-7

Forchhammer, L., Møller, P., Riddervold, I.S., Bønløkke, J., Massling, A., Sigsgaard, T., Loft, S., 2012. Controlled human wood smoke exposure: Oxidative stress, inflammation and microvascular function. Part. Fibre Toxicol. 9, 7. https://doi.org/10.1186/1743-8977-9-7

Fullerton, D.G., Bruce, N., Gordon, S.B., 2008. Indoor air pollution from biomass fuel smoke is a major health concern in the developing world. Trans. R. Soc. Trop. Med. Hyg. 102, 843–851. https://doi.org/10.1016/j.trstmh.2008.05.028

Girotti, S., Ferri, E.N., Fumo, M.G., Maiolini, E., 2008. Monitoring of environmental pollutants by bioluminescent bacteria. Anal. Chim. Acta. https://doi.org/10.1016/j.aca.2007.12.008

Gonçalves, C., Alves, C., Fernandes, A.P., Monteiro, C., Tarelho, L., Evtyugina, M., Pio, C., 2011. Organic compounds in $PM_{2.5}$ emitted from fireplace and woodstove combustion of typical Portuguese wood species. Atmos. Environ. 45, 4533–4545. https://doi.org/10.1016/j.atmosenv.2011.05.071

Guo, L., Lewis, J.O., McLaughlin, J.P., 2008. Emissions from Irish domestic fireplaces and their impact on indoor air quality when used as supplementary heating source. Glob. Nest J. 10, 209–216.

Gurjar, B.R., Molina, L.T., Ojha, C.S. (Eds.), 2010. Air pollution. Health and environmental impacts. CRC Press, Taylor & Francis Group, New York, USA.

Happo, M.S., Uski, O., Jalava, P.I., Kelz, J., Brunner, T., Hakulinen, P., Mäki-Paakkanen, J., Kosma, V.M., Jokiniemi, J., Obernberger, I., Hirvonen, M.R., 2013. Pulmonary inflammation and tissue damage in the mouse lung after exposure to PM samples from biomass heating appliances of old and modern technologies. Sci. Total Environ. 443, 256–266. https://doi.org/10.1016/j.scitotenv.2012.11.004

Health Effects Institute, 2020. State of Global Air 2020. Special Report, Health Effects Institute. Boston, MA, USA.

Health Effects Institute, 2019. State of Global Air 2019. Special Report., Health Effects Institute. Boston, MA.

Hinds, W.C., 1999. Aerosol Technology: Properties, Behavior, and Measurement of Airborne Particles, 2nd Edition, John Wiley & Sons. New York, USA.

Hofmann, W., 2011. Modelling inhaled particle deposition in the human lung - A review. J. Aerosol Sci. https://doi.org/10.1016/j.jaerosci.2011.05.007

Hussain, M., Madl, P., Khan, A., 2011. Lung deposition predictions of airborne particles and the emergence of contemporary diseases Part I. theHealth 2, 51–59.

IARC, 2010. Household use of solid fuels and high-temperature frying, IARC monographs on the evaluation of carcinogenic risks to humans, Nº 95. World Health Organization, International Agency for Research on Cancer. Lyon, France

ICRP, 1994. Human Respiratory Tract Model for Radiological Protection. Publication 66. Volume 24. Pergamon, Oxford, UK.

Jack, D.W., Asante, K.P., Wylie, B.J., Chillrud, S.N., Whyatt, R.M., Ae-Ngibise, K.A., Quinn, A.K., Yawson, A.K., Boamah, E.A., Agyei, O., Mujtaba, M., Kaali, S., Kinney, P., Owusu-Agyei, S., 2015. Ghana randomized air pollution and health study (GRAPHS): Study protocol for a randomized controlled trial. Trials 16, 420. https://doi.org/10.1186/s13063-015-0930-8

Jalava, P.I., Happo, M.S., Kelz, J., Brunner, T., Hakulinen, P., Mäki-Paakkanen, J., Hukkanen, A., Jokiniemi, J., Obernberger, I., Hirvonen, M.R., 2012. *In vitro* toxicological characterization of particulate emissions from residential biomass heating systems based on old and new technologies. Atmos. Environ. 50, 24–35. https://doi.org/10.1016/j.atmosenv.2012.01.009

Jalava, P.I., Salonen, R.O., Nuutinen, K., Pennanen, A.S., Happo, M.S., Tissari, J., Frey, A., Hillamo, R., Jokiniemi, J., Hirvonen, M.R., 2010. Effect of combustion condition on cytotoxic and inflammatory activity of residential wood combustion particles. Atmos. Environ. 44, 1691–1698. https://doi.org/10.1016/j.atmosenv.2009.12.034

Jeguirim, M., Kraiem, N., Lajili, M., Guizani, C., Zorpas, A., Leva, Y., Michelin, L., Josien, L., Limousy, L., 2017. The relationship between mineral contents, particle matter and bottom ash distribution during pellet combustion: molar balance and chemometric analysis. Environ. Sci. Pollut. Res. 24, 9927–9939. https://doi.org/10.1007/s11356-017-8781-3

Johansson, L.S., Tullin, C., Leckner, B., Sjövall, P., 2003. Particle emissions from biomass combustion in small combustors. Biomass Bioenergy 25, 435–446. https://doi.org/10.1016/S0961-9534(03)00036-9

Kasurinen, S., Jalava, P.I., Happo, M.S., Sippula, O., Uski, O., Zimmermann, R., Jokiniemi, J., Koponen, H., Hirvonen, M., 2017. Particulate emissions from the combustion of birch, beech, and spruce logs cause different cytotoxic responses in A549 cells. Environ. Toxicol. 32, 1487–1499. https://doi.org/10.1002/tox

Kasurinen, S., Jalava, P.I., Uski, O., Happo, M.S., Mäki-paakkanen, J., Jokiniemi, J., Obernberger, I., Hirvonen, M., 2016. Toxicological characterization of particulate emissions from straw, Miscanthus, and poplar pellet combustion in residential boilers. Aerosol Sci. Technol. 50, 41–51. https://doi.org/10.1080/02786826.2015.1121198

Ke, S., Liu, Q., Deng, M., Zhang, X., Yao, Y., Shan, M., 2018. Cytotoxicity analysis of indoor air pollution from biomass combustion in human keratinocytes on a multilayered dynamic cell culture platform. Chemosphere 208, 1008–1017. https://doi.org/10.1016/j.chemosphere.2018.06.058

Kelly, F.J., Fussell, J.C., 2012. Size, source and chemical composition as determinants of toxicity attributable to ambient particulate matter. Atmos. Environ. 60, 504–526. https://doi.org/10.1016/j.atmosenv.2012.06.039

Kim, C.S., 2009. Deposition of aerosol particles in human lungs: *in vivo* measurement and modelling. Biomarkers 14, 54–58. https://doi.org/10.1080/13547500902965286

Kim, C.S., Fisher, D.M., Lutz, D.J., Gerrity, T.R., 1994. Particle deposition in bifurcating airway models with varying airway geometry. J. Aerosol Sci. 25, 567–581.

Kim, K.H., Jahan, S.A., Kabir, E., 2011. A review of diseases associated with household air pollution due to the use of biomass fuels. J. Hazard. Mater. 192, 425–431. https://doi.org/10.1016/j.jhazmat.2011.05.087

Kim, K.H., Kabir, E., Kabir, S., 2015. A review on the human health impact of airborne particulate matter. Environ. Int. https://doi.org/10.1016/j.envint.2014.10.005

Kim, Y.H., Warren, S.H., Krantz, Q.T., King, C., Jaskot, R., Preston, W.T., George, B.J., Hays, M.D., Landis, M.S., Higuchi, M., DeMarini, D.M., Gilmour, M.I., 2018. Mutagenicity and lung toxicity of smoldering vs. flaming emissions from various biomass fuels: implications for health effects from wildland fires. Environ. Health Perspect. 126, 017011. https://doi.org/10.1289/EHP2200

King, T.C., 2007. Cell Injury, Cellular Responses to Injury, and Cell Death, in: Elsevier's Integrated Pathology. Elsevier, pp. 1–20. https://doi.org/10.1016/b978-0-323-04328-1.50007-3

Knaapen, A.M., Borm, P.J.A., Albrecht, C., Schins, R.P.F., 2004. Inhaled particles and lung cancer. Part A: mechanisms. Int. J. Cancer 109, 799–809. https://doi.org/10.1002/ijc.11708

Knudsen, J.N., Jensen, P.A., Dam-Johansen, K., 2004. Transformation and release to the gas phase of Cl, K, and S during combustion of annual biomass. Energ. Fuel. 18, 1385–1399. https://doi.org/10.1021/ef049944q

Kocbach, A., Inge, J., Låg, M., Refsnes, M., Schwarze, P.E., 2008a. Particles from wood smoke and traffic induce differential pro-inflammatory response patterns in co-cultures. Toxicol. Appl. Pharmacol. 232, 317–326. https://doi.org/10.1016/j.taap.2008.07.002

Kocbach, A., Namork, E., Schwarze, P.E., 2008b. Pro-inflammatory potential of wood smoke and traffic-derived particles in a monocytic cell line. Toxicology 247, 123–132. https://doi.org/10.1016/j.tox.2008.02.014

Kováts, N., Ács, A., Ferincz, Á., Kovács, A., Horváth, E., Kakasi, B., Jancsek-Turóczi, B., Gelencsér, A., 2013. Ecotoxicity and genotoxicity assessment of exhaust particulates from diesel-powered buses. Environ. Monit. Assess. 185, 8707–8713. https://doi.org/10.1007/s10661-013-3206-3

Kováts, N., Ács, A., Kovács, A., Ferincz, Á., Turóczi, B., Gelencsér, A., 2012. Direct contact test for estimating the ecotoxicity of aerosol samples. Environ. Toxicol. Pharmacol. 33, 284–287. https://doi.org/10.1016/j.etap.2011.12.021

Kováts, N., Horváth, E., 2016. Bioluminescence-based assays for assessing eco- and genotoxicity of airborne emissions. Luminescence 31, 918–923. https://doi.org/10.1002/bio.3102

Kulkarni, P., Baron, P.A., Willeke, K. (Eds.), 2011. Aerosol Measurement. Principles, techniques, and applications, 3rd Edition, John Wiley & Sons, Inc., New Jersey, USA. https://doi.org/10.1002/9781118001684

Kurmi, O.P., Semple, S., Simkhada, P., Cairns S Smith, W., Ayres, J.G., 2010. COPD and chronic bronchitis risk of indoor air pollution from solid fuel: A systematic review and meta-analysis. Thorax 65, 221–228. https://doi.org/10.1136/thx.2009.124644

Lamberg, H., Nuutinen, K., Tissari, J., Ruusunen, J., Yli-Pirilä, P., Sippula, O., Tapanainen, M., Jalava, P., Makkonen, U., Teinilä, K., Saarnio, K., Hillamo, R., Hirvonen, M.R., Jokiniemi, J., 2011a. Physicochemical characterization of fine particles from small-scale wood combustion. Atmos. Environ. 45, 7635–7643. https://doi.org/10.1016/j.atmosenv.2011.02.072

Lamberg, H., Sippula, O., Tissari, J., Jokiniemi, J., 2011b. Effects of air-staging and load on fine particle and gaseous emissions from a small-scale pellet boiler. Energ. Fuel. 4952–4960. https://doi.org/10.1021/ef2010578

Lamberg, H., Tissari, J., Jokiniemi, J., Sippula, O., 2013. Fine particle and gaseous emissions from a small-scale boiler fueled by pellets of various raw materials. Energ. Fuel. 27, 7044–7053. https://doi.org/10.1021/ef401267t

Laumbach, R.J., Kipen, H.M., 2012. Respiratory health effects of air pollution: update on biomass smoke and traffic pollution. J. Allergy Clin. Immunol. https://doi.org/10.1016/j.jaci.2011.11.021

Lazaridis, M., Broday, D.M., Hov, O., Georgopoulos, P.., 2001. Integrated exposure and dose deposition of inhaled particles in the human respiratory tract. Environ. Sci. Technol. 35, 3727–3734.

Leskinen, J., Tissari, J., Uski, O., Virén, A., Torvela, T., Kaivosoja, T., Lamberg, H., Nuutinen, I., Kettunen, T., Joutsensaari, J., Jalava, P.I., Sippula, O., Hirvonen, M.R., Jokiniemi, J., 2014. Fine particle emissions in three different combustion conditions of a wood chip-fired appliance - Particulate physico-chemical properties and induced cell death. Atmos. Environ. 86, 129–139. https://doi.org/10.1016/j.atmosenv.2013.12.012

Lewtas, J., 2007. Air pollution combustion emissions: Characterization of causative agents and mechanisms associated with cancer, reproductive, and cardiovascular effects. Mutat. Res. - Rev. Mutat. Res. https://doi.org/10.1016/j.mrrev.2007.08.003

Li, N., Hao, M., Phalen, R.F., Hinds, W.C., Nel, A.E., 2003. Particulate air pollutants and asthma: A paradigm for the role of oxidative stress in PM-induced adverse health effects. Clin. Immunol. https://doi.org/10.1016/j.clim.2003.08.006

Lippmann, M., Yeates, D.B., Albert, R.E., 1980. Deposition, retention, and clearance of inhaled particles. Br. J. Ind. Med. https://doi.org/10.1136/oem.37.4.337

Löndahl, J., Möller, W., Pagels, J.H., Kreyling, W.G., Swietlicki, E., Schmid, O., 2014. Measurement techniques for respiratory tract deposition of airborne nanoparticles: a critical review. J. Aerosol Med. Pulm. Drug Deliv. 27, 229–254. https://doi.org/10.1089/jamp.2013.1044

Löndahl, J., Pagels, J.H., Boman, C., Swietlicki, E., Massling, A., Rissler, J., Blomberg, A., Bohgard, M., Sandstrom, T., 2008. Deposition of biomass combustion aerosol particles in the human respiratory tract. Inhal. Toxicol. 20, 923–933. https://doi.org/10.1080/08958370802087124

Loomis, D., Grosse, Y., Lauby-Secretan, B., Ghissassi, F. El, Bouvard, V., Benbrahim-Tallaa, L., Guha, N., Baan, R., Mattock, H., Straif, K., 2013. The carcinogenicity of outdoor air pollution. Lancet Oncol. 14, 1262–1263. https://doi.org/10.1016/S1470-2045(13)70487-X

Ma, X.Y., Wang, X.C., Ngo, H.H., Guo, W., Wu, M.N., Wang, N., 2014. Bioassay based luminescent bacteria: Interferences, improvements, and applications. Sci. Total Environ. 468–469, 1–11. https://doi.org/10.1016/j.scitotenv.2013.08.028

Marabini, L., Ozgen, S., Turacchi, S., Aminti, S., Arnaboldi, F., Lonati, G., Fermo, P., Corbella, L., Valli, G., Bernardoni, V., Dell'Acqua, M., Vecchi, R., Becagli, S., Caruso, D., Corrado, L.G., Marinovich, M., 2017. Ultrafine particles (UFPs) from domestic wood stoves: genotoxicity in human lung carcinoma A549 cells. Mutat. Res. - Genet. Toxicol. Environ. Mutagen. 820, 39–46. https://doi.org/10.1016/j.mrgentox.2017.06.001

Marchetti, S., Longhin, E., Bengalli, R., Avino, P., Stabile, L., Buonanno, G., Colombo, A., Camatini, M., Mantecca, P., 2019. *In vitro* lung toxicity of indoor PM_{10} from a stove fueled with different biomasses. Sci. Total Environ. 649, 1422–1433. https://doi.org/10.1016/j.scitotenv.2018.08.249

Mazzoli-Rocha, F., Fernandes, S., Einicker-Lamas, M., Zin, W.A., 2010. Roles of oxidative stress in signaling and inflammation induced by particulate matter. Cell Biol. Toxicol. 26, 481–498. https://doi.org/10.1007/s10565-010-9158-2

McCracken, J.P., Smith, K.R., Díaz, A., Mittleman, M.A., Schwartz, J., 2007. Chimney stove intervention to reduce long-term wood smoke exposure lowers blood pressure among Guatemalan women. Environ. Health Perspect. 115, 996–1001. https://doi.org/10.1289/ehp.9888

McCracken, J.P., Wellenius, G. a., Bloomfield, G.S., Brook, R.D., Tolunay, H.E., Dockery, D.W., Rabadan-Diehl, C., Checkley, W., Rajagopalan, S., 2012. Household air pollution from solid fuel use. Glob. Heart 7, 223–234. https://doi.org/10.1016/j.gheart.2012.06.010

McNamara, M., Thornburg, J., Semmens, E., Ward, T., Noonan, C., 2013. Coarse particulate matter and airborne endotoxin within wood stove homes. Indoor Air 23, 498–505. https://doi.org/10.1111/ina.12043

Mortimer, K., Ndamala, C.B., Naunje, A.W., Malava, J., Katundu, C., Weston, W., Havens, D., Pope, D., Bruce, N.G., Nyirenda, M., Wang, D., Crampin, A., Grigg, J., Balmes, J., Gordon, S.B., 2017. A cleaner burning biomass-fuelled cookstove intervention to prevent pneumonia in children under 5 years old in rural Malawi (the Cooking and Pneumonia Study): a cluster randomised controlled trial. Lancet 389, 167–175. https://doi.org/10.1016/S0140-6736(16)32507-7

Muala, A., Nicklasson, H., Boman, C., Swietlicki, E., Nyström, R., Pettersson, E., Bosson, J.A., Rissler, J., Blomberg, A., Sandström, T., Löndahl, J., 2015. Respiratory tract deposition of inhaled wood smoke particles in healthy volunteers. J. Aerosol Med. Pulm. Drug Deliv. 28, 237–246. https://doi.org/10.1089/jamp.2014.1122

Naeher, L.P., Brauer, M., Lipsett, M., Zelikoff, J.T., Simpson, C.D., Koenig, J.Q., Smith, K.R., 2007. Woodsmoke health effects: A review. Inhal. Toxicol. 19, 67–106. https://doi.org/10.1080/08958370600985875

Nemmar, A., Holme, J.A., Rosas, I., Schwarze, P.E., Alfaro-moreno, E., 2013. Recent advances in particulate matter and nanoparticle toxicology: a review of the *in vivo* and *in vitro* studies. Biomed Res. Int. 2013.

Nussbaumer, T., 2010. Overview on Technologies for Biomass Combustion and Emission Levels of Particulate Matter. Verenum, Switzerland.

Nussbaumer, T., 2003. Combustion and co-combustion of biomass: fundamentals, technologies, and primary measures for emission reduction. Energ. Fuel. 17, 1510–1521. https://doi.org/10.1021/ef030031q

Obaidullah, M., Bram, S., Verma, V.K., Ruyck, J. De, 2012. A review on particle emissions from small scale biomass combustion. Int. J. Renew. Energy Res. 2, 147-159.

Obernberger, I., Brunner, T., Bärnthaler, G., 2006. Chemical properties of solid biofuels-significance and impact. Biomass Bioenergy 30, 973–982. https://doi.org/10.1016/j.biombioe.2006.06.011

OECD, 1997. Test Guideline 471. Bacteria reverse mutation. In: OCED Guidelines for the Testing of Chemicals. Organisation for Economic Co-operation and Development, Paris, France.

Oldham, M.J., Phalen, R.F., Heistracher, T., 2000. Computational fluid dynamic predictions and experimental results for particle deposition in an airway model. Aerosol Sci. Technol. 32, 61–71. https://doi.org/10.1080/027868200303939

Olsen, Y., Nøjgaard, J.K., Olesen, H.R., Brandt, J., Sigsgaard, T., Pryor, S.C., Ancelet, T., Viana, M. del M., Querol, X., Hertel, O., 2020. Emissions and source allocation of carbonaceous air pollutants from wood stoves in developed countries: A review. Atmos. Pollut. Res. https://doi.org/10.1016/j.apr.2019.10.007

Onyeneke, R.U., Nwajiuba, C.A., Munonye, J., Uwazie, U.I., Uwajumogu, N., Uwadoka, C.O., Aligbe, J.O., 2019. Improved cook-stoves and environmental and health outcomes: Lessons from cross river state, Nigeria. Int. J. Environ. Res. Public Health 16. https://doi.org/10.3390/ijerph16193520

Orasche, J., Schnelle-Kreis, J., Schön, C., Hartmann, H., Ruppert, H., Arteaga-Salas, J.M., Zimmermann, R., 2013. Comparison of emissions from wood combustion. Part 2: Impact of combustion conditions on emission factors and characteristics of particle-bound organic species and polycyclic aromatic hydrocarbon (PAH)-related toxicological potential. Energ. Fuel. 27, 1482–1491. https://doi.org/10.1021/ef301506h

Orozco-Levi, M., Garcia-Aymerich, J., Villar, J., Ramírez-Sarmiento, A., Antó, J.M., Gea, J., 2006. Wood smoke exposure and risk of chronic obstructive pulmonary disease. Eur. Respir. J. 27, 542–546. https://doi.org/10.1183/09031936.06.00052705

Parajuli, I., Lee, H., Shrestha, K.R., 2016. Indoor Air Quality and ventilation assessment of rural mountainous households of Nepal. Int. J. Sustain. Built Environ. 5, 301–311. https://doi.org/10.1016/j.ijsbe.2016.08.003

Pathak, U., Gupta, N.C., Suri, J.C., 2020. Risk of COPD due to indoor air pollution from biomass cooking fuel: a systematic review and meta-analysis. Int. J. Environ. Health Res. 30, 75–88. https://doi.org/10.1080/09603123.2019.1575951

Peixoto, M.S., de Oliveira Galvão, M.F., Batistuzzo de Medeiros, S.R., 2017. Cell death pathways of particulate matter toxicity. Chemosphere 188, 32–48. https://doi.org/10.1016/j.chemosphere.2017.08.076

Pereira, T.C., Pina, A., Canaveira, P., Amaro, A., Borges, M., Silva, R., 2020. Portuguese informative inventory report 1990 – 2018. Submitted under the NEC Directive (EU) 2016/2284 and the UNECE Convention on Long-range Transboundary Air Pollution. Portuguese Environmental Agency, Amadora, Portugal.

Pettersson, E., Boman, C., Westerholm, R., Bostr, D., 2011. Stove performance and emission characteristics in residential wood log and pellet combustion, Part 2: Wood stove. Energ. Fuel. 25, 315–323. https://doi.org/10.1021/ef1007787

Pintér, M., Utry, N., Ajtai, T., Kiss-Albert, G., Jancsek-Turóczi, B., Imre, K., Palágyi, A., Manczinger, L., Vágvölgyi, C., Horváth, E., Kováts, N., Gelencsér, A., Szabó, G., Bozóki, Z., 2017. Optical properties, chemical composition and the toxicological potential of urban particulate matter. Aerosol Air Qual. Res. 17, 1415–1426. https://doi.org/10.4209/aaqr.2016.09.0395

Pope, C.A., 2000. Epidemiology of fine particulate air pollution and human health: Biologic mechanisms and who's at risk? Environ. Health Perspect. 108, 713–723. https://doi.org/10.2307/3454408

Pope, C.A., Dockery, D.W., 2006. Health effects of fine particulate air pollution: Lines that connect. J. Air Waste Manag. Assoc. 56, 709–742. https://doi.org/10.1080/10473289.2006.10464485

Risom, L., Møller, P., Loft, S., 2005. Oxidative stress-induced DNA damage by particulate air pollution. Mutat. Res. 592, 119–137. https://doi.org/10.1016/j.mrfmmm.2005.06.012

Rogge, W.F., Hildemann, L.M., Mazurek, M. a., Cass, G.R., 1998. Sources of fine organic aerosol. 9. Pine, oak, and synthetic log combustion in residential fireplaces. Environ. Sci. Technol. 32, 13–22. https://doi.org/10.1021/es960930b

Roig, N., Sierra, J., Rovira, J., Schuhmacher, M., Domingo, J.L., Nadal, M., 2013. *In vitro* tests to assess toxic effects of airborne PM_{10} samples. Correlation with metals and chlorinated dioxins and furans. Sci. Total Environ. 443, 791–797. https://doi.org/10.1016/j.scitotenv.2012.11.022

Romano, S., Perrone, M.R., Becagli, S., Pietrogrande, M.C., Russo, M., Caricato, R., Lionetto, M.G., 2020. Ecotoxicity, genotoxicity, and oxidative potential tests of atmospheric PM_{10} particles. Atmos. Environ. 221, 117085. https://doi.org/10.1016/j.atmosenv.2019.117085

Romieu, I., Riojas-Rodríguez, H., Marrón-Mares, A.T., Schilmann, A., Perez-Padilla, R., Masera, O., 2009. Improved biomass stove intervention in rural Mexico: Impact on the respiratory health of women. Am. J. Respir. Crit. Care Med. 180, 649–656. https://doi.org/10.1164/rccm.200810-1556OC

Salthammer, T., Schripp, T., Wientzek, S., Wensing, M., 2014. Impact of operating wood-burning fireplace ovens on indoor air quality. Chemosphere 103, 205–211. https://doi.org/10.1016/j.chemosphere.2013.11.067

Saraga, D.E., Makrogkika, A., Karavoltsos, S., Sakellari, A., Diapouli, E., Eleftheriadis, K., Vasilakos, C., Helmis, C., Maggos, T., 2015. A pilot investigation of PM indoor/outdoor mass concentration and chemical analysis during a period of extensive fireplace use in Athens. Aerosol Air Qual. Res. 15, 2485–2495. https://doi.org/10.4209/aaqr.2015.02.0100

Schins, R.P.F., Knaapen, A.M., 2007. Genotoxicity of poorly soluble particles, in: Inhalation Toxicology. Taylor & Francis, pp. 189–198. https://doi.org/10.1080/08958370701496202

Schlesinger, R.B., Bohning, D.E., Chan, T.L., Lippmann, M., 1977. Particle deposition in a hollow cast of the human tracheobronchial tree. J. Aerosol Sci. 8, 429–445.

Schmidl, C., Luisser, M., Padouvas, E., Lasselsberger, L., Rzaca, M., Ramirez-Santa Cruz, C., Handler, M., Peng, G., Bauer, H., Puxbaum, H., 2011. Particulate and gaseous emissions from manually and automatically fired small scale combustion systems. Atmos. Environ. 45, 7443–7454. https://doi.org/10.1016/j.atmosenv.2011.05.006

Schulze, A.L., Büchner, D., Klix, V., Lenz, V., Kaltschmitt, M., 2019. Biological effects of particulate matter emissions from residential pellet boilers in bacterial assays: influence of an electrostatic precipitation. Biomass Convers. Biorefinery 9, 227–239. https://doi.org/10.1007/s13399-018-0358-y

Schwarze, P.E., Øvrevik, J., Lag, M., Refsnes, M., Nafstad, P., Hetland, R., Dybing, E., 2006. Particulate matter properties and health effects: consistency of epidemiological and toxicological studies. Hum. Exp. Toxicol. 25, 559–579.

Sehlstedt, M., Dove, R., Boman, C., Pagels, J., Swietlicki, E., Löndahl, J., Westerholm, R., Bosson, J., Barath, S., Behndig, A.F., Pourazar, J., Sandström, T., Mudway, I.S., Blomberg, A., 2010. Antioxidant airway responses following experimental exposure to wood smoke in man. Part. Fibre Toxicol. 7, 21. https://doi.org/10.1186/1743-8977-7-21

Shen, G., 2017. Mutagenicity of particle emissions from solid fuel cookstoves: A literature review and research perspective. Environ. Res. https://doi.org/10.1016/j.envres.2017.05.001

Sigsgaard, T., Forsberg, B., Annesi-Maesano, I., Blomberg, A., Bølling, A., Boman, C., Bønløkke, J., Brauer, M., Bruce, N., Héroux, M.E., Hirvonen, M.R., Kelly, F., Künzli, N., Lundbäck, B., Moshammer, H., Noonan, C., Pagels, J., Sallsten, G., Sculier, J.P., Brunekreef, B., 2015. Health impacts of anthropogenic biomass burning in the developed world. Eur. Respir. J. 46, 1577–1588. https://doi.org/10.1183/13993003.01865-2014

Simoneit, B.R., 2002. Biomass burning - a review of organic tracers for smoke from incomplete combustion. Appl. Geochem. 17, 129–162. https://doi.org/10.1016/S0883-2927(01)00061-0

Sippula, O., Hytönen, K., Tissari, J., Raunemaa, T., Jokiniemi, J., 2007. Effect of wood fuel on the emissions from a top-feed pellet stove. Energ. Fuel. 21, 1151–1160. https://doi.org/10.1021/ef060286e

Sippula, O., Lamberg, H., Leskinen, J., Tissari, J., Jokiniemi, J., 2017. Emissions and ash behavior in a 500 kW pellet boiler operated with various blends of woody biomass and peat. Fuel 202, 144–153. https://doi.org/10.1016/j.fuel.2017.04.009

Skodras, G., Grammelis, P., Prokopidou, M., Kakaras, E., Sakellaropoulos, G., 2009. Chemical, leaching and toxicity characteristics of CFB combustion residues. Fuel 88, 1201–1209. https://doi.org/10.1016/j.fuel.2007.06.009

Smith, K.R., McCracken, J.P., Weber, M.W., Hubbard, A., Jenny, A., Thompson, L.M., Balmes, J., Diaz, A., Arana, B., Bruce, N., 2011. Effect of reduction in household air pollution on childhood pneumonia in Guatemala (RESPIRE): A randomised controlled trial. Lancet 378, 1717–1726. https://doi.org/10.1016/S0140-6736(11)60921-5

Sood, A., 2012. Indoor fuel exposure and the lung in both developing and developed countries: An update. Clin. Chest Med. https://doi.org/10.1016/j.ccm.2012.08.003

Stockfelt, L., Sallsten, G., Almerud, P., Basu, S., Barregard, L., 2013. Short-term chamber exposure to low doses of two kinds of wood smoke does not induce systemic inflammation, coagulation or oxidative stress in healthy humans. Inhal. Toxicol. 25, 417–425. https://doi.org/10.3109/08958378.2013.798387

Tapanainen, M., Jalava, P.I., Mäki-paakkanen, J., Hakulinen, P., Happo, M.S., Lamberg, H., Ruusunen, J., Tissari, J., Nuutinen, K., Yli-pirilä, P., Hillamo, R., Salonen, R.O., Jokiniemi, J., Hirvonen, M., 2011. *In vitro* immunotoxic and genotoxic activities of particles emitted from two different small-scale wood combustion appliances. Atmos. Environ. 45, 7546–7554. https://doi.org/10.1016/j.atmosenv.2011.03.065

Tissari, J., Sippula, O., Kouki, J., Vuorio, K., Jokiniemi, J., 2008. Fine particle and gas emissions from the combustion of agricultural fuels fired in a 20 kW burner. Energ. Fuel. 22, 2033–2042. https://doi.org/10.1021/ef700766y

Tositti, L., Brattich, E., Parmeggiani, S., Bolelli, L., Ferri, E., Girotti, S., 2018. Airborne particulate matter biotoxicity estimated by chemometric analysis on bacterial luminescence data. Sci. Total Environ. 640–641, 1512–1520. https://doi.org/10.1016/j.scitotenv.2018.06.024

Traboulsi, H., Guerrina, N., Iu, M., Maysinger, D., Ariya, P., Baglole, C.J., 2017. Inhaled pollutants: The molecular scene behind respiratory and systemic diseases associated with ultrafine particulate matter. Int. J. Mol. Sci. 18, 243. https://doi.org/10.3390/ijms18020243

Turner, M.D., Nedjai, B., Hurst, T., Pennington, D.J., 2014. Cytokines and chemokines: At the crossroads of cell signalling and inflammatory disease. Biochim. Biophys. Acta 1843, 2563–2582. https://doi.org/10.1016/j.bbamcr.2014.05.014

Turóczi, B., Hoffer, A., Tóth, Á., Kováts, N., Ács, A., Ferincz, Kovács, A., Gelencsér, A., 2012. Comparative assessment of ecotoxicity of urban aerosol. Atmos. Chem. Phys. 12, 7365–7370. https://doi.org/10.5194/acp-12-7365-2012

Unosson, J., Blomberg, A., Sandström, T., Muala, A., Boman, C., Nyström, R., Westerholm, R., Mills, N.L., Newby, D.E., Langrish, J.P., Bosson, J.A., 2013. Exposure to wood smoke increases arterial stiffness and decreases heart rate variability in humans. Part. Fibre Toxicol. 10, 1–8. https://doi.org/10.1186/1743-8977-10-20

Uski, O., Jalava, P.I., Happo, M.S., Leskinen, J., Sippula, O., Tissari, J., Mäki-paakkanen, J., Jokiniemi, J., Hirvonen, M., 2014. Different toxic mechanisms are activated by emission PM depending on combustion efficiency. Atmos. Environ. 89, 623–632. https://doi.org/10.1016/j.atmosenv.2014.02.036

Uski, O.J., Happo, M.S., Jalava, P.I., Brunner, T., Kelz, J., Obernberger, I., Jokiniemi, J., Hirvonen, M.R., 2012. Acute systemic and lung inflammation in C57Bl/6J mice after intratracheal aspiration of particulate matter from small-scale biomass combustion appliances based on old and modern technologies. Inhal. Toxicol. 24, 952–965. https://doi.org/10.3109/08958378.2012.742172

Valavanidis, Athanasios, Fiotakis, Konstantinos, Vlachogianni, Thomais, Valavanidis, A, Fiotakis, K, Vlachogianni, T, 2008. Airborne particulate matter and human health: Toxicological assessment and importance of size and composition of particles for oxidative damage and carcinogenic mechanisms. J. Environ. Sci. Heal. Part C 26, 1532–4095. https://doi.org/10.1080/10590500802494538

Van Lith, S.C., Alonso-Ramírez, V., Jensen, P.A., Frandsen, F.J., Glarborg, P., 2006. Release to the gas phase of inorganic elements during wood combustion. Part 1: Development and evaluation of quantification methods. Energ. Fuel. 20, 964–978. https://doi.org/10.1021/ef050131r

Vassilev, S. V., Baxter, D., Andersen, L.K., Vassileva, C.G., 2010. An overview of the chemical composition of biomass. Fuel 89, 913–933. https://doi.org/10.1016/j.fuel.2009.10.022

Vicente, E.D., Alves, C.A., 2018. An overview of particulate emissions from residential biomass combustion. Atmos. Res. 199, 159–185. https://doi.org/10.1016/J.ATMOSRES.2017.08.027

Vouitsis, E., Ntziachristos, L., Pistikopoulos, P., Samaras, Z., Chrysikou, L., Samara, C., Papadimitriou, C., Samaras, P., Sakellaropoulos, G., 2009. An investigation on the physical, chemical and ecotoxicological characteristics of particulate matter emitted from light-duty vehicles. Environ. Pollut. 157, 2320–2327. https://doi.org/10.1016/j.envpol.2009.03.028

Vu, B., Alves, C.A., Gonçalves, C., Pio, C., Gonçalves, F., Pereira, R., 2012. Mutagenicity assessment of aerosols in emissions from wood combustion in Portugal. Environ. Pollut. 166, 172–181. https://doi.org/10.1016/j.envpol.2012.03.005

WHO, 2016. Burning Opportunity: Clean Household Energy for Health, Sustainable Development, and Wellbeing of Women and Children, Clean Household Energy. World Health Organization, Geneva, Switzarland.

Wiinikka, H., Gebart, R., 2005. The influence of fuel type on particle emissions in combustion of biomass pellets. Combust. Sci. Technol. 177, 741–763. https://doi.org/10.1080/00102200590917257

Williams, A., Jones, J.M., Ma, L., Pourkashanian, M., 2012. Pollutants from the combustion of solid biomass fuels. Prog. Energy Combust. Sci. 38, 113–137. https://doi.org/10.1016/j.pecs.2011.10.001

Wylie, B.J., Coull, B. a, Hamer, D.H., Singh, M.P., Jack, D., Yeboah-Antwi, K., Sabin, L., Singh, N., MacLeod, W.B., 2014. Impact of biomass fuels on pregnancy outcomes in central East India. Environ. Health 13, 1. https://doi.org/10.1186/1476-069X-13-1

Yang, X.Y., Igarashi, K., Tang, N., Lin, J.M., Wang, W., Kameda, T., Toriba, A., Hayakawa, K., 2010. Indirect- and direct-acting mutagenicity of diesel, coal and wood burning-derived particulates and contribution of polycyclic aromatic hydrocarbons and nitropolycyclic aromatic hydrocarbons. Mutat. Res. - Genet. Toxicol. Environ. Mutagen. 695, 29–34. https://doi.org/10.1016/j.mrgentox.2009.10.010

Zelikoff, J.T., Chen, L.C., Cohen, M.D., Schlesinger, R.B., 2002. The toxicology of inhaled woodsmoke. J. Toxicol. Environ. Heal. Part B 269–282. https://doi.org/10.1080/1093740029007006

Zhou, Y., Cheng, Y.S., 2005. Particle deposition in a cast of human tracheobronchial airways. Aerosol Sci. Technol. 39, 492–500. https://doi.org/10.1080/027868291001385

CHAPTER 2

Chapter 2. An overview of particulate emissions from residential biomass combustion

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Abstract

Residential biomass burning has been pointed out as one of the largest sources of fine particles in the global troposphere with serious impacts on air quality, climate and human health. Quantitative estimations of the contribution of this source to the atmospheric particulate matter levels are hard to obtain, because emission factors vary greatly with wood type, combustion equipment and operating conditions. Updated information should improve not only regional and global biomass burning emission inventories, but also the input for atmospheric models. In this work, an extensive tabulation of particulate matter emission factors obtained worldwide is presented and critically evaluated. Existing quantifications and the suitability of specific organic markers to assign the input of residential biomass combustion to the ambient carbonaceous aerosol are also discussed. Based on these organic markers or other tracers, estimates of the contribution of this sector to observed particulate levels by receptor models for different regions around the world are compiled. Key areas requiring future research are highlighted and briefly discussed.

Keywords: Biomass, Emission factors, Organic tracers, PM, Residential heating, Source apportionment

2.1. Residential biomass burning: importance and impacts

The term aerosol refers to solid and liquid particles suspended in the atmosphere that may vary in size from a few nanometers to tens of microns (Calvo et al., 2013). Atmospheric aerosol particles can have natural or anthropogenic sources and are either primarily emitted or formed in the atmosphere from precursor gases (secondary aerosols). Aerosols consist of complex mixtures of organic and inorganic compounds, exhibiting a wide spectrum of physical and chemical properties, which determine their climate and health-related effects (Boucher, 2015; Pöschl, 2005). The World Health Organisation (WHO) reported that in 2012 around 7 million people died as a result of air pollution exposure (WHO, 2014). Particulate matter (PM) is one of the pollutants of major concern in Europe, since the daily average limit levels in the ambient air established by the EU Directive 2008/50/EC are frequently surpassed in many regions. According to the most recent data from the European Environment Agency, in 2013, exceedances of the daily limit values were observed in 22 Member States, particularly in urban or suburban areas (EEA, 2015). It was estimated that, in 2015, small scale residential combustion has been responsible for > 45% of total $PM_{2.5}$ emissions in Europe (DUH and DEC, 2016). In residential areas impacted by wood burning, concentrations of fine particles can reach the same magnitude as the values recorded on the most polluted streets during rush hour (DUH and DEC, 2016). Biomass combustion for residential heating is a major source of atmospheric contaminants, which was estimated to contribute to a large share of PM emissions in different European countries, e.g. Portugal and other Southern nations (Amato et al., 2016), Sweden (Krecl et al., 2008), Switzerland (Szidat et al., 2007), Austria (Caseiro et al., 2009), Germany (Bari et al., 2010), France (Favez et al., 2009) and Belgium (Maenhaut et al., 2012).

An investigation carried out in Greece (Saffari et al., 2013) indicated that air quality in the Greek city of Thessaloniki has worsened during the recent economic crisis, because residents burn more wood and other types of biomass to keep warm. Saffari et al. (2013) have found a 30% increase in the concentration of $PM_{2.5}$ emissions associated with residential wood combustion in 2012 and 2013. Evening samples encompassed a higher proportion of organic matter (74%) compared to the morning samples (58%), again suggesting that more wood and biomass were used for heating in the evening. Also, the concentrations of V and Ni, which imply combustion of residential fuel oil and industrial activity, were 30 – 40% lower in 2013 compared with 2012 (Saffari et al., 2013). Karagulian et al. (2015) performed a systematic literature review and analysed available source apportionment studies on PM conducted in cities to estimate typical shares of the sources of pollution by country and by region. Domestic fuel burning emerged as the main contributor to the PM mass concentrations in Africa (34%), and in Central and Eastern Europe (32%), although based on very few records in this region. Domestic fuel burning was also important in the rest of the Americas (25%), Northwestern Europe (22%), the Southern China region (21%), South Eastern Asia (19%), and India (16%). A recent literature review performed by Chen et al. (2017) regarding the dominant PM sources in China revealed that the contribution of biomass burning can represent from 19% to 37%, depending on the season.

The biomass based market for domestic heating has been in strong growth, not only in order to meet the household demand, but also to promote the use of renewable sources. The use of solid biomass for energy in the EU has been strongly encouraged as a measure to mitigate greenhouse gas emissions by replacing fossil fuels. As regards the fuels employed in the residential biomass heating sector, a wide range of options is available. Among them, wood logs (including softwoods and hardwoods), briquettes and pellets are the most common. The development of new combustion technologies allowed launching improved, automated and cleaner heating systems, which can compete with the traditional oil and gas appliances. One of the reasons for the better performance of such systems is the use of densified fuels. The use of pellets in automatic heating systems proved to be advantageous since this fuel requires less space for storage and is ready to use. The global pellet production has considerably increased over the last years. Between 2006 and 2012, pellet production worldwide increased from 7 to 19 million tons, with Europe and North America being responsible for almost all the production and consumption of densified products (Miranda et al., 2015). International standards, such as the ISO 17225- series, have stablished general requirements for all kind of pellets, including household and commercial applications, as well as industrial use. Despite the technological advances and rapid developments in the biofuel market, it is worthwhile to mention that in Portugal, as in many other countries, the old type manually operated combustion appliances still predominate (Gonçalves et al., 2012). In Europe, there are > 70 million solid fuel appliances and the majority is outdated and often operated improperly (DUH and DEC, 2016).

The exposure to ambient particulate matter has been linked with a wide range of adverse health outcomes. Among them, it is possible to highlight increased risk of dead from cardiovascular and respiratory illnesses (Samet et al., 2000), exacerbation of existing allergic symptoms of mucous membranes, including asthma (Rohr et al., 2014), aggravation of skin diseases, such as atopic dermatitis (Ahn, 2014), decline in lung function (Roy et al., 2012) and increase in the blood pressure (McCracken et al., 2007). Studies on the contribution of biomass combustion to pollution levels in Europe provided evidence on the premature mortality in Europe which totals at least 40,000 premature deaths per year (Sigsgaard et al., 2015). Several epidemiological and experimental studies have reported associations between wood smoke exposure and adverse health effects including eye, nose, and throat irritation, decrements in lung function, reduced resistance to infections and increased severity/incidences of acute asthma, especially in sensitive groups. Moreover, inhalation studies have demonstrated that wood smoke exposure may induce systemic effects, providing a possible link to cardiovascular effects (Bølling et al., 2009, and references therein; Sigsgaard et al., 2015). Ambient PM from wood smoke, which suffered physicochemical alterations in the atmosphere, have shown equivalent or greater lung deposition fractions than primary wood smoke PM (Sigsgaard et al., 2015). Naeher et al. (2007), in their review paper, addressed two questions: i) whether wood smoke should be regulated and/or managed separately, even though some of its separate constituents are already regulated in many jurisdictions; ii) whether wood smoke particles pose different levels of risk than other ambient particles of similar size. Because wood smoke is made up of such a large mixture of different chemicals, the authors concluded that it is impossible at present to accurately assess its health impacts by simply summing the potential effects of individual constituents. It was also stressed that although there is a large and growing body of evidence linking exposure to wood/biomass smoke itself with both acute and chronic illness, the existing information is still scarce to answer firmly to the above questions. Bølling et al. (2009) reviewed the physicochemical properties of smoke particles from different combustion conditions in relation to wood smoke-induced health effects. It was concluded that the influence of the physicochemical properties of wood smoke particles, and of the combustion conditions, on various biological endpoints is presently largely unknown, although *in vitro* studies suggest that particles from incomplete combustion conditions are more toxic than particles generated under more complete combustion conditions. Major gaps in knowledge were also identified: i) characterisation of the atmospheric transformations of wood smoke particles, ii) characterisation of the physicochemical properties of wood smoke particles in ambient and indoor environments, and iii) identification of the physicochemical properties that influence the biological effects of wood smoke particles.

Aerosols are also a topic of great concern because of their influence on atmospheric chemistry, radiative forcing, biogeochemical cycles, visibility, etc. (Frosch et al., 2011; Grantz et al., 2003; Hodzic et al., 2007; Kim et al., 2006; Pöschl, 2005). A recent study (Bond et al., 2013) found that the influence of soot generated by wood burning on climate change has been greatly underestimated. This study, which was the first comprehensive and quantitative analysis of the role of soot (also called black carbon, BC) in the climate system, concluded that particles from wood burning have twice the warming effect calculated in previous estimates. It was shown that BC has a warming effect approximately two thirds that of carbon dioxide. Most climate models treat BC as the sole light-absorbing carbonaceous particulate. Nevertheless, some organic aerosols (OA), designated as brown carbon and mainly associated with biomass burning emissions, also absorb light. Unlike BC, whose light absorption properties are relatively well understood (Bond and Sun, 2005), brown carbon encompasses a wide range of very little known compounds that exhibit highly variable absorptivities, with reported values spanning two orders of magnitude (Chen and Bond, 2010; Saleh et al., 2013). Saleh et al. (2014) performed smog chamber experiments to characterise the effective absorptivity of OA from biomass burning under a range of conditions, showing that brown carbon in emissions from this source is associated mostly with organic compounds of extremely low volatility. Moreover, the researchers found that the effective absorptivity of OA in biomass burning emissions can be parameterised as a function of the ratio of BC to OA, suggesting that aerosol absorptivity depends largely on burn conditions, not fuel type. It was concluded that BC from biomass burning can be an important factor in aerosol radiative forcing.

The mechanisms leading to the formation of secondary organic aerosol (SOA) are an important subject of ongoing research for both air quality and climate. Recent laboratory experiments suggest that reactions taking place in the atmospheric liquid phase represent a potentially significant source of SOA mass. Gilardoni et al. (2016) reported direct ambient observations of SOA mass formation from processing of biomass burning emissions in the aqueous phase. Aqueous SOA (aqSOA) formation was observed both in fog water and in wet aerosol. It was found that aqSOA from biomass burning contributes to the “brown” carbon budget and exhibits light absorption wavelength dependence close to the upper bound of the values found in laboratory experiments for fresh and processed biomass burning emissions. It was estimated that the aqSOA from residential wood combustion can account for up to 0.1 – 0.5 Tg of OA per year in Europe, equivalent to 4 – 20% of the total OA emissions. Organic gases leading to SOA during atmospheric aging are broadly unidentified, particularly in regions influenced by biomass burning. The lack of knowledge associated with SOA, which dominates the atmospheric OA burden, contributes to huge uncertainties when estimating the effects on climate and human health. Bruns et al. (2016) characterised primary and aged emissions from residential wood combustion using high resolution mass spectrometry to identify SOA precursors. It was argued that SOA precursors usually included in models account for only about 3 – 27% of the observed SOA, while the authors could explain ~84 – 116% of the SOA by inclusion of nontraditional precursors. It was also noticed that although hundreds of organic gases are emitted during wood combustion, SOA is dominated by the aging products of only 22 compounds. In some cases, oxidation products of phenol, naphthalene and benzene alone encompass up to ~80% of the observed SOA.

The few laboratory studies investigating SOA formation from residential wood burning have shown that it can be very significant. It has been reported that aged OA was 1.8 – 5.3 times that of primary OA for log wood burners during stable burning conditions (Grieshop et al., 2009a, 2009b; Hennigan et al., 2011). SOA formation from residential wood combustion was also observed in ambient measurements (Iinuma et al., 2010; Mohr et al., 2013). The SOA fractional composition attributable to wood combustion in ambient measurements is largely unknown and more work is needed to characterise quantities and composition. It has been observed, for example, that 59% of the carbon in semi- and low-volatility oxygenated organic aerosol (largely secondary) in winter in Barcelona consisted of non-fossil carbon, suggesting an origin in sources such as biomass burning and cooking (Mohr et al., 2012).

In a “potential aerosol mass” (PAM) flow reactor, substantial new OA mass was observed from aging biomass burning smoke, resulting in total OA average of 1.42 ± 0.36 times the initial primary OA after oxidation (Ortega et al., 2013). This study confirmed that the net secondary- to-primary OA ratio of biomass burning smoke is far lower on average than that observed for urban emissions. In smog chamber experiments, Bruns et al. (2015) observed that OA concentrations in aged aerosols from wood combustion increased by a factor of 3 ± 1 for high load experiments compared to 1.6 ± 0.4 for average-load experiments. In the aerosol mass spectrometer, an increase in aromatic signature ions at lower m/z values, likely fragments from larger functionalized polyaromatic hydrocarbons (PAHs), was observed with aging. Filter samples also showed an increase in functionalised PAHs in the particles with aging, particularly oxidised naphthalene species. This raises serious health concerns because it is known that many of these oxidised species often have higher toxicity than their precursors (Yu, 2002). Photochemical aging of smoke from biomass burning can account for a significant enhancement of initial emitted OA mass. These secondary processes, which include functionalisation and fragmentation reactions, need to be included in climate- and air-quality models (Ortega et al., 2013).

A better understanding of the role of wood biomass heating as a major source of globally harmful outdoor air pollutants is needed among national, regional and local administrations, politicians and the public in general. It is difficult to tackle outdoor air pollution problems in many parts of the world without addressing this source. It has been recognised that this is a sector in which PM and BC emissions can potentially be reduced with greater cost-effectiveness than many other emission reduction options (WHO, 2015).

The environmental and health effects are not only related to physical characteristics, such as particle number, surface area, mass concentration, size, density and morphology, but also to chemical properties (Bølling et al., 2009; Pöschl, 2005). These physicochemical properties are determined by the technology employed, quality and type of fuels and operating practices. Substantial efforts have been made into categorising particles from biomass combustion processes. Taking into account the physical and chemical characteristics of wood smoke particles, three main types were proposed by Bølling et al. (2009) and Obaidullah et al. (2012) including soot, spherical organic carbon (OC) particles and inorganic ash particles. The terms elemental carbon (EC), black barbon (BC) and soot have often been used loosely and interchangeably in the literature. Soot, the product of incomplete combustion of any carbon containing fuels, is used by the Intergovernmental Panel on Climate Change to denote any light absorbing, combustion generated aerosols, whereas BC denotes the optical properties of soot defined as an ideally light-absorbing substance composed of carbon (Karanasiou et al., 2015; Petzold et al., 2013). Light-absorbing is not strictly specific to carbon, but BC features a much larger mass absorption cross-section than other aerosol constituents. In contrast, EC refers to chemical properties, i.e. to thermally-refractory carbon, including graphitic structures. The term EC is used when total carbon is volatilised from the sample, and EC is differentiated from OC based on refractiveness properties (i.e. thermal methods) or optical measurements during the course of the thermal analysis (thermal-optical methods) (Karanasiou et al., 2015). Sigsgaard et al. (2015), within their position paper, gave broader information on particle size distributions by type, as well as new findings on biomass combustion particle formation and toxicity. Inefficient traditional combustion appliances generate an aerosol mainly composed of carbonaceous compounds, while during efficient combustion conditions particles are mainly formed by ash related material (Alves et al., 2011; Calvo et al., 2015; Fine et al., 2001; Frey et al., 2009; Kelz et al., 2010; Lamberg et al., 2011a; Leskinen et al., 2014; Orasche et al., 2012; Sippula et al., 2007; Tissari et al., 2008a, 2008b; Vicente et al., 2015a).

This paper critically reviews the extensive literature regarding particulate emissions from biomass combustion for residential heating purposes to give an overview of the present state of knowledge. Special attention is paid to particulate emissions and composition from different technologies and fuels employed in residential combustion, as well as the dependence on the user's behaviour. The main biomass burning organic tracers and their utilisation in receptor modelling to assign the contribution of this source to the ambient particulate matter concentrations are also discussed. This will contribute with updated databases to improve emission inventories, source apportionment and climate models, and will help in the adoption of air pollution control measures. Some of the research gaps and needs are also outlined.

2.2. Particulate emission factors

In the past years, a wealth of publications has reported on the particulate emissions from residential biomass combustion. An emission factor (EF) is defined as the mass of targeted pollutant emitted per unit mass of fuel burned or per unit of energy produced. The EF is based on pollutant concentration and flue gas volume flow rate in relation to the fuel burned (g PM kg^{-1} fuel burned) or energy input (mg PM MJ^{-1}). The detailed description of the calculation methods can be found in several studies (e.g. Calvo et al., 2014; Ozgen et al., 2014). The PM EF can be also calculated based on the carbon mass balance method. Following this method, the EF is obtained from the ratio between the pollutant mass concentration and the total carbon emitted (gaseous CO, CO_2, total hydrocarbons and total particulate carbon) multiplied by the mass fraction of carbon in the dry fuel (Shen et al., 2010; Zhang et al., 2000). The extrapolation of laboratory measurements is associated with large uncertainties, not only due to the different PM EF calculation methodologies, but mainly due to the variability in fuels, combustion appliances and household behaviour. Furthermore, although an extensive amount of work has been carried out to quantify the PM emissions, different sampling strategies for evaluating emissions are employed, which makes it difficult to compare the values reported in the literature.

2.2.1. Sampling strategies

A significant number of different standard methods for PM sampling is available (Table A1). Several researchers have followed different standards based on sampling from the undiluted flue gas in the chimney (Fig. 2.1A), such as the EPA Method 5H, the VDI 2066 (Bari et al., 2011; Bologa et al., 2011a; Carvalho et al., 2013) and the DIN-plus 13240 standard (Verma et al., 2012). The EPA Method 5H allows the determination of PM and condensable emissions through a dual filter sampling train. The two filters are separated by impingers, which are cooled such that the temperature in the second filter is lower than 20 °C. The first filter, heated to 120 °C, collects the solid PM (Fig. A1). According to the German standard VDI 2066, PM sampling is performed inside the stack (in-stack sampling). The flue gas temperature in the chimney prevents water condensation on the filter and for that reason the filter holder is not heated. Nevertheless, according to the standard, when the flue gas is saturated, an out-stack filter should be used and the filter and sampling line must be heated to prevent condensation.

Flue gas dilution before sampling is an alternative method that has been widely used to assess particulate emissions. There are two main strategies: (i) partial flue gas dilution (Fig. 2.1B) using a dilution tunnel according to the standard ISO 8178 (Frey et al., 2009; Lamberg et al., 2011b, 2013; Tissari et al., 2008a, 2009; Sippula et al., 2007) and (ii) full flue gas dilution (Fig. 2.1C) based on hood dilution systems (Alves et al., 2011; Calvo et al., 2014, 2015; Fernandes et al., 2011; Gonçalves et al., 2010, 2011; Vicente et al., 2015a, 2015b, 2015c). Although it is not mentioned in any standard, some authors perform the dilution using a compact dilution system which comprises two dilution steps. In the first step, a sample flow is taken from the chimney and diluted with heated and filtered air, to prevent particle losses and transformation, in a porous tube diluter. In the second step the samples are further diluted with an ejector diluter to stabilise the sample (Lamberg et al., 2011a; Nuutinen et al., 2014; Sippula et al., 2009a, 2009b; Tissari et al., 2007).

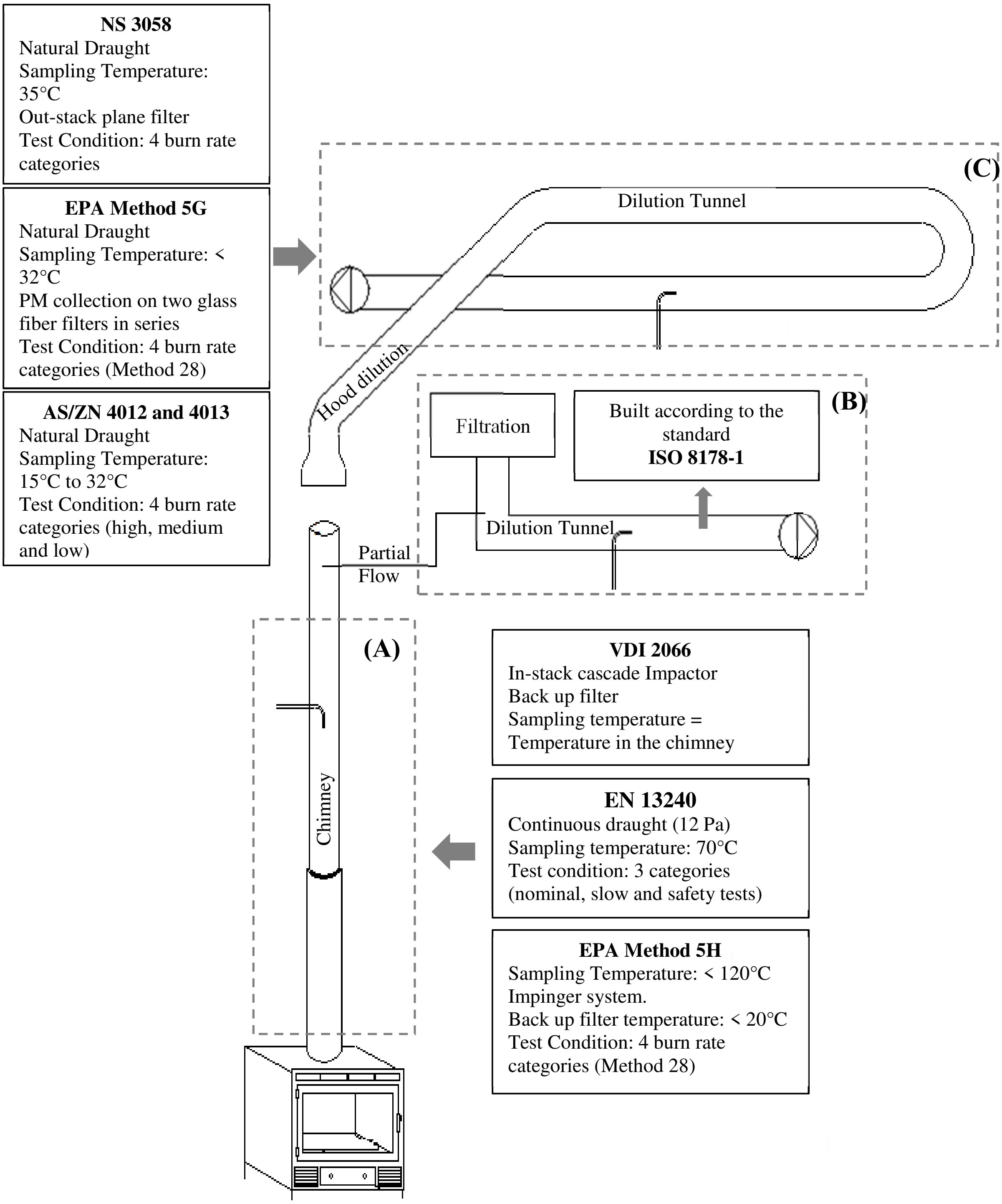

Figure 2.1. PM sampling standards and procedures for wood combustion appliances.

The partial flue gas dilution is performed by carrying a portion of flue gas from the chimney to a dilution tunnel through a heated sampling line, to prevent cooling and condensation. The dilution in the tunnel is achieved with filtered air. The full gas dilution is achieved using a hood after the chimney stack. The space between the stack and the hood ensures flue gas dilution (with ambient air) and effective mixing due to the turbulence generated. The NS 3058 standard (Ozgen et al., 2014; Win and Persson, 2014), the EPA Method 5G (Purvis et al., 2000), and the AS/NZS 4012 and 4013 standards (Jordan and Seen, 2005) are examples of procedures relying on the full flue gas dilution before PM sampling. The Norwegian and the Australian/New Zealand PM sampling train resemble in many aspects the one used in EPA Method 5G (Fig. 2.1C). Apart from the PM sampling train, there are significant differences in the test procedures among standards. Key differences include the draught, fuel, reporting units, dilution, and sampling time. The EPA and the Norwegian standards require four burn rate categories, while the Australian/New Zealand standard comprises three test burns for three different flow settings (high, medium and low). The fuel is also specified in each standard (e.g. softwood and hardwood, Norwegian and Australian/New Zealand, respectively). Although the EN 13240 European standard does not comprise requirements for particulate matter emissions, it describes the test method for heating appliances fired by solid fuels. The standard comprises three test categories (nominal, slow and safety tests), which are performed with constant forced draught at 12 Pa. The weight of the test fuel is the one defined by the manufacturer. The German DIN-plus 13240 standard follows the test procedures of EN 13240.

The way of reporting emission values also requires standardisation. The most common forms are: i) mass of PM per mass of fuel burned or, when the heating value of the fuel is known, mass of PM per MJ (e.g. Alves et al., 2011; Bäfver et al., 2011; Calvo et al., 2014, 2015; Lamberg et al., 2011a; Sippula et al., 2007; Vicente et al., 2015b, 2015c), or ii) mass of PM per volume sampled, which might be normalised to different O_2 reference concentrations (e.g. Bologa et al., 2010; Carroll and Finnan, 2013; Fernandes and Costa, 2012; Limousy et al., 2013; Migliavacca et al., 2014; Verma et al., 2011, 2012, 2013; Wiinikka et al., 2013). There are also significant differences in the reporting units across standards. The Australian/New Zealand and the Norwegian standards set g kg^{-1} as the PM emission unit, the German DIN-plus 13240 and VDI 2066 establish mg Nm^{-3} at 13% O_2 and according to the EPA methods the emissions are expressed as particulate emission rate (g $hour^{-1}$).

The definition of dilution ratio can also be based on different principles: i) volumetric flow rates (Calvo et al., 2014; Toscano et al., 2014; Vicente et al., 2015a, 2015b, 2015c) or ii) CO_2 concentrations (Hukkanen et al., 2012; Lamberg et al., 2013; Nuutinen et al., 2014; Ozgen et al., 2013, 2014; Tissari et al., 2008a). An international standard method to determine PM emissions from residential heating appliances should be implemented to allow the comparability of results and a reliable assessment of the source impact.

Nussbaumer et al. (2008a) carried out a comparative study of PM sampling strategies and reported that particulate EFs determined in dilution tunnels coupled to the exhaust stack are between 2.5 and 10 times higher compared with the ones obtained from measurements of solid particles in the chimney. A dilution stack sampler simulates the cooling and dilution processes that occur in the plume downwind a combustion source, enabling the collection of organic compounds as PM after their condensation under ambient conditions. Hildemann et al. (1989) conducted a field comparison of a dilution stack sampler with EPA Method 5 concluding that this sampler collects about 10 times as much organic material as the hot filter portion of the Method 5 train. Because the size and complexity of dilution samplers is a major obstacle to more extensive application of these systems, a more portable dilution sampler, without residence tank, was designed by Lipsky and Robinson (2005) to provide measurements consistent with the widely cited Caltech dilution sampler (Hildemann et al., 1989). Intercomparison experiments were performed using emissions from a woodstove. Bias errors of 10% or less were observed between the portable field tunnel sampler and the sampler based on the Caltech design for $PM_{2.5}$ total mass, carbonaceous constituents measured with filters, and integrated volume measured with a scanning mobility particle sizer (SMPS). Large differences in total particle number were registered between the two samplers in experiments during which nucleation occurred in the larger, laboratory sampler tunnel, but not in the smaller, field sampler. These variations were attributed to differences in mixing rates between the two systems. Experiments were also carried out to evaluate the effects of residence time on diluted exhaust. No difference was observed in simultaneous measurements made 2.5 and 40 s after dilution. Theoretical analysis indicated that the aerosol should achieve phase equilibrium in < 1 s. Thus, it was concluded that the elimination of the residence time tank simplifies the design and operation of dilution samplers. Additional experiments were conducted to observe the effects of dilution on fine particle mass emissions from a woodstove. Filter measurements were made simultaneously using three dilution sampling systems operating at dilution ratios ranging from 20:1 to 510:1 (Lipsky and Robinson, 2006). Large decreases in fine particle mass emissions were observed with increases in dilution. At low levels of dilution, semivolatile species mainly occur in the particle phase, but increasing dilution reduces the concentration of these species, shifting the material to the gas phase in order to maintain phase equilibrium. Emissions of EC did not vary with dilution. The application of the partitioning theory indicated that dilution samplers need to be operated such that the diluted exhaust achieves atmospheric levels of dilution. In fact, too little dilution can potentially overestimate the fine particle mass emissions, while too much dilution can underestimate them.

To study the influence of sampling conditions, Ozgen et al. (2014) performed simultaneous sampling in the hot and diluted flue gas from an advanced stove and found that the diluted EFs were on average 4 times higher than the ones obtained in the hot flue gas. Mitchell et al. (2016) used two different measurement methodologies to determine the PM emissions from a fixed bed stove and found significant differences between the two approaches. The major difference between the methods was the sampling temperature (sampling at 170 °C using the cyclone method and at 70 °C using the gravimetric method). The higher PM EF for sampling at lower temperature is due to the condensation of organic material on the filter. Sampling at higher temperatures can significantly underestimate the organic PM fraction.

Different PM fractions can also be sampled (e.g. PM_1, $PM_{2.5}$ and PM_{10}). However, several studies have reported that residential biomass combustion typically generates emissions dominated by particles with mass median diameter between 0.1 and 1 µm (Bäfver et al., 2011; Boman et al., 2004, 2011; Garcia-Maraver et al., 2014; Lamberg et al., 2011a; Pettersson et al., 2011; Tissari et al., 2008a; Verma et al., 2012). Thus, when comparing emissions of different size fractions, the error is predictably low.

2.2.2. Emission values for different appliances, biofuels and operating conditions

The variability in particulate emissions reported in the literature depends not only on the sampling procedure, but also arises from the use of different fuels, combustion technologies and operating conditions. Table 2.1 presents a compilation of bibliographical results for PM EFs (mg MJ^{-1}) obtained in biomass combustion experiments based on flue gas dilution, comprising different appliances, fuels and operating practices. Numerous models and designs of biomass burning appliances (boilers, stoves and fireplaces) are available on the market. Emissions from domestic combustion are highly technology-dependent and the standardisation of the burning appliances is crucial to guide the transition to cleaner systems. Countries like Germany, Austria and Switzerland have their own very strict national standards regarding the emissions of space heating appliances. The European Commission has already established the framework on Ecodesign requirements for domestic heating systems in order to regulate, among other parameters, the $PM_{2.5}$ emissions.

2.2.2.1. Fireplaces

For open fireplaces, PM EFs range from values exceeding one hundred to over 1600 mg MJ^{-1}. The wide amplitude may be related not only to variations in sampling strategies, but also to the great impact of operating conditions and/or fuels burned. McDonald et al. (2000) reported PM emissions from combustion tests carried out in a fireplace for various types of wood with different moisture contents. For softwood combustion, a maximum difference of 3 times in the PM EF was observed, while between hardwood species emissions differed almost 2 times. Differences in the moisture content and burn rates were the factors originating these variations. Although firewood exhibits a wide range of different characteristics, with strong repercussions on emissions, its market is almost entirely unregulated and unsurveilled. Alves et al. (2011) tested different wood types in a fireplace and observed a difference of around 2-fold between the lowest and the highest PM EF. These results were further corroborated by Calvo et al. (2015). Purvis et al. (2000) reported PM emissions from two standard closed fireplaces (one incorporated a room air blower) and one low emission closed fireplace with secondary air injection. The authors included cold starts and full loads in the emissions and tested different fuels, wood moistures and burn rates. The differences reported were 4.5-fold higher for the less efficient fireplace compared with the fireplace with secondary air injection. Particulate emissions from burning firewood in boilers, stoves or fireplaces are highly dependent on the fuel moisture content (e.g. McDonald et al., 2000; Shen et al., 2013a), size of the logs and batch (Johansson et al., 2004; Shen et al., 2013b; Tissari et al., 2009; Vicente et al., 2015b). Tissari et al. (2009) found that big batch sizes increase the emissions significantly. Doubling the batch size caused particle EFs to increase almost twice. Using equal batch sizes, emissions from small logs were 4.8-fold greater than from big logs. When small batch sizes were used, but the logs in them were small, PM EFs were 2.5 times higher than when big batches and big logs were burned. Because glass fronted fireplaces keep fire temperatures for longer, produce higher heat outputs and higher efficiency ratings, they allow better combustion to occur, thereby contributing to a reduction of global emissions. Ozgen et al. (2014) reported a 4-fold difference between a closed and an open fireplace.

2.2.2.2. Woodstoves

The PM EFs from wood combustion in woodstoves can be anywhere between 20 and nearly 1500 mg MJ^{-1} (Table 2.1). Once again, both fuels and combustion practices have shown to play an important role on particulate emissions. Calvo et al. (2014) investigated the particulate emissions from softwood and hardwood combustion in a traditional brick fireplace and a cast iron woodstove. Irrespective of the combustion appliance, PM emissions were about 1.5-fold higher for hardwood combustion. Besides the influence of the type of firewood, a difference in the PM emissions reaching 2.8-fold was observed between the fireplace and the woodstove. Wood combustion in modern woodstoves generates generally lower particulate EFs, in the range of about 20 to 220 mg MJ^{-1}. Fernandes et al. (2011) reported PM emission factors from the combustion in a fireplace, woodstove and eco-labelled woodstove. The average EF obtained by the authors for the fireplace was, on average, around 7-fold higher compared to the modern ecolabelled woodstove.

Table 2.1. PM emission factors (mg MJ^{-1}) obtained from biomass combustion based on measurements with flue gas dilution.

Combustion appliance	Fuel	Fraction Sampled	PM EF (mg MJ^{-1})	OC (wt.% PM)	EC (wt.% PM)	Reference
Fireplaces						
Open fireplace	Hardwoods and softwoods	$PM_{2.5}$	161 - 500 [a], (1)	55.1 - 58.3 [a]	6.5 - 14.2 [a]	McDonald et al. (2000)
Open fireplace	Portuguese woods (excluding golden wattle) and briquettes	$PM_{2.5}$	330 - 1610[a], (1)	20 - 48 [a]	1.1 -17 [a]	Gonçalves et al. (2011)
Open fireplace	Portuguese woods and briquettes	$PM_{2.5}$	550 - 1122	38.7 - 53.0	2.2 - 7.5	Alves et al. (2011)
Open fireplace	Pine logs	PM_{10}	742 ± 243(1)	N/A	N/A	Calvo et al. (2014)
	Eucalypt logs		1124 ± 158(1)	N/A	N/A	
Open fireplace	Beech, false acacia, hornbeam, oak and spruce logs	PM_{tot}	434 - 611	N/A	N/A	Ozgen et al. (2014)
Closed fireplace	Beech, false acacia, hornbeam, oak and spruce logs	PM_{tot}	152 -219	N/A	N/A	
Open fireplace	Three common Southern and mid-European woods	$PM_{2.5}$	322 - 778 (1)	67.2 - 75.0	4.63 - 7.41	Calvo et al. (2015)
Woodstoves						
Woodstove	Mixed hardwoods, oak	$PM_{2.5}$	128 - 400 [a] (1)	64.9	8.19	McDonald et al. (2000)
Modern woodstove	Logwood in accordance with ÖNORM CEN/TS 14961 and ÖNORM M 7132	PM_1	46.1- 47.2	N/A	N/A	Kelz et al. (2010)
Conventional woodstove			55.5- 74.2	N/A	N/A	
Woodstove	Birch, pine and spruce logs	PM_{tot}	38 - 350[a]	N/A	N/A	Pettersson et al. (2011)
Woodstove	Portuguese woods and briquettes	$PM_{2.5}$	233 – 906	45.0 - 53.6	1.9 - 7.7	Alves et al. (2011)
Woodstove	Portuguese woods (excluding golden wattle) and briquettes	$PM_{2.5}$	92.2 - 1433[a] (1)	30 - 50[a]	0.82 - 9.3[a]	Gonçalves et al. (2011)
Woodstove	Spruce logs	PM_{tot}	85 - 250[a]	12.9 -21.6 [a]	1.88 - 10.9 [a]	Orasche et al. (2012)
	Beech logs		120 - 410[a]	12.5	34.2	
Conventional woodstove	Beech, false acacia, hornbeam, oak and spruce logs	N/A	140 - 225	N/A	N/A	Ozgen et al. (2014)
Modern woodstove			120 - 176	N/A	N/A	
Woodstove	Pine logs	PM_{10}	263 ± 131(1)	N/A	N/A	Calvo et al. (2014)
	Eucalypt logs		423 ± 137(1)	N/A	N/A	
Woodstove	Pine logs	PM_{10}	282 - 1083 [a] (1)	32.2 - 51.6 [a]	8.37 - 30.8 [a]	Vicente et al. (2015a)
	Beech logs		270 - 611 [a] (1)	34.1 -42.9 [a]	12.2 - 35.2 [a]	
Woodstove	Three common Southern and mid-European woods	$PM_{2.5}$	157 - 744 (1)	56.7 - 67.9	6.72 - 20.0	Calvo et al. (2015)

Chimney woodstove	Beech, oak and spruce logs and briquettes	PM_{10}	63 - 97	26.8 - 38.8	24.2 - 36.7	Schmidl et al. (2011)
	Spruce logs	PM_{10}	110 - 303[a]	35.1 - 51.6[a]	16.8 - 40.3[a]	
Modern chimney type woodstove	Beech, oak and spruce logs and briquettes	PM_{10}	73 - 89	22.2 - 35.6	29.8 - 37.6	
	Spruce logs	PM_{10}	49 - 91[a]	15.8 - 42.8[a]	7.3 - 41.7[a]	
Chimney type woodstove	Pine, eucalypt, cork oak and golden wattle logs	PM_{10}	62 – 161(1)	19.7 - 42.8	11.3 - 37.1	Gonçalves et al. (2010)
Chimney type woodstove	Dry pine needles and leaves	PM_{10}	85 - 626	N/A	N/A	Kistler et al. (2012)
	Seven hardwoods and five softwoods		20 - 222	N/A	N/A	
Pellet stoves and boilers						
Pellet boiler	Wood pellets in accordance with ÖNORM M 7135	PM_1	6.0 - 6.2	N/A	N/A	Kelz et al. (2010)
Pellet boiler with burner A	Six fuels: fresh and six-month stored material from softwood sawdust, logging residues and bark	PM_{tot}	114 - 377	N/A	N/A	Boman et al. (2004)
Pellet boiler with burner B			57 - 157	N/A	N/A	
Pellet boiler with burner C			64 - 192	N/A	N/A	
Modern Scandinavian pellet stove	Pellets made of unknown mixture of pine and spruce and pellets made with >90% pine and spruce	PM_{tot}	15 - 43[a]	N/A	N/A	Boman et al. (2011)
Conventional American pellet stove			22 - 47[a]	N/A	N/A	
Pellet stove	Wood pellets in accordance with ÖNORM M 7135	PM_{10}	3.0 - 8.5[a]	4.7 - 22[a]	13.7 - 15.8[a]	Schmidl et al. (2011)
Pellet boiler	Pine steam wood pellets	PM_1	3.0 - 29[a]	2.30 - 10.6[a]	0.0 - 51.2[a]	Lamberg et al (2011b)
Pellet stove	Wood pellets	PM_{10}	16 - 31[a]	N/A	N/A	Kistler et al. (2012)
Pellet boiler	Softwood pellets in accordance with SS 187120	$PM_{2.5}$	62 - 84[a]	N/A	N/A	Win et al. (2012)
Pellet stove	Spruce pellets in accordance with ÖNORM M 7135	PM_{tot}	36 - 110[a]	8.33 - 32.7[a]	1.42 - 7.45[a]	Orasche et al. (2012)
Pellet boiler			14 - 19[a]	5.07 - 17.4[a]	0.07 - 2.05[a]	
Pellet boiler	Pellets made of wood and/or bark material	PM_1	9.7 - 46	0.0 - 9.14	0.46 - 40.2	Lamberg et al (2013)
	Pellets made of peat		2.9 - 5.1	0.0 - 14.5	1.18 - 3.10	
	Pellets made of of woody biomass and peat		5.2 - 28	0.98 - 9.81	0.43 - 16.0	
	Pellets made of straw		126 - 196	0.94 - 1.75	0.63 - 18.4	
	Pellets made of wood and reed canary grass		23	9.00	11.4	
Pellet stove		PM_{tot}	75 - 139	N/A	N/A	Ozgen et al. (2014)

Pellet boiler	Low-quality pellets and pellets in accordance with DIN-PLUS		30 - 103	N/A	N/A	
Pellet boiler – bottom fed	Softwood pellets in accordance with SS 187120	$PM_{2.5}$	51 - 62[a]	N/A	N/A	Win and Persson (2014)
Pellet boiler – top fed 1			53 - 65[a]	N/A	N/A	
Pellet boiler – top fed 2			50 - 65[a]	N/A	N/A	
Pellet stove			43 -55[a]	N/A	N/A	
Pellet stove	Pellets made of golden wattle, cedar and pine.	PM_{10}	26.6 ± 3.14[a]	27.8	13.6	Vicente et al. (2015b)
	Pellets made of lignocellulosic residues and dust from the furniture manufacturing industry (75/25).		86.4 ± 13.6[a]	16.6	42.6	
	Pellets made of lignocellulosic residues and dust from the furniture manufacturing industry (65/35).		102 ± 8.63[a]	8.22	7.52	
	Pellets made of waste woodchips and dust from the furniture manufacturing industry (50/50).		75.6 ± 9.39[a]	20.1	27.1	
	Olive pit		169 ± 23.6[a]	28.8	5.24	
	Shell of pine nuts		117 ± 33.9[a]	16.0	32.6	
	Almond shell		112 ± 4.05[a]	10.8	7.86	
Other appliances						
Conventional masory heater	Birch logs	PM_1	100 - 617[a] (1)	N/A	N/A	Tissari et al. (2008b)
Modern tiled stove	Logwood in accordance with ÖNORM CEN/TS 14961	PM_1	28.0 - 31.3	N/A	N/A	Kelz et al. (2010)
Conventional sauna stove	Birch logs	PM_1	391 ± 101	N/A	N/A	Hukkanen et al. (2012)
Conventional Masonry Heater (small)	Birch logs	PM_1	56.3 - 69.1	46.4	33.0	Nuutinen et al. (2014)
Modern Masonry Heater (small)			40.2 - 49.0	29.5	65.3	
Conventional Masonry Heater (large)			94.1 - 106	37.4	51.1	
Modern Masonry Heater (large)			44.5 - 44.8	22.6	73.5	

[a]different combustion conditions; (1)assuming 18 MJ.kg^{-1}; N/A: information not available.

Although the emissions during cold start/kindling are known to be significantly higher (Gonçalves et al., 2011; Vicente et al., 2015b), usually the values reported in the literature only include the hot start phase, i.e., PM sampling starts after loading a fuel batch to a hot charcoal bed. This may lead to an underestimation of emissions, since the ignition phase is neglected.

In batch mode operated combustion appliances, the household behavior can make the emissions fluctuate significantly. Schmidl et al. (2011) studied the influence of the operator's behaviour on emissions from manually fired systems by changing the amount of fuel loaded and the airflow setting. The authors reported that the operator can have an influence up to a factor of 6 on particulate emissions from woodstoves. Tissari et al. (2008a) tested two different conditions, designated as “normal combustion” and “smouldering combustion”, on a conventional masonry heater. A PM_1 EF about 6 times higher was obtained for smouldering combustion. Other authors found high particulate emissions during smouldering conditions at reduced load and air starved conditions (Vicente et al., 2015b). Vicente et al. (2015b) studied the influence of operating conditions on emissions from a woodstove, including two ignition techniques (upside-down and bottom-up lighting), hot start versus cold start, different fuel loads (low, medium and high load) and secondary combustion air supply. In the case of high loads, the emissions of whole logs versus split pieces were compared. This study showed that large variations in emissions can be easily achieved. In particular, the ignition technique and combustion air supply exert a remarkable influence on emissions. The lowest emissions were observed when secondary air was supplied to the combustion chamber. The top-down ignition technique can reduce the PM_{10} EF to less than half compared with the traditional technique of lighting from the bottom. A similar result, i.e., a noteworthy reduction of PM emissions by modifying the ignition technique, has been previously reported by Nussbaumer et al. (2008b).

2.2.2.3. Pellet stoves and boilers

EFs of pellet stoves and boilers are significantly lower than those from woodstoves and fireplaces. The particulate emissions described in the literature for the combustion of wood pellets range from around 3 to 140 mg MJ^{-1} (Table 2.1). Lamberg et al. (2011a) collected particulate samples from six combustion appliances: five woodstoves (including one modern combustion technology, three conventional woodstoves and one sauna stove) and a modern pellet boiler. Advanced combustion in the pellet boiler produced the lowest PM emissions whereas inefficient batch combustion in a sauna stove released the highest emissions. Improved batch combustion with air-staging produced PM_1 emissions about 2.5-fold higher compared to the modern pellet boiler. Improved batch combustion and conventional batch combustion showed similar PM_1 emissions. Schmidl et al. (2011) investigated the particulate emissions from two automatically and two manually fired combustion appliances and eight fuel types. The authors concluded that the combustion of wood pellets and chips in automatically fired appliances emit almost one order of magnitude less PM. The age of the combustion appliance is a factor influencing PM emissions. Johansson et al. (2004) tested old and modern boilers and observed EFs ranging from 87 to 2200 mg MJ^{-1} and between 18 and 89 mg MJ^{-1}, respectively.

A noticeable increase in the particulate emissions from automatically fired combustion systems is achieved using pellets made with other raw material than wood or when burning non-pelletised fuels (Boman et al., 2004; Garcia-Maraver et al., 2014; Lamberg et al., 2013; Limousy et al., 2013; Verma et al., 2012; Vicente et al., 2015c). Besides the fuel properties, the emission variations can also be related to the full or partial load operating mode (Boman et al., 2011; Lamberg et al., 2011b; Tissari et al., 2008b; Verma et al., 2013; Wöhler et al., 2017). Moreover, some researchers include the non-steady-state phases (e.g. start-up, transient and shut-down phases) in the reported particulate emissions, considering this to be more representative of the daily use pattern (Toscano et al., 2014; Win and Persson, 2014; Wöhler et al., 2017), while others contemplate only the steady-state phases (Fernandes and Costa, 2012; Sippula et al., 2007; Vicente et al., 2015c), claiming that the duration of non-steady phases are much shorter than the steady operation.

Ozgen et al. (2014) tested low quality cheap pellets and high quality pellets with DIN-plus certification in a pellet stove and a boiler. Average EFs of 109 mg MJ^{-1} and 61 mg MJ^{-1} were observed, respectively, for the pellet stove and boiler. Vicente et al. (2015c) tested four different types of wood pellets (high quality pellets made of wood and pellets composed of lignocellulosic residues, waste woodchips and dust from the furniture manufacturing industry) and three agro-fuels (olive pit, almond shell and shell of pine nuts) in a pellet stove. The non-pelletised agro-fuels resulted in higher PM_{10} EFs, possibly due to the fuel physical characteristics, which affect the fuel supply to the burner and consequently the combustion behaviour. A 6-fold difference was found between the PM_{10} EF obtained for the combustion of high quality pellets and olive pit. The fuel chemical composition (e.g. K content) may also be related to the higher particulate emissions observed for the agricultural fuels. A 3.8-fold difference between the PM_{10} EF for the various types of pellets was observed. For three types of non-certified pellets, high contents of zinc (14.6 to 19.9 wt% of total inorganic mass) and lead (7.6 to 17.6 wt% of total inorganic mass) were recorded. It is important to highlight that some woods, wood products and wastes arising from specific industrial sectors, such as the furniture industry, may be subjected to phyto-treatments and if these products are directly used as biofuels or as raw material for manufacturing pellets, upon burning, the emission into the atmosphere of heavy metals, including copper, chromium and arsenic, as well as preservatives (e.g. pentachorophenol) will take place. As regards the use of pellets, the physical characteristics like dimensions (length and diameter), fine content and particle density can have great effect on the particulate emissions since those can affect the fuel supply to the burner and the combustion behavior (Carvalho et al., 2013; Garcia-Maraver et al., 2014; Obernberger and Thek, 2004; Verma et al., 2012; Wöhler et al., 2017). In highly efficient and optimised combustion systems, particulate emissions consist mainly of ash-related material (Tissari et al., 2008b). In several studies, the fuel ash content has been found to correlate positively with the PM emissions (e.g. Carroll and Finnan, 2013; Sippula et al., 2007). Furthermore, high concentrations of elements, such as potassium, chlorine and sulphur in the fuel, have also been linked with higher particulate emissions (Sippula et al., 2007).

With the steadily increase in the pellet market, alternative raw materials for pellet production are of great interest. In Portugal, as well as in other southern European countries, several sectors generate large amounts of residues, which can be used for pellet manufacturing (Monteiro et al., 2012). In recent years, attempting to verify the reliability of alternative raw materials for pellets production, the agro-industry residues have been the focus of several researchers. Pellets made of biomass residues, such as tomato, olive stove and cardoon, have been tested in a domestic mural boiler by González et al. (2004). Although the combustion efficiencies obtained with the three residues were very similar to the one obtained with the pellets recommended by the boiler manufacturer, the CO emission was higher. Olsson (2006) studied the combustion behaviour of wheat straw and peat/wood pellets reporting relatively low emissions compared with softwood pellets. However, the authors also observed higher emission of hazardous polycyclic aromatic hydrocarbons (PAHs) from straw and peat/wood pellets. Furthermore, a higher ash content of such biomass fuels generate high amounts of ash that need to be removed from the combustion appliance in order to prevent the undesirable shut down due to ash accumulation and slag formation (Öhman et al., 2004). Vicente et al. (2015b) have also reported slag formation on the pellet stove grate during the combustion of agro-fuels. Therefore, the current pellet systems available on the market are not designed for pellets made of agricultural residues, which can cause ash-related operational problems, such as fouling, slagging and corrosion (Biedermann and Obernberger, 2005; Öhman et al., 2004; Verma et al., 2012). For these reasons, the use of the above mentioned fuels should be reserved for medium and large scale combustion plants, which have more sophisticated and robust combustion systems (Obernberger and Thek, 2004).

It is almost impossible to track beyond the pellets production process to the processing material sources and to determine if the high content in ash forming elements (e.g. K, S and Cl) is a result of harvesting practices, use of waste materials, processing impurities or inappropriate handling during production and distribution. Given the interest in increasing the use of pellets as a renewable fuel, pellets standardisation is important to avoid the inclusion of hazardous materials during their manufacturing and in this way preventing environmental impacts of toxic species that would be emitted during the burning. Pellets standardisation and certification is a step towards the European pellet market development. For that reason and in order to follow the European standards for solid fuels the ENplus quality label was introduced and is now used across the world. The quality requirements of ENplus certification are based on the international standard ISO 17225-2, which has replaced the European Standard EN 14961-2. This quality label requires even stricter quality criteria than the international standard and addresses producers, traders and service providers.

2.2.3. Mitigation of emissions

In the past few years, the evaluation of emission reduction strategies for the residential biomass combustion sector has been investigated with increasing interest. These strategies can be oriented to the optimization of the combustion process and/or fuel improvement (primary measures) or can be focused on flue gas cleaning technologies (secondary measures). As regards the employment of primary measures into the combustion concept, a few studies have addressed the air supply design, for example, through the implementation of air staged combustion (Carvalho et al., 2016; Lamberg et al., 2011b; Nuutinen et al., 2014; Vicente et al., 2015b) or by pre-heating the primary combustion air (Carvalho et al., 2016), as well as the household behaviour, as discussed above. Other possible method to reduce the particulate emissions is the fuel improvement by using additives to capture gaseous alkali compounds, and thus decreasing the formation of particles (Bäfver et al., 2009; Fournel et al., 2015). With respect to secondary measures, there are several pollution control devices that can be applied to the flue gases, such as electrostatic precipitators (Bologa et al., 2010, 2011a, 2011b; Kaivosoja et al., 2013; Migliavacca et al., 2014; Sippula et al., 2009a, 2009b), condensing scrubbers (Grigonyte et al., 2014; Sippula et al., 2009a) and catalytic converters (Fine et al., 2004; Hukkanen et al., 2012). In practice, small-scale electrostatic precipitators (ESPs) are not options in the present, as they are not economically viable to control PM emissions from small scale combustion appliances (Karvosenoja et al., 2007). Moreover, the removal efficiency of ESPs is reliant on the particle resistivity. Therefore, the removal efficiency greatly changes with the composition of the emitted particles (Migliavacca et al., 2014). According to Nussbaumer and Lauber (2010), ESPs are designed to remove inorganic particles from the flue gases. Thus, depollution of the flue gas from traditional residential combustion appliances, such as fireplaces and woodstoves, is very problematic, because of incomplete combustions and high emission of condensables, which can lead to a higher aerosol load at filter outlet compared to filter inlet (Nussbaumer and Lauber, 2010). Furthermore, the use of such depollution devices may alter the particulate emission composition and, as result, some compounds might become enriched in the flue gas after the ESP, changing the toxicity of the released particles. Kaivosoja et al. (2013) reported higher cytotoxicity for particles collected after ESP rather than before, in the same wood powered district heating plant.

According to the authors, that might be related to the relative enrichment in Ca, Zn and PAHs in the particulate samples. Sippula et al. (2009a) also observed a change in the PM composition after an ESP in a wood fired grate boiler. The same conclusion was drawn by Nuutinen et al. (2014) after the implementation of air-staging in small scale heating appliances. An increase in the PAH particle bound emissions, as well as in EC, from a catalytic woodstove in comparison with the emissions observed during the non-catalytic mode tests of the same tree species was reported by Fine et al. (2004).

Catalytic combustors have been widely used, including in the residential heating sector. The main problem arising from the use of such devices is related to the low temperature of the flue gases when using these devices in inefficient combustion appliances. Most of the chemical compounds in wood smoke are only combustible at temperatures higher than 550 – 600 °C. When installed in the early part of the chimney, connected to the outlet of the combustion chamber of small-scale traditional appliances, these temperatures are hardly achieved. This is an issue especially problematic during the start-up, when the emissions can be really high but temperature is very low. Another disadvantage is associated with the ash/soot clogging and creosote fouling that may take place on the surface of the catalyst, decreasing its efficiency. Thus, catalytic converters need to be cleaned in a regular basis. Hukkanen et al. (2012) reported a decrease in the PM_1 emissions from a sauna stove with catalytic converter (391 to 252 mg MJ^{-1}). The reduction occurred mainly during the gasification stage through oxidation of condensable organic vapours and oxidation of soot particles. Fine et al. (2004) used a catalyst equipped woodstove in order to assess the effects of the catalyst on fine particle emissions. However, the catalyst was only engaged when the appliance reached the recommended operating temperature. For that reason, it was not possible to record a large reduction on the PM emissions, since a large share was likely emitted prior to catalytic operation.

Sippula et al. (2009a) studied the particle emissions of a fire-tube boiler based on rotating grate combustion technology (district heating unit) equipped with a condensing flue gas scrubber. The filtration efficiency of the particle removal device was, on average, 44% and 84% for PM_1 and total suspended particles (TSP), respectively.

2.3. Carbonaceous content and organic tracers

Scientific effort has been devoted to identify the composition of organic aerosols due to the potential use of statistically based techniques to estimate the contribution of various emission sources to the ambient PM. However, to estimate the contribution of residential biomass combustion to the atmospheric aerosol loading, only a small number of individual compounds are suitable. An ideal tracer should be source specific, resistant to degradation in the environment, its emission should be relatively constant and should allow high precision of measurement (Khalil and Rasmussen, 2003). Finding suitable tracers for residential biomass combustion is not an easy task due to the complex nature of combustion chemistry, which results in high variability of the particle chemical composition. Data reported in the literature show the influence of several factors, such as the stove design, operating conditions, combustion conditions and biomass fuel burned (Eriksson et al., 2014; Fine et al., 2004; Frey et al., 2009; Jordan and Seen, 2005; Lamberg et al., 2011a; Leskinen et al., 2014; Vicente et al., 2015a, 2015c, 2016; Weimer et al., 2008). Soot and organic particles are formed during incomplete combustion in small-scale biomass combustion (Bølling et al., 2009; Obaidullah et al., 2012), while during efficient combustion in modern domestic heating systems, the aerosol is dominated by ash compounds (Kaivosoja et al., 2013; Lamberg et al., 2011a; Leskinen et al., 2014; Orasche et al., 2012; Tissari et al., 2008b) and the carbonaceous content in the particulate mass can be below 1% (Löndahl et al., 2008).

2.3.1. Carbonaceous components

Table 2.1 displays the carbonaceous particulate mass fraction obtained in distinct biomass combustion appliances. Calvo et al. (2015) reported the carbonaceous matter resulting from the combustion of three different wood species in a fireplace and a woodstove. The EC mass fractions in particles emitted from the woodstove (6.72 – 20 wt%) were higher than those of the fireplace (4.63 – 7.41 wt%), while the opposite was observed for OC (67 – 75 wt% and 57 – 68 wt% for the fireplace and woodstove, respectively). Vicente et al. (2015a, 2015c) assessed the effects of biofuel type and operating practices on the particle chemical composition for two combustion appliances. In the case of the woodstove, total carbon represented 54 – 73 wt% of the particulate mass, regardless of fuel or operating conditions. The carbonaceous component was dominated by OC, especially when high loads of fuel were burned (Vicente et al., 2015a). Vicente et al. (2015c) found a lower carbonaceous content in the PM released during the combustion in a pellet stove than that reported previously during the combustion of several wood fuels in traditional woodstoves and fireplaces. The OC mass fraction in PM_{10} ranged from 8 to 29 wt%, while EC ranged from 3 to 47 wt%. Higher carbonaceous emissions were observed for agricultural fuels than for wood pellets. Fernandes et al. (2011) compared the particulate carbonaceous content resulting from the combustion in a fireplace, a traditional woodstove and a more efficient chimney type woodstove. The authors reported particles with the lowest OC and the highest EC contents for the chimney type woodstove. An improved combustion efficiency with higher combustion temperatures and vigorous flaming conditions in this latter device contributed to enhanced EC emissions. Torvela et al. (2014) also reported a higher OC content in PM_1 in intermediate and smouldering combustions than in efficient combustion conditions. Gonçalves et al. (2011) evaluated the influence of cold and hot start-up conditions on the total carbon content in particles emitted by traditional combustion appliances. However, the maximum temperatures reached in these appliances do not exceed 600 °C and for that reason the starting combustion temperature does not have significant influence on the particulate OC and EC fractions, resulting essentially in the formation of organic particles. Soot formation occurs at high temperatures in the fuel-rich zones. The total amount of produced soot is defined by the carbon-to-oxygen ratio. Equilibrium considerations indicate that soot is formed when the mentioned ratio is > 1 (Wiinikka, 2005). Particles from residential biomass combustion present highly variable OC/EC ratios (Table 2.2), depending on the efficiency of the combustion equipment, burning rates, fuel moisture content, etc. (Fernandes et al., 2011). Thus, the ratio is an indicator of the combustion temperatures and the fuel burned (Fernandes et al., 2011; Gonçalves et al., 2011; Khalil and Rasmussen, 2003; McDonald et al., 2000). Average ratios of 14.4 ± 7.2 and 16.4 ± 7.6 were obtained by Alves et al. (2011) for combustion experiments using Portuguese biomass fuels in a fireplace and a woodstove, respectively. Low-combustion temperatures in traditional appliances produce large amounts of OC while hot, flaming combustion results mostly in EC. Vicente et al. (2015c) recorded OC/EC ratios ranging from 0.9 to 4.2 for the combustion of wood pellets in a pellet stove. Similar ratios were observed by Gonçalves et al. (2010). The authors reported OC to EC ratios in the range of 1.0 to 4.4 for hardwood combustion in a chimney type woodstove and a ratio of 0.9 for softwood combustion. OC/EC biomass burning emission ratios are a function of combustion conditions. However, in new and more efficient burners, both OC and EC emissions are much lower compared to old combustion appliances (Table 2.2). Obtaining lower ratios for softwood combustion than those observed for hardwood combustion is consistent with the results reported by McDonald et al. (2000). The authors found a ratio of 3.9 and 7.9 for softwood and hardwood combustion in a woodstove, respectively.

2.3.2. Major organic markers

Biomass is composed essentially of cellulose, hemicelluloses, and lignin, and in a lesser extent of extractives and ash. Cellulose is a glucose polymer whereas hemicelluloses contain, besides glucose, several other sugar monomers (e.g. galactose and mannose). Lignin is a phenolic polymer that holds together cellulose and hemicellulose making up the plant cell wall (Agarwal et al., 2014; Anwar et al., 2014; Saarnio et al., 2010). When biomass combustion takes place, large amounts of numerous organic compounds are produced from the combustion of cellulose and hemicellulose, including, among others, anhydrosugars, PAHs, methoxyphenols and resin acids. The particulate bound organic compounds can result either from the volatilisation of the biomass organic molecules, followed by its condensation, or from the biomass biopolymers thermal breakdown (Fine et al., 2001). Alves (2008) presented a comprehensive overview of organic tracers in biomass burning aerosols. The detailed analysis of organic particle-bound compounds emitted from biomass burning is very useful to apply source assignment methodologies. However, it is noteworthy to mention that the amount of organic compounds released during biomass combustion decrease with increasing combustion efficiency (Kjällstrand and Olsson, 2004; Pagels et al., 2013; Weimer et al., 2008).

2.3.2.1. Methoxyphenols

Methoxyphenols are major lignin pyrolysis products in biomass burning particulate samples (Fine et al., 2004; Gonçalves et al., 2010; Mazzoleni et al., 2007; McDonald et al., 2000), but are thermally decomposed above 800 °C (Kjällstrand and Olsson, 2004; Kjällstrand and Petersson, 2001). They have been also detected in smoke-impacted atmospheric samples (e.g. Bari et al., 2009; Nolte et al., 2001; Simpson et al., 2005). Lignins are polymers biosynthesised only by vascular plants from substituted cinnamyl alcohol units with p-hydroxyphenyl, vanillyl, or syringyl residues. Proportions of these alcohols differ between gymnosperm and angiosperm lignins. Gymnosperm lignins are made up almost solely from coniferyl alcohol (vanillyl), while angiosperm lignins are formed from both coniferyl and sinapyl alcohol (syringyl) units. Grass lignins have high proportions of the coumaryl alcohol (p-hydroxyphenyl) units. Hence substitution patterns of simple phenols produced by mild oxidation of lignins have been used as a geochemical tracer in identifying the contribution of different vegetation types to smoke particles. Fine et al. (2004) found vanillin mass fractions in the ranges 5.62 – 7.18 mg g^{-1} OC and 4.80 – 9.02 mg g^{-1} OC emitted by the combustion of hardwoods and softwoods in a stove, respectively. Gonçalves et al. (2011) found higher methoxyphenol emissions during the cold start rather than during hot star-up using both a woodstove (10.6 – 236.5 mg g^{-1} OC) and a fireplace (47.8 – 242.1 mg g^{-1} OC). The predominant methoxyphenols found by the authors were vanillic and syringic acids. Methoxyphenols have been also detected in emissions from small-scale pellet combustion (Alves et al., 2017; Kjällstrand and Olsson, 2004). Alves et al. (2017) reported vanillin-to-OC mass fractions (mg g^{-1} OC) in the ranges 4.77 – 29.3 and 4.67 – 8.64 for the combustion of wood pellets and agro fuels in a pellet stove, respectively. These organic compounds have been pointed out as tracers for wood combustion processes. However, since they are semi-volatile compounds partitioned between the gas and the particulate phases (Hays et al., 2002; Mazzoleni et al., 2007; Schauer et al., 2001; Simpson et al., 2005), they can suffer transformations in the atmosphere. Several studies have shown the reactivity of methoxyphenols with OH radicals (Coeur-Tourneur et al., 2010; Lauraguais et al., 2012, 2014) and ozone (Net et al., 2011), which has significant implications for the use of such compounds as molecular markers of biomass burning.

2.3.2.2. Resin acids

Resin acids, such as dehydroabietic, abietic, isopimaric acid, and pimaric acids, are diterpenic compounds pointed out as tracers emitted only from the burning of resinous higher plants (Alves et al., 2017; Fine et al., 2004; Fine et al., 2001; Gonçalves et al., 2010, 2011; Mazzoleni et al., 2007; McDonald et al., 2000; Rogge et al., 1998; Zhang et al., 2013). Some constituents, such as abietic acid, are released in their unaltered form when the wood is burned, while others, such as dehydroabietic acid, are formed from other resin acids during combustion (Alves, 2008). Resin acids are resistant to chemical degradation in the atmosphere, however, dehydroabietic acid in the air can be affected by relative humidity as it can be degraded under UV light when dissolved in water (Corin et al., 2000). Mazzoleni et al. (2007) argued that fuel moisture may play an important role on the abundance of the resin acids as compared to other carbonaceous species. Resin acids have been shown to have toxic effects on the liver and the potential to damage DNA (Peng and Roberts, 2000; Rigol et al., 2003). Dehydroabietic, abietic and isopimaric acids were detected at mass fractions of 4.42 – 10.8, 1.67 – 3.69 and 0.677 – 3.01 mg g^{-1} OC, respectively, in fine particles from the woodstove combustion of prevalent US softwood tree species, but were undetectable or unquantifiable in emissions from hardwoods (Fine et al., 2004). Average isopimaric acid-to-OC mass fractions (mg g^{-1}) of 24, 17.8 and 31.2 were reported in particles from softwood combustion in a fireplace, traditional woodstove and ecolabelled woodstove, respectively (Gonçalves et al., 2010, 2011). The mass fractions for hardwood combustion were 0.77, 1.29 and 0.37 mg g^{-1} OC, correspondingly. These three combustion residential devices, in the same order, emitted dehydroabietic acid at 187, 119 and 5.44 mg g^{-1} OC for softwood burning, while the equivalent mass ratios for hardwood were 8.84, 7.17 and 0.12 mg g^{-1} OC. Alves et al. (2017) reported that dehydroabietic and isopimaric acids were represented in emissions whether from all type of pellets or from shell of pine nuts, while abietic acid was only quantifiable in $PM_{2.5}$ from the combustion of pellets made of coniferous wood.

2.3.2.3. PAHs

PAHs have been reported to be emitted in large amounts during biomass combustion (Boman et al., 2011; Eriksson et al., 2014; Gonçalves et al., 2011; Jordan and Seen, 2005; Kaivosoja et al., 2013; Lamberg et al., 2011a; Leskinen et al., 2014; Orasche et al., 2012, 2013; Pettersson et al., 2011; Riva et al., 2011; Shen et al., 2013a; Vicente et al., 2016). The growing concern over PAHs and their derivatives is a result of their associated health risk since some individual compounds have been recognised to have mutagenic, genotoxic and carcinogenic properties (Abdel-Shafy and Mansour, 2015; Canha et al., 2016; Claxton et al., 2004; Happo et al., 2013; Jalava et al., 2010, 2012; Oanh et al., 2002; Bølling et al., 2009; Pedersen et al., 2004; Vu et al., 2012; Yu, 2013). Previous studies reported significantly higher PAH emissions from softwood than those for hardwood (Gonçalves et al., 2011; Vicente et al., 2016) during residential wood combustion. Apart from the fuel type, several studies have shown the influence of combustion conditions on the PAH emissions (Gonçalves et al., 2011; Johansson et al., 2004; Jordan and Seen, 2005; Leskinen et al., 2014; Orasche et al., 2012; Pagels et al., 2013; Shen et al., 2013a). Vicente et al. (2016) reported PAH emissions from the combustion of different biofuels in two combustion appliances (woodstove and pellet stove). The authors observed that emissions from traditional appliances may be up to 145 times higher than those observed for automatic stoves. The devolatilisation phase during the combustion of conifer logs (softwood) in the woodstove showed that benzo[a]pyrene (BaP) emissions can be > 1000 times higher than the values recorded for any other combustion stage, appliance or biofuel. Resinous woods are characterized by higher burning rates, which result in very hot flame and short, local drop of oxygen concentration during the combustion. BaP, classified as the most potent carcinogen, is formed on the way of pyrolysis and further pyrosynthesis, and depends strongly on temperature and oxygen concentration in the burning chamber. In the literature, the lowest BaP levels have been reported for pellet stoves and the highest for sauna stoves. Open fireplaces depict lower BaP, due to easy access of air to the combustion chamber and low combustion temperatures. Chimney stoves with closed chamber are characterised by variable BaP emissions. The highest BaP emissions are noticeable for modern appliances, characterised by higher burning rates (Kistler, 2012, and references therein). Thus, although a “new” combustion technology contributes to the reduction of the overall PM emissions compared with “old” burning appliances, higher combustion temperatures in modern logwood stoves may lead to higher PAH emissions. Among the PAHs determined in their study, Vicente et al. (2016) described retene as the polyaromatic with the highest EF for almost all the fuels. This pyrolysis product of resin acids has been pointed out as a tracer for softwood burning (Ramdahl, 1983). However, retene and other PAHs have been identified in the emissions from other combustion sources. In particular, retene was found to be one of the dominant PAHs in atmospheric PM collected in a road tunnel (Alves et al., 2016). Besides biomass burning, there are other anthropogenic activities responsible for the introduction of PAHs into the atmosphere, such as traffic, coal burning and steel industry (Abdel-Shafy and Mansour, 2015; Jang et al., 2013; Shen et al., 2012), thereby limiting their use as unique tracers. In order to distinguish among PAH sources in environmental media, diagnostic ratios have been widely used (Gonçalves et al., 2011; Li and Kamens, 1993; Vicente et al., 2016). Nevertheless, the use of this simple tool to accurately and uniquely identify sources has been criticised (Galarneau, 2008; Zhang et al., 2005). Galarneau (2008) pointed out that due to the large variability in the reported ratios within each source type, it is unlikely that any single ratio will be representative of a source. Furthermore, the author mentions that PAH concentrations are not conserved in the atmosphere.

2.3.2.4. Monosaccharide anhydrides

Although a rather extensive amount of chemical groups has been associated with biomass combustion, the monosaccharide anhydrides (MA) represent the most frequently quantified. Levoglucosan and its isomers are formed from the thermal breakdown of wood constituents at low temperatures (Bølling et al., 2009; Simoneit, 2002; Simoneit et al., 1999). Moreover, these compounds are in the particulate phase in the atmosphere due to their low vapour pressures (Saarnio et al., 2010). Levoglucosan has been the most widely used organic tracer for assessing the impact of biomass burning emissions on ambient particulate loads. Schkolnik and Rudich (2006) reviewed and compared both established and emerging analytical methods for levoglucosan quantification in ambient aerosol samples. More recently, Yttri et al. (2015) reported a European-wide intercomparison on the analysis of MA based on ambient aerosol quartz fibre filter samples collected at a Norwegian urban background site impacted by residential wood combustion during winter. Thirteen laboratories participated, of which three applied high-performance anion exchange chromatography (HPAEC), four used high-performance liquid chromatography (HPLC) or ultra-performance liquid chromatography (UPLC) and six resorted to gas chromatography (GC). The accuracy for levoglucosan, presented as the mean percentage error (PE) for each participating laboratory, varied from 63 to 20%; however, for 62% of the laboratories the mean PE was within ± 10%, and for 85% the mean PE was within ± 20%.

The emissions of levoglucosan have shown to be highly variable depending on the type of appliance, fuel burned, and operating practices (Fine et al., 2001, 2002, 2004; Gonçalves et al., 2010; Hedberg et al., 2006; Schmidl et al., 2008; Yttri et al., 2015). In fact, in addition to differences in the cellulosic content of the different biofuels, the emission of saccharidic compounds may strongly depend on combustion characteristics. Under controlled combustion conditions (150 – 1050 °C), Kuo et al. (2008) determined the levoglucosan content in samples from 3 wood species. The anhydrosugar was only detectable in low temperature samples (150 – 350 °C), with maximum yield obtained from samples produced at 250 °C, regardless of plant species.

Table 2.2. OC to EC and levoglucosan to OC ratios reported in the literature for residential biomass combustion.

Appliance	Fuel	Fraction Sampled	OC/EC	Levo/OC	Reference
Fireplaces					
Fireplace	Softwoods	$PM_{2.5}$	3.88	N/A	McDonald et al. (2000)
	Hardwoods		9.01	N/A	
Fireplace	Softwood	PM_{10}	40	0.258	Schauer et al. (2001)
	Hardwoods		16.8 – 18.5	0.234 – 0.522	
Fireplace	Softwoods	$PM_{2.5}$	2.35 - 18.9	0.052 - 0.095	Fine et al. (2001)
	Hardwoods		3.95 - 23.0	0.109 - 0.168	
Fireplace	Softwoods	$PM_{2.5}$	5.61 - 7.08	0.099 - 0.159	Fine et al. (2002)
	Hardwoods		12.0 – 61.8	0.036 - 0.047	
Fireplace	Portuguese woods and briquettes	$PM_{2.5}$	2.7 - 35.5[a]	0.101 - 0.582[a]	Gonçalves et al. (2011)
			2.2 - 22.9[b]	0.080 - 0.506[b]	
Fireplace	Hardwoods	$PM_{2.5}$	10.7 - 23.7	N/A	Fernandes et al. (2011)
	Softwood		4.84	N/A	
	Briquettes		19.9	N/A	
Fireplace	Hardwoods	$PM_{2.5}$	5.86 - 24.1	N/A	Alves et al. (2011)
	Softwood		5.76	N/A	
	Briquettes		8.83	N/A	
Fireplace	Hardwoods	$PM_{2.5}$	10.3 - 24.0	0.078 - 0.357	Gonçalves et al. (2012)
	Softwood		4.68	0.208	
	Briquettes		20.3	0.125	
Fireplace	Oak logs	$PM_{2.5}$	15.0 ± 4.1	0.112 ± 0.027	Calvo et al. (2015)
	Poplar logs		13.3 ± 1.1	0.063 ± 0.008	
	Beech logs		9.9 ± 2.7	0.091 ± 0.016	
Woodstoves					
Woodstove	Pine, cedar, fir and jeffery pine logs	$PM_{2.5}$	2.8±1.3	N/A	Zhang et al. (2013)
	Leaves/duff		12.1±3.3	N/A	
Catalyst-equipped woodstove	Softwood	$PM_{2.5}$	2.95	0.253	Fine et al. (2004)
	Hardwood		5.30	0.213	
Woodstove	Softwoods		3.25 - 10.2	0.397 - 0.409	
	Hardwoods		2.61 - 16.8	0.108 - 0.210	
Woodstove	Hardwoods	$PM_{2.5}$	7.92	N/A	McDonald et al. (2000)
Woodstove	Portuguese woods and briquettes	$PM_{2.5}$	4.1 - 52.6[a]	0.126 - 0.506[a]	Gonçalves et al. (2011)
			4.0 - 19.1[b]	0.099 - 0.948[b]	
Woodstove	Hardwoods	$PM_{2.5}$	10.0 - 19.4	0.031 - 0.555	Gonçalves et al. (2012)
	Softwood		4.1	0.170	
	Briquettes		20.6	0.409	

Woodstove	Hardwoods	$PM_{2.5}$	12.9 - 18.7	N/A	Fernandes et al. (2011)
	Softwood		4.52	N/A	
	Briquettes		20.5	N/A	
Woodstove	Hardwoods	$PM_{2.5}$	5.92 - 28.2	N/A	Alves et al. (2011)
	Softwood		12.6	N/A	
	Briquettes		12.1	N/A	
Woodstove	Softwood	PM_{10}	1.11 - 6.16	0.074 - 0.192[c]	Vicente et al. (2015a)
	Hardwood		1.07 - 3.43	0.100 - 0.207[c]	
Woodstove	Oak logs	$PM_{2.5}$	10.1 ± 1.8	0.122 ± 0.022	Calvo et al. (2015)
	Poplar logs		3.2 ± 1.1	0.069 ± 0.028	
	Beech logs		3.8 ± 0.48	0.129 ± 0.026	
Woodstove	Beech logs	PM_{tot}	0.37	0.100	Orasche et al. (2012)
	Spruce logs		1.18 - 11.5[c]	0.204 – 0.209[c]	
Chimney type woodstove	Hardwoods	PM_{10}	1.0 - 4.4	0.096 - 0.462	Gonçalves et al. (2010)
	Softwood		0.85	0.146	
Chimney type woodstove	Softwood	PM_{10}	1.24 | 0.87 - 3.07[c]	0.180	Schmidl et al. (2011)
	Hardwoods		1.11 - 1.23	0.07 - 0.29	
	Briquettes		0.95	0.080	
Modern chimney type woodstove	Softwood	PM_{10}	0.86 | 0.38 - 5.86[c]	0.170	
	Hardwoods		0.74 - 0.96	0.03 - 0.39	
	Briquettes		0.88	0.060	
Pellet stoves and boilers					
Pellet stove	Wood pellets	PM_{10}	0.34 - 1.39[c]	0.180[d]	Schmidl et al. (2011)
Pellet stove	Spruce pellets	PM_{tot}	4.39 - 5.88[c]	0.113 - 0.181[c]	Orasche et al. (2012)
Pellet boiler	Spruce pellets		8.46 - 71.0[c]	0.197 - 0.209[c]	
Pellet boiler	Pellets made of wood and/or bark material	PM_1	0.00 - 3.8	N/A	Lamberg et al. (2013)
	Pellets made of peat		0.00 - 12.3	N/A	
	Pellets made of of woody biomass and peat		0.48- 4.0	N/A	
	Pellets made of straw		0.10 - 1.5	N/A	
	Pellets made of wood and reed canary grass		0.79	N/A	
Pellet stove	Wood pellets	PM_{10}	0.9 - 4.2	0.002 – 0.087[d]	Vicente et al. (2015b)
	Agricultural fuels (olive pit, shell of pine nuts and almond shell)		0.3 - 9.4	0.008 – 0.022[d]	
Other appliances					

Modern masonry heater	Birch logs	PM_1	0.46	N/A	Tissari et al. (2007)
Baking oven	Birch logs and construction wood		0.54	N/A	
Sauna stove	Alder and aspen logs		0.75	N/A	
Conventional masonry heater	Birch, spruce and alder logs		1.33 - 2.81[c]	N/A	
Soapstone stove	Spruce logs		0.41	N/A	
Tiled stove (*Kachelofen*)	Softwoods	PM_{10}	2.6 - 5.7	0.199 - 0.272	Schmidl et al. (2008)
	Hardwoods		2.7 - 3.2	0.080 - 0.273	
	Briquettes		1.3	0.248	
Masory heater	Birch logs	$PM_{2.5}$	0.64 - 1.96[c]	0.050 - 0.142[c]	Frey et al. (2009)
Biomass boiler	Wood chips	PM_{10}	0.06 - 8.60[c]	0.240[d]	Schmidl et al. (2011)
	Triticale pellets		0.61 - 19.6[c]	0.020[d]	
	Miscanthus pellets		0.49 - 1.50[c]	0.020[d]	
	Wood pellets		0.14 - 10.0[c]	0.020[d]	

[a] cold start; [b] hot start; [c] different combustion conditions; [d]anhydrous sugars only emitted during specific operation conditions, N/A: information not available.

A laboratory emission study of wood and pellet boilers gave 0.3 wt% to 22 wt% levoglucosan to particle mass, indicating that the levoglucosan fraction may be highly dependent on combustion parameters, making it uncertain to use it as a quantitative tracer under real-world burning conditions (Hedberg et al., 2006). Another variable that has a strong influence on the yield of levoglucosan from cellulose is the presence of inorganic ions (Dobele et al., 2005; Khelfa et al., 2008). It has been observed that the presence of mineral matter in wood decreases the temperature of cellulose pyrolysis (Williams and Horne, 1994). Lately, some researchers have questioned the levoglucosan atmospheric stability because of degradation: i) at high OH concentrations (e.g. Hennigan et al., 2010), ii) in high relative humidity conditions (e.g. Hoffmann et al., 2010), and iii) during air masses aging (e.g. Lai et al., 2014). It has also been shown that compounds like $(NH_4)_2SO_4$ or NaCl internally mixed with levoglucosan clearly inhibit its degradation (Lai et al., 2014). Large discrepancies are found in the literature regarding the levoglucosan atmospheric lifetime. The main factors contributing to such differences are the detection methods used, experimental OH concentration ranges tested and environmental conditions considered. Depending on these parameters, researchers estimated levoglucosan atmospheric lifetimes in the order of weeks (Kessler et al., 2010; Slade and Knopf, 2014), days (Hennigan et al., 2010; Hoffmann et al., 2010; Lai et al., 2014; Slade and Knopf, 2014) or hours (Hennigan et al., 2010). Thus, quantitative estimates of wood burning inputs to atmospheric particles may be very doubtful using exclusively levoglucosan as a tracer. It can be taken as a good tracer if the receptor site is close to the source and the above-mentioned conditions are of little significance (Alves et al., 2017).

The stereoisomers of levoglucosan, galactosan and mannosan, can also be abundant compounds in smoke. Although the three MA are concurrently emitted by biomass burning sources, the proportions between them depend on what biofuel is being burnt. Thus, the simultaneous determination of the three stereoisomers is recommended in order to apportion the contribution from distinct biomass burning emissions (e.g. softwood versus hardwood) or to differentiate combustion conditions (smouldering vs. flaming). The relative proportions of levoglucosan to mannosan (L/M) have been used for source reconstruction of combustion derived byproducts in atmospheric aerosols. For example, inputs from very specific poor-quality brown coals gave L/M ratios > 50 in atmospheric aerosols (Fabbri et al., 2009). Differences in the L/M ratio in smoke from softwood and hardwood/ grass combustion (~5 versus ~10 – 20, respectively) can further support discrimination between inputs from these combustion sources to the atmosphere (Louchouarn et al., 2009, and references therein). Herbaceous tissues can produce relatively high L/M ratios, in the range from 25 to 50 (Engling et al., 2009). Schmidl et al. (2011) investigated two automatically and two manually fired appliances, and eight biofuels. Automatically fired systems only emitted detectable amounts of anhydrousugars during the start-up phase. The authors found L/M ratios of around 14 – 17 for hardwoods and of 2.5 – 3.5 for softwoods combustion using manually fired appliances. During the combustion in a biomass boiler the authors observed also lower L/M ratios for wood pellets (2.3 – 2.9) and wood chips (1.7) made of softwood and higher values for miscanthus and triticale pellets which behave similar to hardwoods. Alves et al. (2017) reported that anhydrousugars represented 2.3 – 3.5 and 0.73 – 1.7 wt% of the OC mass in emissions from the combustion of pellets and agro-fuels in a pellet stove, respectively. The authors concluded that the anhydrosugar particle mass fractions were 30 to 70 times lower than the values reported for manually fired systems.

As noted by a number of studies, the levoglucosan to OC ratio has been shown to be highly variable in biomass burning emissions (Table 2.2). Fine et al. (2001) conducted tests to determine the chemical composition of fine particle emissions from the fireplace combustion of six species of woods grown in the northeastern United States. The authors found that hardwoods emit more levoglucosan than softwoods. Levoglucosan yields in the ranges from 0.109 to 0.168 g g^{-1} OC and between 0.052 and 0.095 g g^{-1} OC were reported for hardwood and softwood combustion, respectively. On the other hand, softwood combustion usually generated higher mannosan emissions than hardwoods. The mannosan emission ranged between 0.0013 and 0.0047 and between 0.0090 and 0.025 g g^{-1} OC for hardwoods and softwoods combustion, respectively (Fine et al., 2001). Fine et al. (2002) reported a levoglucosan-to-OC mass ratio of 0.136 g g^{-1} for fireplace combustion of four hardwood species grown in the southern US, which is consistent with the previous results. Furthermore, the researchers also proved the importance of combustion conditions on the anhydrosugars yield. After testing the same wood in a fireplace and in a woodstove, the authors reported a difference of about 7 fold in the levoglucosan to OC ratio between both appliances. They observed that, in general, the levoglucosan content in emissions from woodstove (average 0.245 ± 0.114 g g^{-1} OC) were higher than those obtained from fireplace (average 0.129 ± 0.078 g g^{-1} OC) combustion (Fine et al., 2001, 2002, 2004). Gonçalves et al. (2011) evaluated the effect of the appliance and the combustion temperature on MA emissions. The combustion experiments included the use of a fireplace and a woodstove (cold and hot start), as well as eight typical Portuguese biofuels. The anhydrosugar emissions were generically higher for the higher combustion temperature experiments. Average values of 0.426 and 0.379 g g^{-1} OC were, respectively, obtained for the hot and cold start tests in the fireplace. Frey et al. (2009) used a typical masonry heater in order to assess the influence of different combustion conditions on the different chemical components of particulate emissions. The authors tested two different combustion conditions corresponding to a normal (flaming) and smouldering combustion. The levoglucosan emissions ranged from 0.050 (smouldering) to 0.142 (normal) g g^{-1} OC.

2.3.3. Biomarkers for wood smoke exposure

Several organic compounds emitted from biomass burning, such as different methoxyphenols, levoglucosan and 1-hydroxypyrene, have been suggested as potential urinary biomarkers for wood smoke exposure (Bergauff et al., 2010; Clark et al., 2007; Dills et al., 2001, 2006; Hinwood et al., 2008; Kato et al., 2004; Naeher et al., 2013; Sankaranarayanan et al., 2016; Wallner et al., 2013). It was suggested that human biomonitoring of levoglucosan may be suitable to detect differences in regional exposure to wood smoke (Wallner et al., 2013). Sankaranarayanan et al. (2016) conducted a study among 33 children living in homes that used woodstoves for residential heating. Indoor $PM_{2.5}$ concentrations and corresponding urine samples from participants were collected during pre- and a post-intervention winter sampling periods. Interventions included the installation of an air filtration unit and a woodstove change out. Results showed a strong reduction in indoor $PM_{2.5}$ among the air filter homes, while the woodstove replacement did not show a significant $PM_{2.5}$ decrease from pre- to post-intervention observations. Children living in the air filter homes did not reveal a corresponding reduction in urinary levoglucosan concentrations. Further analysis did not display an association between overall changes in indoor $PM_{2.5}$ concentrations and changes in urinary levoglucosan levels. These findings indicate that urinary levoglucosan is not a suitable indicator of smoke exposure in residential wood heating settings. Naeher et al. (2013) also concluded that other sources apart from wood smoke may affect the urinary levels of this MA. Therefore, urinary levoglucosan may not be effective as a biomarker of woodsmoke exposure. Bergauff et al. (2010) suggested that diet is a major factor in determining urinary levoglucosan levels and recent dietary history needs to be taken into account for future work involving this compound as a biomarker of wood smoke exposure. The use of urinary levoglucosan as a quantitative marker of exposure to wood smoke would be affected by variability in its EF, and would benefit from the concurrent determination of the levoglucosan content of the specific wood smoke. Moreover, levoglucosan is a constituent of tobacco smoke (Saint-Jalm, 1981), so exposure to this emission source would either need to be eliminated or corrected.

Clark et al. (2007) demonstrated that the urinary concentrations of specific methoxyphenols may be effective biomarkers of short-term exposures to inhaled woodsmoke in field conditions. One drawback to using methoxyphenols as tracers for wood smoke exposure is that they are widely found in foods and can be released into the air by industrial processes. Another limitation is related to the variability of metabolisms and, thus, highly fluctuating inter-individual detection times (Rylance et al., 2013). Li et al. (2016) investigated urinary hydroxylated PAH metabolites (OH-PAHs) as wood smoke biomarkers in non-smoking volunteers experimentally exposed to a wood fire. Concentrations of nine OH-PAHs increased by 1.8 – 7.2 times within 2.3 – 19.3 h, and returned to baseline approximately 24 h after the exposure. 2-Naphthol (2-NAP) had the largest post-exposure increase and exhibited a clear excretion pattern in all volunteers. The level of urinary OH-PAHs, except 1-hydroxypyrene (1-OHP), correlated with those of $PM_{2.5}$, levoglucosan and PAHs in personal $PM_{2.5}$ samples. This finding indicates that several urinary OH-PAHs, in particular 2-NAP, are potential exposure biomarkers to wood smoke. On the contrary, 1-OHP may not be a reliable biomarker. Compared with levoglucosan and methoxyphenols, OH-PAHs might be better biomarkers, based on sensitivity, robustness and stability, especially under suboptimal sampling and storage conditions, like in epidemiological studies carried out in less developed areas. A disadvantage of 1-OHP as a marker of wood smoke exposure is that it is not very selective due to the ubiquitous nature of PAHs in the environment.

The current concerns to promote clean residential biomass burning solutions provide an opportunity to produce robust, specific, and fieldready biomarkers of wood smoke exposure to identify populations at greatest risk and to monitor the effectiveness of interventions (Rylance et al., 2013).

2.4. Contribution of residential biomass combustion to the atmospheric levels

Several studies have addressed the ambient levels of carbonaceous aerosol across the world aiming to quantify and identify the sources of OA. Quite a few showed the impact of biomass burning on the reported concentrations at rural background sites (e.g. Pio et al., 2007; Querol et al., 2008, 2013; Ricard et al., 2002; Salvador et al., 2011; Yttri et al., 2007; Zappoli et al., 1999) and at urban environments (e.g. Glasius et al., 2006; Querol et al., 2008; Saarikoski et al., 2008; Sillanpää et al., 2005; Viidanoja et al., 2002; Yttri et al., 2007, 2009). Residential biomass combustion can have a substantial contribution to the PM carbonaceous levels. In Finland (Helsinki), the contribution of biomass burning to the PM_1 OC content was estimated to be 41% during winter (Saarikoski et al., 2008). In Switzerland (Zurich), the contribution of this source to OC in PM_{10} was approximately 41% in winter (Szidat et al., 2006). In Spain (Barcelona), 60% of OC in PM_1 was reported to arise from non-fossil carbon sources (Minguillón et al., 2011). Within the CARBOSOL project (Present and retrospective state of organic versus inorganic aerosol over Europe: implication for climate, EVK2- 2001-00113), source apportionment of $PM_{2.5}$ aerosol in five rural/remote sites in Europe was performed. It was observed that, in winter, primary OA from biomass burning had a significant contribution in all sites, ranging from 11 to 64% (Gelencsér et al., 2007). In Berlin (Germany), Wagener et al. (2012) also reported that biomass burning dominates the organic fraction in the cooler months. Fountoukis et al. (2016) found out that a major source of total primary OA concentrations in the Paris urban atmosphere was residential wood combustion, contributing to approximately 40% during the winter season. Even in Las Vegas (USA), where most homes are heated by natural gas or electricity, biomass burning OA comprised 9 to 14% of the organic matter (Brown et al., 2016). In China, as illustrated by a recent review, the particle-phase mass in biomass burning emissions tends to be dominated by carbonaceous matter. The reviewed data showed that despite being present over the whole year it was possible to observe seasonality in biomass burning contribution to PM pollution in the country. The contribution of the biomass burning related OA was in the range of 15% (summer) to 30% (winter) (Chen et al., 2017).

The atmospheric mass concentrations of levoglucosan have been reported in several studies, ranging from 0.32 ng m^{-3} at a maritime background site (Chichi-jima), in the western-north Pacific during summer, to 3040 ng m^{-3} at an urban site (Libby, Montana) in winter. From Table 2.3, it is possible to observe a difference > 150 between the levoglucosan mean concentration at urban sites in winter (3040 ng m^{-3}, Libby) and summer (19.4 ng m^{-3}, Gent). Very wide mean levoglucosan concentration ranges are also found in the literature for traffic (14.9 – 947 ng m^{-3}), rural background (20 – 916 ng m^{-3}) and urban background sites (19.1 – 963 ng m^{-3}). Ambient levoglucosan concentrations at continental and maritime background sites have been reported to be in the range of 7.8 – 24.4 and 0.32 – 5.2 ng m^{-3}, respectively. Marked seasonal variations in concentrations have been documented by several authors for different types of monitoring sites. The mean concentration of levoglucosan observed in winter was reported to be > 20 times higher compared to summer by several authors (Yttri et al., 2005; Giannoni et al., 2012; Puxbaum et al., 2007; Zdráhal et al., 2002).

The assessment of the impact of the different source emissions at receptor sites has been performed using different techniques, such as the multivariate statistical models Positive Matrix Factorisation (PMF) (e.g. Maenhaut et al., 2016; Nava et al., 2015), Chemical Mass Balance (CMB) (e.g. El Haddad et al., 2011; Perrone et al., 2012), radiocarbon method (e.g. Budhavant et al., 2015; Szidat et al., 2006; Zhang et al., 2015) and the aethalometer model (e.g. Favez et al., 2009; Herich et al., 2011). More recently, following the development of the Source Finder (SoFi) interface, the multilinear engine (ME-2) factorisation tool is being widely used in source apportionment studies (e.g. Canonaco et al., 2013; Milic et al., 2016). Over the years, several researchers have performed intercomparison studies to evaluate the different source apportionment approaches (e.g. Bullock et al., 2008; Favez et al., 2010; Lee et al., 2008; Martinsson et al., 2016). The identification of PM sources is the key to design effective abatement measures in areas where the legislation thresholds are exceeded. In recent years, many researchers have paid special attention to source apportionment, and new insights regarding the PM sources have been gained. A wealth of publications, with focus on identification and apportionment of airborne PM in the atmosphere, pointed out biomass burning as a major contributor to the atmospheric levels in wintertime.

The AIRUSE (Testing and development of air quality mitigation measures in Southern Europe) project main goal was to generate a harmonised data set of particulate matter sources across the Mediterranean region. In doing so, a one-year sampling campaign was performed in order to determine the PM_{10} and $PM_{2.5}$ levels and composition following the same sampling and analysis protocol in Barcelona (Spain), Porto (Portugal), Florence and Milan (Italy) and Athens (Greece). The particulate 24 h samples were analysed for carbonaceous content, ions, major and trace elements and levoglucosan. In order to conduct the source apportionment of PM_{10} and $PM_{2.5}$, the USEPA PMF5 receptor model was applied to the data sets for each city (Amato et al., 2016). Large variability in biomass burning contribution among Porto (traffic site), Florence, Milan and Barcelona (urban background sites) and Athens (suburban background site) were observed. While a very high degree of natural gas penetration in the Spanish city is clearly reflected in very low contributions from biomass burning to the atmospheric PM levels, the extensive use of wood in residential combustion appliances in other cities, especially in Portugal and Italy, contributes to high inputs from this source. Within the European project TRANSPHORM (Transport related Air Pollution and Health impacts - Integrated Methodologies for Assessing Particulate Matter), source apportionment results for PM_{10} and $PM_{2.5}$ were obtained for 20 urban areas in Europe (Table 2.3). The sampling campaigns were conducted between October 2008 and April 2011 and covered an entire year in each of the study areas. At each site, samples were taken over three 14-day periods spread over a year, in different seasons. In each area, five stations and a reference site were monitored simultaneously, representing all different site types (regional background, urban background and traffic). PMF was employed to determine PM sources for two particle size fractions, $PM_{2.5}$ and PM_{10}. For $PM_{2.5}$ mass, cities included in the study were grouped into four main clusters. The first cluster included northern European cities such as Copenhagen (Denmark), Helsinki (Finland), Oslo (Norway) and Manchester and London/Oxford (United Kingdom). The second cluster was Vienna (Austria) and Gyor (Hungary), geographically close and similar (landlocked) cities. The third cluster included cities as geographically diverse as Paris (France), Athens (Greece) and Kaunas (Lithuania). The third cluster was, however, spatially distinct from the first cluster. The fourth cluster consisted of Gyor (Hungary) and Turin (Italy). With the exception of Gyor (Hungary), there was a clear north/south divide in the cities. Southern cities (e.g. Athens, Rome and Barcelona) were in the first cluster, while cities further north (e.g. Helsinki, Copenhagen, and Oslo) were in a different cluster. Due to climatic and social differences, there is a north/south divide to wood burning across Europe, and this has been reflected in the clustering pattern (NILU, 2011).

Table 2.3. Levoglucosan levels reported for several locations worldwide.

Location and type of site	Period	Mean (ng m^{-3})	Range (ng m^{-3})	PM fraction	References
Traffic					
Vienna (Austria)	2004 (winter)		230 – 240	PM_{10}	Caseiro et al. (2009)
	2004 (summer)		30 – 40		
Graz (Austria)	2004 (winter)	740			
	2004 (summer)	90			
Salzburg (Austria)	2004 (winter)	300			
	2004 (summer)	50			
Sondrio (Italy)	2005 Feb 21-27	885		PM_{10}	Piazzalunga et al. (2010)
Milan (Italy)	2006-2009 (winter)	947±189		$PM_{2.5}$	Perrone et al. (2012)
	2006-2009 (summer)	33±11			
Florence (Italy)	2009 - 2010 (winter)	355		$PM_{2.5}$	Giannoni et al. (2012)
	2009 (summer)	14.9			
Porto (Portugal)	2013 Jan - 2014 Jan	387		$PM_{2.5}$	Amato et al. (2016)
Urban					
Bakersfield (California)	1995 Dec - 1996 Jan	2390		$PM_{2.5}$	Nolte et al. (2001)
Fresno (California)	1995 Dec - 1996 Jan	2980			
Gent (Belgium)	1998 (winter)	477	121 – 1133	PM_{10}	Zdráhal et al. (2002)
	1998 (summer)	19.4	4.1 – 34.6		
Missoula (Montana)	2003 Aug 14-18		860 – 6091	$PM_{2.5}$	Ward et al. (2006)
Graz (Austria)	2004 (winter)	860		PM_{10}	Caseiro et al. (2009)
	2004 (summer)	100			
Salzburg (Austria)	2004 (winter)	330			
	2004 (summer)	50			
Libby (Montana)	2004 Nov - 2005 Feb	3040		$PM_{2.5}$	Bergauff et al. (2008)
Dettenhausen (Germany)	2005 Nov - 2006 Mar	806	35 – 3223	PM_{10}	Bari et al. (2010)
Brno (Czech Republic)	2009 (winter)	326		$PM_{2.5}$	Křůmal et al. (2010)
	2009 (summer)	47.1			
Šlapanice (Czech Republic)	2009 (winter)	572			
	2009 (summer)	55.6			
Geeveston (Tasmania)	2009 Mar - 2010 Nov	2430	720 - 6020	PM_{10}	Reisen et al. (2013)
Bologna (Italy)	2011 Nov - 2011 Dez	1043±490.4		$PM_{2.5}$	Pietrogrande et al. (2015)
	2012 Oct - 2012 Nov	288.9±143.9			
	2013 Jan - 2013 Feb	259.4± 98.9			
	2013 Sep – 2013 Oct	34.6±23.8			

	2014 Jan – 2014 Feb	300.8±117.8			
Urban Background					
Gent (Belgium)	2000 Nov - 2001Mar	420	96 – 1900	PM_{10}	Pashynska et al. (2002)
	2001 May - 2001 Sep	19.1	9.1 – 27		
Zurich (Switzerland)	2002 Aug - 2002 Sep	70±30		PM_{10}	Szidat et al. (2006)
	2003 - Feb	620±160			
Lycksele (Sweden)	2002 Jan - 2002 Mar	897	16.5 - 2335	PM_{10}	Hedberg et al. (2006)
Oslo (Norway)	2001 Nov - 2001 Dec	166	nd – 475	PM_{10}	Yttri et al. (2005)
Vienna (Austria)	2004 (winter)		190 – 220	PM_{10}	Caseiro et al. (2009)
	2004 (summer)		20 – 30		
Graz (Austria)	2004 (winter)	450			
	2004 (summer)	80			
Salzburg (Austria)	2004 (winter)	250			
	2004 (summer)	30			
Cantù (Italy)	2005 Feb 21-27	963		PM_{10}	Piazzalunga et al. (2010)
Milan (Italy)		385			
Mantova (Italy)		569			
Helsinki (Finland)	2006 Mar - 2007 Feb	64±87		PM_1	Saarikoski et al. (2008)
Vindinge (Denmark)	2005 Feb - 2005 Abr	313±237	55 – 917	$PM_{2.5}$	Glasius et al. (2008)
Göteborg (Sweden)	2005 Feb - 2005 Mar	60±30		$PM_{2.5}$	Szidat et al. (2009)
Šlapanice (Czech Republic)	2009 - Feb	420		PM_1	Křůmal et al. (2010)
		570		$PM_{2.5}$	
Brno (Czech Republic)	2009 - Feb	220		PM_1	
		320		$PM_{2.5}$	
Barcelona (Spain)	2009 Feb - 2009 Mar	60		$PM_{2.5}$	Reche et al. (2012)
Florence (Italy)	2009 - 2010 (winter)	371		$PM_{2.5}$	Giannoni et al. (2012)
Ealing (United Kingdom)	2010 Jan – 2010 Feb	190±21		PM_{10}	Fuller et al. (2014)
Kensington (United Kingdom)		180±20			
Westminster (United Kingdom)		162±18			
Islington (United Kingdom)		171±19			
Greenwich (United Kingdom)		180±20			
Bexley (United Kingdom)		190±21			
Borgerhout (Belgium)	2010 Feb - 2011Feb	81*	11.9 – 300*	PM_{10}	Maenhaut et al. (2012)
Gent (Belgium)		69*	14.8 – 330*		
Antwerpen (Belgium)	2011 Jun - 2012 Jul	61*	17.9 – 185*	PM_{10}	Maenhaut et al. (2016)
Gent (Belgium)		82*	23 – 191*		
Brugge (Belgium)		62*	11.5 – 142*		
Oostende (Belgium)		39*	8.6 – 122*		
Lens (France)	2011 Mar - 2012 Mar		10 – 310	PM_{10}	Waked et al. (2014)

Granada (Spain)	2012 Nov -2013 Feb	250		PM_{10}	Titos et al. (2017)
Florence (Italy)	2013 Jan - 2014 Jan	255		$PM_{2.5}$	Amato et al. (2016)
Milan (Italy)		274			
Barcelona (Spain)		20			
Suburban background					
Elverum (Norway)	2002 Feb - 2002 Mar	407	134 – 971	PM_{10}	Yttri et al. (2005)
Livorno (Italy)	2009 - 2010 (winter)	117		$PM_{2.5}$	Giannoni et al. (2012)
	2009 (summer)	6.2			
Mechelen (Belgium)	2010 Feb - 2011 Feb	95*	13.8 – 330*	PM_{10}	Maenhaut et al. (2012)
Riccione (Italy)	2011 Mar – 2011Apr	200±100		$PM_{2.5}$	Vassura et al. (2014)
Athens (Greece)	2013 Jan - 2014 Jan	37		$PM_{2.5}$	Amato et al. (2016)
Rural Background					
Košetice (Czech Republic)	2009 Feb - 2010 Apr	125±111		$PM_{2.5}$	Schwarz et al. (2016)
	2009 - 2010 (winter)	237			
	2009 - 2010 (summer)	20			
Hamme (Belgium)	2010 Feb - 2011 Feb	200*	18.1 – 640*	PM_{10}	Maenhaut et al. (2012)
Lier (Belgium)		82*	13.2 – 300*		
Retie (Belgium)		78*	10.9 – 270*		
Houtem (Belgium)		34	5.2 – 138		
San Pietro (Italy)	2011 Nov - 2011 Dez	916.0±389.3		$PM_{2.5}$	Pietrogrande et al. (2015)
	2012 Oct - 2012 Nov	233.2±114.6			
	2013 Jan - 2013 Feb	252.9± 110.7			
	2013 Sep - 2013 Oct	38.8± 25.9			
	2014 Jan - 2014 Feb	341.9±129.6			
Rural					
Aveiro (Portugal)	2002 Jul - 2004 Jul	517	19.6 – 1651	$PM_{2.5}$	Puxbaum et al. (2007)
K-Puszta (Hungary)	2002 Jul - 2004 May	309	13.0 – 922		
Råö (Sweden)	2005 Feb - 2005 Mar	40±20		PM_{10}	Szidat et al. (2009)
Lille Valby (Denmark)	2005 Feb - 2005 Abr	168±89	21 – 312	$PM_{2.5}$	Glasius et al. (2008)
Dettenhausen (Germany)	2005 Nov - 2006 Mar	806	35 – 3223	PM_{10}	Bari et al. (2010)
Bosco Fontana (Italy)	2005 Feb 21-27	405		PM_{10}	Piazzalunga et al. (2010)
Reserve Oasi Le Bine (Italy)	2006-2009 (winter)	502±134		$PM_{2.5}$	Perrone et al. (2012)
	2006-2009 (summer)	13±2			
Grove (Tasmania)	2009 Mar - 2010 Nov	400	170 – 940	PM_{10}	Reisen et al. (2013)
Continental background					
Puy de Dôme (France)	2002 Oct - 2004 Oct	17.0	1.6 - 46.5	$PM_{2.5}$	Puxbaum et al. (2007)

Schauinsland (Germany)	2002 Oct - 2004 Oct	24.4	7.2 - 55.5		
Sonnblick (Austria)	2002 Oct - 2004 Oct	7.8	<0.7- 55.6		
Maritime background					
Chichi-jima (western-north Pacific)	2001 -2004 (winter)	2.2	0.43 – 15	TSP	Mochida et al. (2010)
	2001-2004 (summer)	0.32	0.017 - 1.6		
Azores Islands (Portugal)	2002 Jul - 2004 Jul	5.2	0.3 - 19.2	$PM_{2.5}$	Puxbaum et al. (2007)

nd – not determined; *median concentrations

In Athens and Catalonia, two regions in common to both the TRANSPHORM and AIRUSE projects, domestic heating was estimated to contribute up to 37% of the PM levels. However, mixed signals of long range transport, domestic heating and other industrial and combustion sources made it difficult to separate biomass burning itself. It should be noted, however, that the TRANSPHORM and AIRUSE data are not directly comparable. In fact, while the source apportionment results of TRANSPHORM refer to multi-station monitoring, within AIRUSE one urban site was monitored in each target city. For example, in TRANSPHORM, the Catalonia study area covered two cohorts placed in the cities of Sabadell and Barcelona, and a third cohort spread over the Girona region. These cohorts comprised urban background, traffic and rural sites, covering towns next to the sea to countryside and Pyrenean locations, where biomass burning is much more entrenched. Contrary to what happens in Barcelona, where natural gas is the main energy source, in rural areas and small towns of Catalonia, due to the widespread use of wood fuels, emissions of biomass burning in wintertime have been found to contribute to exceedances of the BaP target value (annual average) of 1 ng m^{-3} (Querol, 2014). The regional emission inventory carried out in 2008 in the Italian region of Lombardy showed that residential wood combustion in small appliances is the major source of BaP, representing 77% of the total emissions. In particular, traditional woodstoves, closed fireplaces and open fireplaces are the major contributors accounting, respectively, for 32%, 23% and 19% (Gianelle et al., 2013). It should be noted that, due to its carcinogenicity, BaP is regulated in the European Union by the 4th Air Quality Daughter Directive (2004/107/EC). Belis et al. (2011) conducted a study in 2007 and 2009 at ten air quality monitoring stations in the North Italian Po Plain and Valtelline Valley. Emissions from biomass burning accounted for 74 ± 32%, 79 ± 18%, 85 ± 33%, and 84 ± 46% of all BaP sources, respectively, at a kerbside in Milan, six urban background stations in the Po Plain, two rural background stations in the Po Plain, and an urban background station in the Valtelline Valley. BaP measurements in 2010 were above the threshold value at 38% of the EMEP monitoring stations. Exceedances are most predominant in central and eastern Europe, although they are also observed in Bulgaria, Germany, Ireland, the United Kingdom, France and Greece (EEA, 2012).

As already stated, biomass burning can significantly contribute to the aerosol loads in many regions of the world (Tables 2.4 and 2.5). In previous works, the input of this source was estimated to account for 11 – 13% of the PM mass at some traffic sites in Switzerland and Germany (Gianini et al., 2012; Gu et al., 2011). Contributions from 0.8% (Izmir, Turkey) to 44% (Rockwood, USA) have been apportioned in suburban background sites (Kim et al., 2003; Yatkin and Bayram, 2008). Annual average inputs of 12 – 13% have been found at urban background sites in French and Swiss cities (Bressi et al., 2014; Gianini et al., 2012; Waked et al., 2014).

Table 2.4. Contribution of wood combustion and/or domestic heating to PM levels in different European regions, as estimated by the TRANSPHORM project (NILU, 2011).

Location and type of site	Source	Key compounds	PM fraction	Source contribution (%)
Belgium and Netherlands	Combustion	K, Zn, Br, Pb, AC, S	$PM_{2.5}$	52.5
	Wood combustion	K, levoglucosan, Br, Zn, Pb	$PM_{2.5\ (inc.\ org)}$	36.9
Denmark, Copenhagen	Domestic heating	Pb, K, Zn, Se, Br, AC	$PM_{2.5}$	33.1
		Pb, OC, Zn, K, S	$PM_{2.5\ (inc.\ org)}$	27.6
		Pb, Zn, As, AC, S, K	PM_{10}	32.0
Finland, Helsinki and Turku	Domestic heating	Pb, S, Zn, K, AC	$PM_{2.5}$	35.7
	Long range transport (LRT) heating	Pb, S, Zn, Br, Cr, K	$PM_{2.5\ (inc.\ org)}$	34.6
	Secondary, industrial, domestic heating	Pb, S, Zn, Br, AC	PM_{10}	24.1
France, Paris	Combustion (mixed including LRT)	Cl, Ni, K, Br, Pb, AC, S	$PM_{2.5}$	37.7
	Domestic heating	Cl, PAHs, OC, Ni, K	$PM_{2.5\ (inc.\ org)}$	26.4
	Mixed combustion/Domestic heating/SIA	Pb, S, Se, Ni, Zn, As, AC	PM_{10}	36.6
Germany, Munich	Domestic heating	K, Rb, Pb, Zn, As, AC	$PM_{2.5}$	42.9
		PAHs, levoglucosan, benzanthrone, K	$PM_{2.5\ (inc.\ org)}$	22.2
		Pb, K, AC, S, Zn, As, Se, Br, Rb	PM_{10}	41.2
Greece, Athens	SIA/Combustion	Se, As, S, K	$PM_{2.5}$	25.3
	Domestic heating	PAHs, OC, K	$PM_{2.5\ (inc.\ org)}$	12.8
	Combustion (biomass burning/coal/industry)	Se, Pb, AC, Zn, Ni	PM_{10}	20.1
Greece, Heraklion	Combustion (burning of agricultural waste)	K, As, Br, Ni, V, AC	$PM_{2.5}$	17.5
Germany, Ruhr Area	Domestic heating	Cl, Br, Rb, K, Pb; AC	$PM_{2.5}$	19.3
		Cl, Br, As, V	PM_{10}	20.8
Hungary, Györ	Combustion (domestic heating)	K, Zn, As, Rb, Br, AC, Pb	$PM_{2.5}$	41.7
		Cl, As, K, Zn	PM_{10}	20.8
Italy, Rome	Wood combustion, domestic heating	Rb, K, Br, Pb, AC, Zn	$PM_{2.5}$	38.9
	Biomass combustion	K, Rb, Pb, AC, Br	PM_{10}	24.1

Italy, Turin	Domestic heating	K, Pb, Ni, Br, Zn	$PM_{2.5}$	48.9
	Combustion, heating	Cl, Ni, Rb	PM_{10}	24.4
Lithuania, Kaunas	Combustion (domestic heating)	Zn, Pb, K	$PM_{2.5}$	27.7
		Pb, Zn, K, AC, S	PM_{10}	17.5
Norway, Oslo	Domestic heating	Pb, Zn, K, AC	$PM_{2.5}$	36.1
		PAHs, levoglucosan	$PM_{2.5 \text{ (inc. org)}}$	17.3
	Domestic heating / Other combustion sources	As, AC, Zn, Rb	PM_{10}	28.4
Sweden, Stockholm	Domestic heating	Pb, Zn, AC, S, K	$PM_{2.5}$	23.9
		Pb, S, Na, V, Br, AC	PM_{10}	15.5
Switzerland, Lugano	Domestic heating	Pb, K, AC, Zn, Br, Ni	$PM_{2.5}$	39.5
		Pb, Br, Zn, Ni, AC, K	PM_{10}	38.5
United Kingdom, Manchester	Combustion (including domestic heating)	Pb, Br, K, AC	$PM_{2.5}$	30.3
	Domestic heating/SIA	Pb, Zn, Ni, V, S, AC, K	PM_{10}	24.3
United Kingdom, London and Oxford	Domestic heating	Cl, Na, Pb, Br, K	$PM_{2.5}$	24.7
	Combustion (biomass burning, coal, industry)	Cl, PAHs, Pb, Br, As, Zn, K	$PM_{2.5 \text{ (inc. org)}}$	24.9
	Combustion (domestic heating)	As, Br, Pb, AC, K, Cl, Zn	PM_{10}	30.4
Spain, Catalonia	Domestic heating	K, Br, Pb, AC	$PM_{2.5}$	37.2
Austria, Voralberg	Domestic heating and road salt	Na, Cl, K, Zn, Pb, AC	PM_{10}	25.0

AC: absorption coefficient; SIA: Secondary inorganic aerosols

Around 14 and 27% of the PM wintertime levels have been assigned to biomass burning in the Alpes and in a nature reserve, respectively, in Italy (Perrone et al., 2012). The annual mean contributions in Milan and Florence determined within the AIRUSE project are in the range of these latter percentages. From measurements previously carried out at urban background sites in Athens, it has been estimated that biomass burning emissions represented 15% of the fine particle mass (Karanasiou et al., 2009). This value is in line with the current estimate of the AIRUSE project for the same city (10% of $PM_{2.5}$). In accordance with what has been observed in the AIRUSE project, in earlier works, lower contributions (< 8%) have also been determined for Barcelona (Dall'Osto et al., 2013; Reche et al., 2012; Viana et al., 2013). Despite the sampling campaign in Porto was carried out at a traffic station, it was observed that, following vehicle emissions and sea salt, biomass burning is the most significant source, accounting for 17% of the $PM_{2.5}$ levels. The fractional contribution from this source to $PM_{2.5}$ and PM_{10} doubles on exceedance days ($> 50\ \mu g\ m^{-3}$). It is worth noting that approximately half of the exceedances were recorded in winter months, indicating the input from residential wood combustion to the atmospheric PM levels (Amato et al., 2016).

2.5. Conclusions and future directions

Currently, air pollution from residential biomass burning is a major global environmental and health concern. In the EU, the recent economic crisis increased the practice of household biomass burning as it is cheaper than using the primary energy sources (e.g. oil and natural gas). On the other hand, the replacement of fossil fuels by renewable energies has been politically encouraged. The knowledge of particulate matter emission factors is of utmost importance to define strategies for pollution control. Emission factors are also necessary for updating inventories, which, in turn, are an essential input to mathematical models that estimate air quality. Results from several studies, together with disaggregation of emissions factors by technology and fuel type, lead to quite large differences, especially between old-type residential appliances versus advanced residential energy conversion systems, such as modern woodstoves, and automatic pellet stoves and boilers with higher combustion efficiency. New technologies for biomass burning can perform far better than traditional systems, but their progress and application are advancing gradually. These systems are user-friendly presenting potential advantages, such as automatic control, and enabling a reduction in fuel consumption and emissions. The compilation of a large number of measurements is important since improved emission inventories also require emission factors to be linked to activity data.

Table 2.5. Biomass burning contribution to PM levels estimated by receptor models for different regions around the world.

Receptor model	**Location and type of site**	**Sampling period**	**Sampling campaign**	**PM fraction**	**BB contribution to PM mass (%)**					**References**
					Spring	**Summer**	**Fall**	**Winter**	**Average**	
	Urban background									
PMF (9 factor solution)	Lens (France)	2011-2012	Sampling over 1 year (Mar-Mar). Daily samples. Every third sample was analyzed.	PM$_{10}$	4	-	18	25	13	Waked et al. (2014)
PMF (7 factor solution)	Paris (France)	2009-2010	Sampling over 1 year (Sep-Sep). Daily samples.	PM$_{2.5}$	1	-	18	22	12	Bressi et al. (2014)
PMF (9 factor solution)	Barcelona (Spain)	2009	Sampling from Feb to Mar 2009 (winter) and Jul 2009 (summer). Samples collected every 4 days (24 h samples).	PM$_{2.5}$	-	-	-	-	3	Reche et al. (2012)
PMF (9 factor solution)	Barcelona (Spain)	2010	Sampling from Sep to Oct 2010. Hourly-resolved samples (streaker sampler).	PM$_{2.5}$	-	-	6	-	-	Dall'Osto et al. (2013)
PMF (4 factor solution)	Barcelona (Spain)	2011	Sampling from 12 to 21 Jan. PM concentrations by optical counters (10 min time resolution) and 24 h samples.	PM$_{2.5}$	-	-	-	8	-	Viana et al. (2013)
PMF (8 factor solution)	Barcelona (Spain)	2013-2014	Sampling over one year (Jan-Jan). Samples collected simultaneously every third day (24 h samples).	PM$_{2.5}$	-	-	-	-	-	Amato et al. (2016)
PMF (10 factor solution)	Florence (Italy)				-	-	-	-	20	
PMF (8 factor solution)	Milan (Italy)				-	-	-	-	17	
PMF (9 factor solution)	Zaragoza (Spain)	2003 - 2004	Samples collected every week. Sampling from Apr 2003 to Jul 2004.	PM$_{10}$	-	-	-	-	6	Callén et al. (2009)
PMF (7 factor solution)	Milan (Italy)	2006	Sampling from Jun to Jul (summer) and Nov to Dec (winter). Samples with 4-hour resolution.	PM$_{10}$	-	1	-	14	-	Bernardoni et al. (2011)
PMF (7 factor solution)	Capannori (Italy)	2005 - 2006	Sampling over 1 year (Sep-Sep). Samples collected during 15 days every 15 days (24 h samples).	PM$_{10}$	18.3	12.1	52.2	52.0	36.8	Nava et al. (2015)

PMF (6 factor solution)	Zurich (Switzerland)	2008 - 2009	Sampling from Aug to Jul. Samples collected every 4 day (24 h samples).	PM_{10}	-	-	-	-	13	Gianini et al. (2012)
PMF (10 factor solution)	Antwerpen (Belgium)	2011 - 2012	Sampling from Jun to Jul. Samples collected every 4 day (24 h samples).	PM_{10}	4.6	0.83	14.5	16.4	9.0	Maenhaut et al. (2016)
	Gent (Belgium)				5.6	1.35	18.5	19.0	11.0	
	Brugge (Belgium)				5.4	1.27	16.6	20.1	10.8	
PMF (8 factor solution)	Beijing (China)	2000	Sampling in Jan, Apr, Jul and Oct. Samples collected every 6 day (24 h samples) at five locations in the Beijing metropolitan area.	$PM_{2.5}$	-	-	-	-	11	Song et al. (2006)
PMF (8 factor solution)	San Jose (California, U.S)	2002 - 2012	Sampling from Oct. 2002 to Feb. 2012. Samples collected every 3 day (24 h samples).	$PM_{2.5}$	16.4	13.5	24.3	35.1	24.3	Wang et al. (2013)
				PM_{10}	-	1	-	18	-	
CMB	Elms road observatory site (UK)	2007 - 2008	Sampling from May to Apr. Samples collected every 5 day (24 h samples).	$PM_{2.5}$	-	0.5	-	0.8	0.6	Yin et al. (2010)
CMB	Marseille (France)	2008	Sampling from 30 Jun to 14 Jul. Samples collected continuously on a 12 h basis.	$PM_{2.5}$	-	0.52	-	-	-	El Haddad et al. (2011)
	Urban									
PMF (7 factor solution)	Athens (Greece)	2002	Sampling at three sites located in the Athens urban area from Mar to Dec 2002. 24 h samples except for one sampling site, where four 6-h samples were taken each day.	PM_2	-	-	-	-	15	Karanasiou et al. (2009)
PMF (6 factor solution)	Chengdu (China)	2011	Sampling in Jan, Apr to May, Jul and Oct. Daily samples.	PM_{10}	7	1	19	16	11	Tao et al. (2014)

PMF (7 factor solution)	Bandung (Indonesia)	2002 - 2004	Sampling from Jan to Dec. Samples collected twice a week (24 h samples).	$PM_{2.5}$	-	-	-	-	20	Santoso et al. (2008)
CMB	Izmir (Turkey)	2004 - 2005	Sampling from Jun 2004 to May 2005. Samples collected every 6 days (24 h samples) on two sequential days a week (first day PM_{10} and second day $PM_{2.5}$).	PM_{10}					3.8	Yatkin et al. (2008)
				$PM_{2.5}$	-	0.7	-	1.2	1.0	
CMB	Milan (Italy)	2006 - 2009	Daily samples collected in summer and winter. Shorter campaigns in spring (2007 and 2008) and fall (2007) (24 h samples).	$PM_{2.5}$	8-16	1	30	25	-	Perrone et al. (2012)
COPREM	Copenhagen (Denmark)	2002 - 2003	Sampling from 03 May to 22 Dec. Daily samples.	PM_{10}	-	-	-	-	32.5	Andersen et al. (2007)
	Rural									
PMF (6 factor solution)	Payerne (Switzerland)	2008 - 2009	Sampling from Aug to Jul. Samples collected every 4 day (24 h samples).	PM_{10}	-	-	-	-	15	Gianini et al. (2012)
	Magadino (Switzerland)				-	-	-	-	31	
CMB	Churchill pumping station site (UK)	2007 - 2008	Sampling from May to Apr. Samples collected every 5 day (24 h samples).	$PM_{2.5}$	-	0.5	-	0.7	0.6	Yin et al. (2010)
CMB	Reserve Oasi Le Bine (Italy)	2006 - 2009	Daily samples collected in summer and winter. Shorter campaigns in spring (2007 and 2008) and fall (2007) (24 h samples).	$PM_{2.5}$	-	3	31	27	-	Perronne et al. (2012)
	Remote									
PMF (14 factor solution)	Gosan (Korea)	2001 - 2003	Sampling from 13 to 25 Nov 2001, 29 Mar to 11 Apr 2002, 27 Aug to 11 Sept 2002, 14 to 26 Feb, 6 to 22 Jun 2003 and 18 Aug to 1 Sept 2003 (24 h samples).	$PM_{2.5}$	-	-	-	-	7.1	Moon et al. (2008)
CMB	Alps (Italy)	2006 - 2009	Daily samples collected in summer and winter. Shorter campaigns in spring (2007 and 2008) and fall (2007) (24 h samples).	$PM_{2.5}$	2	-	5	14	-	Perronne et al. (2012)
	Traffic									

PMF (6 factor solution)	Augsburg (Germany)	2006 - 2007	Sampling from Dec to Mar. Daily samples.	PM_{10}	-	-	-	-	13.3	Gu et al. (2011)
PMF (8 factor solution)	Porto (Portugal)	2013-2014	Sampling over one year (Jan-Jan). Samples collected simultaneously every third day (24 h samples).	$PM_{2.5}$	-	-	-	-	17	Amato et al. (2016)
PMF (7 factor solution)	Chennai (India)	2008- 2009	Sampling from 10 Nov to 26 Dec 2008, 17 Jan to 16 Feb 2009 and 23 Mar to 13 Apr 2009. Daily samples.	PM_{10}	-	-	-	-	0.7	Srimuruganandam et al. (2012)
				$PM_{2.5}$	-	-	-	-	14	
PMF (7 factor solution)	Bern (Switzerland)	2008 - 2009	Sampling from Aug to Jul. Samples collected every 4 day (24 h samples).	PM_{10}	-	-	-	-	11	Gianini et al. (2012)
	Suburban									
PMF (5 factor solution)	Tanumshede (Sweden)	2007 - 2008	Daily sampling from 17 Nov. 2007 to 15 Apr. 2008 (24 h samples)	$PM_{2.5}$	-	-	-	-	25	Molnár and Sallsten (2013)
PMF (6 factor solution)	Lembang (Indonesia)	2002 - 2004	Sampling from Jan 2002 to Dec 2003 and from Mar to Dec 2004. Samples collected twice a week (24 h samples).	$PM_{2.5}$	-	-	-	-	40	Santoso et al. (2008)
PMF (7 factor solution)	Rockwood (USA)	1995 - 1997	Sampling from Jan to Dec. Daily samples.	$PM_{2.5}$	-	-	-	-	44	Kim et al. (2003)
PMF (6 factor solution)	Basel (Switzerland)	2008 - 2009	Sampling from Aug to Jul. Samples collected every 4 day (24 h samples).	PM_{10}	-	-	-	-	14	Gianini et al. (2012)
CMB	Izmir (Turkey)	2004 - 2005	Sampling from Jun 2004 to May 2005. Samples collected every 6 days (24 h samples) on two sequential days a week (first day PM_{10} and second day $PM_{2.5}$).	PM_{10}					2.9	Yatkin et al. (2008)
				$PM_{2.5}$	-	0.4	-	1.6	0.8	
	Suburban background									
PMF (8 factor solution)	Athens (Greece)	2013 - 2014	Sampling over one year (Jan-Jan). Samples collected simultaneously every third day (24 h samples).	$PM_{2.5}$	-	-	-	-	10	Amato et al. (2016)

Despite all efforts to estimate PM emissions from biomass burning, there is still a pressing need to implement a common standardized measurement protocol. In the literature, particulate sampling and dilution methods, as well as the way emissions are reported, present numerous discrepancies. PM from incomplete combustion in inefficiently operated manual devices consists mostly of carbonaceous material, i.e., soot and condensable organic compounds, which exhibit high toxicity and carcinogenic properties, whereas emissions from appropriately operated automatic biomass combustion systems are mainly composed of inorganic salts. Thus, for non-ideal conditions, as usually observed in many small scale combustion devices, the concentration of condensable organic compounds in the flue gas can exceed up to 10 times the mass concentration of solid particles collected directly on hot filters in the chimney. Therefore, measurements in dilution tunnels or additional measurements of condensables by liquid quenching lead to far higher PM concentrations when compared to collection of only hot solid particles. Inventories based on emission factors of solid particles may significantly underestimate the contribution of residential biomass burning to PM in the ambient air.

A great deal of improvement with respect to particle mitigation strategies can be made. Improvements in the batch combustion technology may offer the opportunity of a cost-efficient decrease of emissions. As shown in this review, several options can be followed to reduce the formation of pollutants: through the implementation of air staged combustion, by pre-heating the primary combustion air or by improving the characteristics of the fuel and the way of feeding. Secondary emission reduction strategies are also available. However, these technologies are not well-developed for domestic scale applications, would increase costs and maintenance and may even raise safety issues, such as high-tension voltage loss in ESPs. Prior to any market implementation several operational and breakdown risks have still to be tackled. Also the test methods for determining the removal efficiency need improvement and standardisation. Additionally, recent research articles have outlined that these reduction technologies have effects on particulate physicochemical characteristics, which can lead to undesired changes in the triggered toxicological responses. For this reason, it becomes necessary to study and establish relationships between these changes and the toxicological effects in future research. From the data gathered, it seems that it would be more cost-effective, and the reduction of emissions greater, if old-type residential combustion appliances are replaced by new and improved combustion technologies rather than installing depollution technologies. With regard to human health, emission requirements for the eco-labelling of small-scale combustion appliances for wood logs and pellets should be mandatory in all countries. The requirement for selling only certified pellets should also be widespread. Similarly to what has already been implemented in a few countries, other regulations should be imposed so that aspects such as storage of wood logs or pellets and transportation are taken into account. For areas that do not meet the national particle standards due in part to wood smoke, the local jurisdiction may consider banning the use of non-certified woodstoves. National governments and regional authorities should support voluntary woodstove and fireplace replacement/retrofit programmes to motivate households to replace older technologies with safer, more efficient, cleaner burning technologies. A plan for education and outreach to the public should definitely be included when introducing burn ban ordinances or wood burning appliance replacement programmes. Financial incentives may be a necessity to encourage households to replace or retrofit outdated and inefficient stoves. An eco-design framework and testing methods have been established and recently published by the European Committee for standardisation in order to regulate fuel quality, energy efficiency and emissions related to combustion appliances.

Particles from biomass burning are highly complex mixtures of chemical constituents. The physicochemical properties of emissions vary largely according to combustion parameters. As aerosol particles preserve in a certain degree the chemical characteristics of their origin, the detection of specific chemical compounds is very useful to assess the biomass burning input to the aerosol loading. Publications dealing with source apportionment of atmospheric particulate matter were reviewed in the present work. It has been demonstrated that studies worldwide agree on the identification of biomass burning as a major source of atmospheric particulate matter.

Monosaccharide anhydrides, resin acids, and methoxyphenols have been extensively reported as organic tracers for wood-fired residential combustion systems. It has been observed that emissions of individual compounds depend not only on the biofuel, but also on the combustion temperature, and that significant differences exist, either between biofuels or within combustion appliances. Thus, no single compound can be proposed as universal biomass burning tracer. To apply the CMB model, a weighted composite residential combustion source profile based on the usage patterns of stoves in a given region have to be created, before applying the composite profile in the mass balance calculations. In addition, the long-term atmospheric stability of some of these products is still a challenge and remains to be evaluated.

Several aspects related to urinary biomarkers for wood smoke exposure deserve further investigation, namely interfering factors (e.g. diet), sensitivity, robustness and stability, particularly under suboptimal sampling and storage conditions, like in epidemiological studies carried out in less developed areas.

The compilation of emission factors presented herein derived from fresh smoke sampled at the source that had usually cooled to ambient temperature, but undergone minimal photochemical aging. Rather few studies have been focused on the post emission processing and, thus, data for testing or constraining the chemical mechanism in smoke photochemistry models are very limited. Photochemical oxidation produced substantial new OA. Only a small fraction of this new OA can be explained using state-of-the-art secondary organic aerosol models and the measured decay of traditional SOA precursors. The application of models that explicitly track the partitioning and aging of low-volatility organics, including water soluble species, should be compared to measurements with a suite of instruments in chambers.

There is a growing interest in the indirect aerosol effect in climate models, but to fully represent the effect of aerosol emissions on cloud properties, improved particle number emission factors are required. It is recommended that optical properties of smoke particles and their components during aging are studied, as well as morphology, mixing state with urban pollutants and potentially toxic organics. Such data are essential for modelling of residential biomass burning on health and climate effects. There is a growing interest in the indirect aerosol effect in climate models, but to fully represent the effect of aerosol emissions on cloud properties, improved particle number emission factors are also required. The proper measurement of particle-phase light absorbing carbon (including BC, weak absorption by OC, and strong absorption by brown carbon) and the best way to represent this component in models is an area of vigorous research.

In addition to outdoor pollution, indoor smoke particles emitted from cooking and heating are of particular significance in many places worldwide. Therefore, it would be interesting and urgent to compare the biological effects of indoor fresh and aged smoke particles that carry various carcinogenic substances, as ambient fine biomass burning particles are known to contain PAHs and also their nitrated, hydroxylated, and oxygenated derivatives.

It is expected that the scientific study of residential biomass burning will be productive for years to come, improving our understanding of climate, health and air quality impacts. Research should also provide assistance to authorities and relevant stakeholders for the implementation of measures and technical standards.

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References

Abdel-Shafy, H.I., Mansour, M.S.M., 2015. A review on polycyclic aromatic hydrocarbons: source, environmental impact, effect on human health and remediation. Egypt. J. Pet. 25, 107–123. http://dx.doi.org/10.1016/j.ejpe.2015.03.011.

Agarwal, A.K., Pandey, A., Gupta, A.K., Aggarwal, S.K., Kushari, A. (Eds.), 2014. Novel Combustion Concepts for Sustainable Energy Development. Springer, India (ISBN 978-81-322-2211-8).

Ahn, K., 2014. The role of air pollutants in atopic dermatitis. J. Allergy Clin. Immunol. 134, 993–999. http://dx.doi.org/10.1016/j.jaci.2014.09.023.

Alves, C., 2008. Characterisation of solvent extractable organic constituents in atmospheric particulate matter: an overview. An. Acad. Brasil. Ciênc. 80, 21–82. Alves, C., Gonçalves, C., Fernandes, A.P., Tarelho, L., Pio, C., 2011. Fireplace and woodstove fine particle emissions from combustion of western Mediterranean wood types. Atmos. Res. 101, 692–700.

Alves, C.A., Vicente, A.M.P., Gomes, J., Nunes, T., Duarte, M., Bandowe, B.A.M., 2016. Polycyclic aromatic hydrocarbons (PAHs) and their derivatives (oxygenated PAHs, nitrated-PAHs and azaarenes) in size-fractionated particles emitted in an urban road tunnel. Atmos. Res. 180, 128–137. http://dx.doi.org/10.1016/j.atmosres.2016.05.013.

Alves, C.A., Vicente, E.D., Rocha, S., Vicente, A.M., 2017. Organic tracers in aerosols from the residential combustion of pellets and agro-fuels. Air Qual. Atmos. Health 1–9. http://dx.doi.org/10.1007/s11869-016-0406-3.

Amato, F., Alastuey, A., Karanasiou, A., Lucarelli, F., Nava, S., Calzolai, G., Severi, M., Becagli, S., Gianelle, V.L., Colombi, C., Alves, C., Custódio, D., Nunes, T., Cerqueira, M., Pio, C., Eleftheriadis, K., Diapouli, E., Reche, C., Minguillón, M.C., Manousakas, M.I., Maggos, T., Vratolis, S., Harrison, R.M., Querol, X., 2016. AIRUSE-LIFE+: a harmonized PM speciation and source apportionment in five southern European cities. Atmos. Chem. Phys. 16, 3289–3309. http://dx.doi.org/10.5194/acp-16-3289- 2016.

Andersen, Z.J., Wahlin, P., Raaschou-Nielsen, O., Scheike, T., Loft, S., 2007. Ambient particle source apportionment and daily hospital admissions among children and elderly in Copenhagen. J. Expo. Sci. Environ. Epidemiol. 17, 625–636. http://dx.doi.org/10.1038/sj.jes.7500546.

Anwar, Z., Gulfraz, M., Irshad, M., 2014. Agro-industrial lignocellulosic biomass a key to unlock the future bio-energy: a brief review. J. Radiat. Res. Appl. Sci. 7, 163–173. http://dx.doi.org/10.1016/j.jrras.2014.02.003.

Bäfver, L.S., Rönnbäck, M., Leckner, B., Claesson, F., Tullin, C., 2009. Particle emission from combustion of oat grain and its potential reduction by addition of limestone or kaolin. Fuel Process. Technol. 90, 353–359. http://dx.doi.org/10.1016/j.fuproc.2008.10.006.

Bäfver, L.S., Leckner, B., Tullin, C., Berntsen, M., 2011. Particle emissions from pellets stoves and modern and old-type wood stoves. Biomass Bioenergy 35, 3648–3655. http://dx.doi.org/10.1016/j.biombioe.2011.05.027.

Bari, M.A., Baumbach, G., Kuch, B., Scheffknecht, G., 2009. Wood smoke as a source of particle-phase organic compounds in residential areas. Atmos. Environ. 43, 4722–4732. http://dx.doi.org/10.1016/j.atmosenv.2008.09.006.

Bari, M.A., Baumbach, G., Kuch, B., Scheffknecht, G., 2010. Temporal variation and impact of wood smoke pollution on a residential area in southern Germany. Atmos. Environ. 44, 3823–3832. http://dx.doi.org/10.1016/j.atmosenv.2010.06.031.

Bari, M.A., Baumbach, G., Brodbeck, J., Struschka, M., Kuch, B., Dreher, W., Scheffknecht, G., 2011. Characterisation of particulates and carcinogenic polycyclic aromatic hydrocarbons in wintertime wood-fired heating in residential areas. Atmos. Environ. 45, 7627–7634. http://dx.doi.org/10.1016/j.atmosenv.2010.11.053.

Belis, C.A., Cancelinha, J., Duane, M., Forcina, V., Pedroni, V., Passarella, R., Tanet, G., Douglas, K., Piazzalunga, A., Bolzacchini, E., Sangiorgi, G., Perrone, M.-G., Ferrero, L., Fermo, P., Larsen, B.R., 2011. Sources for PM air pollution in the Po Plain, Italy: I. Critical comparison of methods for estimating biomass burning contributions to benzo(a)pyrene. Atmos. Environ. 45, 7266–7275. http://dx.doi.org/10.1016/j.atmosenv.2011.08.061.

Bergauff, M., Ward, T., Noonan, C., Palmer, C.P., 2008. Determination and evaluation of selected organic chemical tracers for wood smoke in airborne particulate matter. Int. J. Environ. Anal. Chem. 88, 473–486. http://dx.doi.org/10.1080/03067310701809110.

Bergauff, M.A., Ward, T.J., Noonan, C.W., Migliaccio, C.T., Simpson, C.D., Evanoski, A.R., Palmer, C.P., 2010. Urinary levoglucosan as a biomarker of wood smoke: results of human exposure studies. J. Expo. Sci. Environ. Epidemiol. 20, 385–392. http://dx.doi.org/10.1038/jes.2009.46.

Bernardoni, V., Vecchi, R., Valli, G., Piazzalunga, A., Fermo, P., 2011. PM_{10} source apportionment in Milan (Italy) using time-resolved data. Sci. Total Environ. 409, 4788–4795. http://dx.doi.org/10.1016/j.scitotenv.2011.07.048.

Biedermann, F., Obernberger, I., 2005. Ash-related problems during biomass combustion and possibilities for a sustainable ash utilisation. In: Proceedings Int. Conf. World Renew. Energy Congr. 8.

Bølling, A.K., Pagels, J., Yttri, K.E., Barregard, L., Sallsten, G., Schwarze, P.E., Boman, C., 2009. Health effects of residential wood smoke particles: the importance of combustion conditions and physicochemical particle properties. Part. Fibre Toxicol. 6, 29. http://dx.doi.org/10.1186/1743-8977-6-29.

Bologa, A., Paur, H.R., Ulbricht, T., Woletz, K., 2010. Particle emissions from small scale wood combustion devices and their control by electrostatic precipitation. Chem. Eng. Trans. 22, 119–124. http://dx.doi.org/10.3303/CET1022019.

Bologa, A., Paur, H.-R., Klaus, W., 2011a. Development and study of an electrostatic precipitator for small scale wood combustion. Int. J. Plasma Environ. Sci. Technol. 5, 168–173.

Bologa, A., Paur, H., Seifert, H., Woletz, K., Ulbricht, T., 2011b. Fine particle generation, evolution and control by small biomass combustion. Manag. Environ. Qual. 23, 36 55. http://dx.doi.org/10.1108/14777831211191584.

Boman, C., Nordin, A., Bostro, D., Marcus, O., 2004. Characterization of inorganic particulate matter from residential combustion of pelletized biomass fuels. Energ. Fuel. 18, 338–348.

Boman, C., Pettersson, E., Westerholm, R., Boström, D., Nordin, A., 2011. Stove performance and emission characteristics in residential wood log and pellet combustion, part 1: pellet stoves. Energ. Fuel. 25, 307–314. http://dx.doi.org/10.1021/ef100774x.

Bond, T.C., Sun, H., 2005. Can reducing black carbon emissions counteract global warming? Environ. Sci. Technol. 39, 5921–5926. http://dx.doi.org/10.1021/es0480421.

Bond, T.C., Doherty, S.J., Fahey, D.W., Forster, P.M., Berntsen, T., DeAngelo, B.J., Flanner, M.G., Ghan, S., Kärcher, B., Koch, D., Kinne, S., Kondo, Y., Quinn, P.K., Sarofim, M.C., Schultz, M.G., Schulz, M., Venkataraman, C., Zhang, H., Zhang, S., Bellouin, N., Guttikunda, S.K., Hopke, P.K., Jacobson, M.Z., Kaiser, J.W., Klimont, Z., Lohmann, U., Schwarz, J.P., Shindell, D., Storelvmo, T., Warren, S.G., Zender, C.S., 2013. Bounding the role of black carbon in the climate system: a scientific assessment. J. Geophys. Res. Atmos. 118, 5380–5552. http://dx.doi.org/10.1002/jgrd.50171.

Boucher, O., 2015. In: Springer Netherlands (Ed.), Atmospheric aerosols - properties and climate impacts, http://dx.doi.org/10.1007/978-94-017-9649-1.

Bressi, M., Sciare, J., Ghersi, V., Mihalopoulos, N., Petit, J.-E., Nicolas, J.B., Moukhtar, S., Rosso, A., Féron, A., Bonnaire, N., Poulakis, E., Theodosi, C., 2014. Sources and geographical origins of fine aerosols in Paris (France). Atmos. Chem. Phys. 14, 8813–8839. http://dx.doi.org/10.5194/acp-14-8813-2014.

Brown, S.G., Lee, T., Roberts, P.T., Collett, J.L., 2016. Wintertime residential biomass burning in Las Vegas, Nevada; marker components and apportionment methods. Atmosphere (Basel) 7, 1–16. http://dx.doi.org/10.3390/atmos7040058.

Bruns, E.A., Krapf, M., Orasche, J., Huang, Y., Zimmermann, R., Drinovec, L., Močnik, G., El Haddad, I., Slowik, J.G., Dommen, J., Baltensperger, U., Prévôt, A.S.H., 2015. Characterization of primary and secondary wood combustion products generated under different burner loads. Atmos. Chem. Phys. 15, 2825–2841. http://dx.doi.org/10.5194/acp-15-2825-2015.

Bruns, E.A., El Haddad, I., Slowik, J.G., Kilic, D., Klein, F., Baltensperger, U., Prévôt, A.S.H., 2016. Identification of significant precursor gases of secondary organic aerosols from residential wood combustion. Sci. Rep. 6, 27881. http://dx.doi.org/10.1038/srep27881.

Budhavant, K., Andersson, A., Bosch, C., Kruså, M., Kirillova, E.N., Sheesley, R.J., Safai, P.D., Rao, P.S.P., Gustafsson, Ö, 2015. Radiocarbon-based source apportionment of elemental carbon aerosols at two South Asian receptor observatories over a full annual cycle. Environ. Res. Lett. 10, 064004. http://dx.doi.org/10.1088/1748-9326/10/6/064004.

Bullock, K.R., Duvall, R.M., Norris, G.A., McDow, S.R., Hays, M.D., 2008. Evaluation of the CMB and PMF models using organic molecular markers in fine particulate matter collected during the Pittsburgh Air Quality Study. Atmos. Environ. 42, 6897–6904. http://dx.doi.org/10.1016/j.atmosenv.2008.05.011.

Callén, M.S., de la Cruz, M.T., López, J.M., Navarro, M.V., Mastral, A.M., 2009. Comparison of receptor models for source apportionment of the PM_{10} in Zaragoza (Spain). Chemosphere 76, 1120–1129. http://dx.doi.org/10.1016/j.chemosphere.2009.04.015.

Calvo, A.I., Alves, C., Castro, A., Pont, V., Vicente, A.M., Fraile, R., 2013. Research on aerosol sources and chemical composition: past, current and emerging issues. Atmos. Res. 120-121, 1–28. http://dx.doi.org/10.1016/j.atmosres.2012.09.021.

Calvo, A.I., Tarelho, L.A.C., Alves, C.A., Duarte, M., Nunes, T., 2014. Characterization of operating conditions of two residential wood combustion appliances. Fuel Process. Technol. 126, 222–232. http://dx.doi.org/10.1016/j.fuproc.2014.05.001.

Calvo, A.I., Martins, V., Nunes, T., Duarte, M., Hillamo, R., Teinilä, K., Pont, V., Castro, A., Fraile, R., Tarelho, L., Alves, C., 2015. Residential wood combustion in two domestic devices: relationship of different parameters throughout the combustion cycle. Atmos. Environ. 116, 72–82. http://dx.doi.org/10.1016/j.atmosenv.2015.06.012.

Canha, N., Lopes, I., Vicente, E.D., Vicente, A.M., Bandowe, B.A.M., Almeida, S.M., Alves, C.A., 2016. Mutagenicity assessment of aerosols in emissions from domestic combustion processes. Environ. Sci. Pollut. Res. 23, 10799–10807. http://dx.doi.org/10.1007/ s11356-016-6292-2.

Canonaco, F., Crippa, M., Slowik, J.G., Baltensperger, U., Prévôt, A.S.H., 2013. SoFi, an IGOR based interface for the efficient use of the generalized multilinear engine (ME-2) for the source apportionment: ME-2 application to aerosol mass spectrometer data. Atmos. Meas. Tech. 6, 3649–3661. http://dx.doi.org/10.5194/amt-6-3649-2013.

Carroll, J., Finnan, J., 2013. Emissions and efficiencies from the combustion of agricultural feedstock pellets using a small scale tilting grate boiler. Biosyst. Eng. 115, 50–55. http://dx.doi.org/10.1016/j.biosystemseng.2013.01.009.

Carvalho, L., Wopienka, E., Pointner, C., Lundgren, J., Verma, V.K., Haslinger, W., Schmidl, C., 2013. Performance of a pellet boiler fired with agricultural fuels. Appl. Energy 104, 286–296. http://dx.doi.org/10.1016/j.apenergy.2012.10.058.

Carvalho, R.L., Jensen, O.M., Vicente, E.D., Tarelho, L.A.C., 2016. Transition to an intelligent use of cleaner biomass stoves. In: 4th European Conference on Behaviour and Energy Efficiency (BEHAVE). Coimbra, Portugal, pp. 8–9.

Caseiro, A., Bauer, H., Schmidl, C., Pio, C.A., Puxbaum, H., 2009. Wood burning impact on PM_{10} in three Austrian regions. Atmos. Environ. 43, 2186–2195. http://dx.doi.org/10.1016/j.atmosenv.2009.01.012.

Chen, Y., Bond, T.C., 2010. Light absorption by organic carbon from wood combustion. Atmos. Chem. Phys. 10, 1773–1787. http://dx.doi.org/10.5194/acp-10-1773-2010.

Chen, J., Li, C., Ristovski, Z., Milic, A., Gu, Y., Islam, M.S., Wang, S., Hao, J., Zhang, H., He, C., Guo, H., Fu, H., Miljevic, B., Morawska, L., Thai, P., LAM, Y.F., Pereira, G., Ding, A., Huang, X., Dumka, U.C., 2017. A review of biomass burning: emissions and impacts on air quality, health and climate in China. Sci. Total Environ. 579, 1000–1034. http://dx.doi.org/10.1016/j.scitotenv.2016.11.025.

Clark, M., Paulsen, M., Smith, K.R., Canuz, E., Simpson, C.D., 2007. Urinary methoxyphenol biomarkers and woodsmoke exposure: comparisons in rural Guatemala with personal CO and kitchen CO, levoglucosan, and $PM_{2.5}$. Environ. Sci. Technol. 41, 3481–3487.

Claxton, L.D., Matthews, P.P., Warren, S.H., 2004. The genotoxicity of ambient outdoor air, a review: salmonella mutagenicity. Mutat. Res. Rev. Mutat. Res. 567, 347–399. http://dx.doi.org/10.1016/j.mrrev.2004.08.002.

Coeur-Tourneur, C., Cassez, A., Wenger, J.C., 2010. Rate coefficients for the gas-phase reaction of hydroxyl radicals with 2-methoxyphenol (guaiacol) and related compounds. J. Phys. Chem. A 114, 11645–11650. http://dx.doi.org/10.1021/jp1071023.

Corin, N.S., Backlund, P.H., Kulovaara, M.A.M., 2000. Photolysis of the resin acid dehydroabietic acid in water. Environ. Sci. Technol. 34, 2231 2236. http://dx.doi.org/10.1021/ES9910816.

Dall'Osto, M., Querol, X., Amato, F., Karanasiou, A., Lucarelli, F., Nava, S., Calzolai, G., Chiari, M., 2013. Hourly elemental concentrations in $PM_{2.5}$ aerosols sampled simultaneously at urban background and road site during SAPUSS – diurnal variations and PMF receptor modelling. Atmos. Chem. Phys. 13, 4375–4392. http://dx.doi.org/10.5194/acp-13-4375-2013.

Dills, R.L., Zhu, X., Kalman, D.A., 2001. Measurement of urinary methoxyphenols and their use for biological monitoring of wood smoke exposure. Environ. Res. 85, 145-158. http://dx.doi.org/10.1006/enrs.2000.4107.

Dills, R.L., Paulsen, M., Ahmad, J., Kalman, D.A., Elias, F.N., Simpson, C.D., 2006. Evaluation of urinary methoxyphenols as biomarkers of woodsmoke exposure. Environ. Sci. Technol. 40, 2163–2170.

Dobele, G., Rossinskaja, G., Dizhbite, T., Telysheva, G., Meier, D., Faix, O., 2005. Application of catalysts for obtaining 1,6-anhydrosaccharides from cellulose and wood by fast pyrolysis. J. Anal. Appl. Pyrolysis 74, 401–405. http://dx.doi.org/10.1016/j.jaap.2004.11.031.

DUH and DEC, 2016. Residential wood burning - environmental impact and sustainable solutions. In: Background Paper - Clean Heat. Deutsche Umwelthilfe and Danish Ecological Council.

EEA, 2012. Air Quality in Europe - 2012 report. In: Report No 4/2012. European Environment Agency, Copenhagen, Denmark. http://dx.doi.org/10.2800/55823.

EEA, 2015. Air quality in Europe - 2015 report. In: Report No 5/2015. European Environment Agency, Copenhagen, Denmark. http://dx.doi.org/10.2800/413142.

El Haddad, I., Marchand, N., Wortham, H., Piot, C., Besombes, J.L., Cozic, J., Chauvel, C., Armengaud, A., Robin, D., Jaffrezo, J.L., 2011. Primary sources of $PM_{2.5}$ organic aerosol in an industrial Mediterranean city, Marseille. Atmos. Chem. Phys. 11, 2039–2058. http://dx.doi.org/10.5194/acp-11-2039-2011.

Engling, G., Lee, J.J., Tsai, Y.-W., Lung, S.-C.C., Chou, C.C.-K., Chan, C.-Y., 2009. Sizeresolved anhydrosugar composition in smoke aerosol from controlled field burning of rice straw. Aerosol Sci. Technol. 43, 662–672. http://dx.doi.org/10.1080/02786820902825113.

Eriksson, A.C., Nordin, E.Z., Nyström, R., Pettersson, E., Swietlicki, E., Bergvall, C., Westerholm, R., Boman, C., Pagels, J.H., 2014. Particulate PAH emissions from residential biomass combustion: time-resolved analysis with aerosol mass spectrometry. Environ. Sci. Technol. 48, 7143–7150. http://dx.doi.org/10.1021/es500486j.

Fabbri, D., Torri, C., Simoneit, B.R.T., Marynowski, L., Rushdi, A.I., Fabiańska, M.J., 2009. Levoglucosan and other cellulose and lignin markers in emissions from burning of Miocene lignites. Atmos. Environ. 43, 2286–2295. http://dx.doi.org/10.1016/j.atmosenv.2009.01.030.

Favez, O., Cachier, H., Sciare, J., Sarda-Estève, R., Martinon, L., 2009. Evidence for a significant contribution of wood burning aerosols to $PM_{2.5}$ during the winter season in Paris, France. Atmos. Environ. 43, 3640–3644. http://dx.doi.org/10.1016/j.atmosenv.2009.04.035.

Favez, O., El Haddad, I., Piot, C., Boréave, A., Abidi, E., Marchand, N., Jaffrezo, J.L., Besombes, J.L., Personnaz, M.B., Sciare, J., Wortham, H., George, C., D'Anna, B., 2010. Inter-comparison of source apportionment models for the estimation of wood burning aerosols during wintertime in an Alpine city (Grenoble, France). Atmos. Chem. Phys. 10, 5295–5314. http://dx.doi.org/10.5194/acp-10-5295-2010.

Fernandes, U., Costa, M., 2012. Particle emissions from a domestic pellets-fired boiler. Fuel Process. Technol. 103, 51–56. http://dx.doi.org/10.1016/j.fuproc.2011.08.020.

Fernandes, A.P., Alves, C.A., Gonçalves, C., Tarelho, L., Pio, C., Schimdl, C., Bauer, H., 2011. Emission factors from residential combustion appliances burning Portuguese biomass fuels. J. Environ. Monit. 13, 3196–3206. http://dx.doi.org/10.1039/c1em10500k.

Fine, P.M., Cass, G.R., Simoneit, B.R., 2001. Chemical characterization of fine particle emissions from fireplace combustion of woods grown in the northeastern United States. Environ. Sci. Technol. 35, 2665–2675.

Fine, P.M., Cass, G.R., Simoneit, B.R.T., 2002. Chemical characterization of fine particle emissions from the fireplace combustion of woods grown in the southern United States. Environ. Sci. Technol. 36, 1442–1451. http://dx.doi.org/10.1021/es0108988.

Fine, P.M., Cass, G.R., Simoneit, B.R.T., 2004. Chemical characterization of fine particle emissions from the wood stove combustion of prevalent United States tree species. Environ. Eng. Sci. 21. https://doi.org/10.1089/ees.2004.21.705

Fountoukis, C., Megaritis, A.G., Skyllakou, K., Charalampidis, P.E., Denier van der Gon, H.A.C., Crippa, M., Prévôt, A.S.H., Fachinger, F., Wiedensohler, A., Pilinis, C., Pandis, S.N., 2016. Simulating the formation of carbonaceous aerosol in a European Megacity (Paris) during the MEGAPOLI summer and winter campaigns. Atmos. Chem. Phys. 16, 3727–3741. http://dx.doi.org/10.5194/acp-16-3727-2016.

Fournel, S., Palacios, J., Godbout, S., Heitz, M., 2015. Effect of additives and fuel blending on emissions and ash-related problems from small-scale combustion of reed canary grass. Agriculture 5, 561–576. http://dx.doi.org/10.3390/agriculture5030561.

Frey, A.K., Tissari, J., Saarnio, K.M., Timonen, H.J., Tolonen-Kivimäki, O., Aurela, M.A., Saarikoski, S.K., Makkonen, U., Hytönen, K., Jokiniemi, J., Salonen, R.O., Hillamo, R.E.J., 2009. Chemical composition and mass size distribution of fine particulate matter emitted by a small masonry heater. Boreal Environ. Res. 14, 225–271.

Frosch, M., Prisle, N.L., Bilde, M., Varga, Z., Kiss, G., 2011. Joint effect of organic acids and inorganic salts on cloud droplet activation. Atmos. Chem. Phys. 11, 3895–3911. http://dx.doi.org/10.5194/acp-11-3895-2011.

Fuller, G.W., Tremper, A.H., Baker, T.D., Yttri, K.E., Butterfield, D., 2014. Contribution of wood burning to PM_{10} in London. Atmos. Environ. 87, 87–94.

Galarneau, E., 2008. Source specificity and atmospheric processing of airborne PAHs: implications for source apportionment. Atmos. Environ. 42, 8139–8149. http://dx.doi.org/10.1016/j.atmosenv.2008.07.025.

Garcia-Maraver, A., Zamorano, M., Fernandes, U., Rabaçal, M., Costa, M., 2014. Relationship between fuel quality and gaseous and particulate matter emissions in a domestic pellet fired boiler. Fuel 119, 141–152. http://dx.doi.org/10.1016/j.fuel.2013.11.037.

Gelencsér, A., May, B., Simpson, D., Sánchez-Ochoa, A., Kasper-Giebl, A., Puxbaum, H., Caseiro, A., Pio, C., Legrand, M., 2007. Source apportionment of $PM_{2.5}$ organic aerosol over Europe: Primary/secondary, natural/anthropogenic, and fossil/biogenic origin. J. Geophys. Res. 112, D23S04. http://dx.doi.org/10.1029/2006JD008094.

Gianelle, V., Colombi, C., Caserini, S., Ozgen, S., Galante, S., Marongiu, A., Lanzani, G., 2013. Benzo(a)pyrene air concentrations and emission inventory in Lombardy region, Italy. Atmos. Pollut. Res. 4, 257–266. http://dx.doi.org/10.5094/APR.2013.028.

Gianini, M.F.D., Fischer, A., Gehrig, R., Ulrich, A., Wichser, A., Piot, C., Besombes, J. L., Hueglin, C., 2012. Comparative source apportionment of PM_{10} in Switzerland for 2008/2009 and 1998/1999 by positive matrix factorisation. Atmos. Environ. 54, 149–158. http://dx.doi.org/10.1016/j.atmosenv.2012.02.036.

Giannoni, M., Martellini, T., Del Bubba, M., Gambaro, A., Zangrando, R., Chiari, M., Lepri, L., Cincinelli, A., 2012. The use of levoglucosan for tracing biomass burning in $PM_{2.5}$ samples in Tuscany (Italy). Environ. Pollut. 167, 7–15. http://dx.doi.org/10.1016/j.envpol.2012.03.016.

Gilardoni, S., Massoli, P., Paglione, M., Giulianelli, L., Carbone, C., Rinaldi, M., Decesari, S., Sandrini, S., Costabile, F., Gobbi, G.P., Pietrogrande, M.C., Visentin, M., Scotto, F., Fuzzi, S., Facchini, M.C., 2016. Direct observation of aqueous secondary organic aerosol from biomass-burning emissions. Proc. Natl. Acad. Sci. U.S.A. 113, 10013–10018. http://dx.doi.org/10.1073/pnas.1602212113.

Glasius, M., Ketzel, M., Wåhlin, P., Jensen, B., Mønster, J., Berkowicz, R., Palmgren, F., 2006. Impact of wood combustion on particle levels in a residential area in Denmark. Atmos. Environ. 40, 7115–7124. http://dx.doi.org/10.1016/j.atmosenv.2006.06.047.

Glasius, M., Ketzel, M., Wåhlin, P., Bossi, R., Stubkjær, J., Hertel, O., Palmgren, F., 2008. Characterization of particles from residential wood combustion and modelling of spatial variation in a low-strength emission area. Atmos. Environ. 42, 8686–8697. http://dx.doi.org/10.1016/j.atmosenv.2008.04.037.

Gonçalves, C., Alves, C., Evtyugina, M., Mirante, F., Pio, C., Caseiro, A., Schmidl, C., Bauer, H., Carvalho, F., 2010. Characterisation of PM_{10} emissions from woodstove combustion of common woods grown in Portugal. Atmos. Environ. 44, 4474–4480. http://dx.doi.org/10.1016/j.atmosenv.2010.07.026.

Gonçalves, C., Alves, C., Fernandes, A.P., Monteiro, C., Tarelho, L., Evtyugina, M., Pio, C., 2011. Organic compounds in $PM_{2.5}$ emitted from fireplace and woodstove combustion of typical Portuguese wood species. Atmos. Environ. 45, 4533–4545. http://dx.doi.org/10.1016/j.atmosenv.2011.05.071.

Gonçalves, C., Alves, C., Pio, C., 2012. Inventory of fine particulate organic compound emissions from residential wood combustion in Portugal. Atmos. Environ. 50, 297–306. http://dx.doi.org/10.1016/j.atmosenv.2011.12.013.

González, J.F., González-García, C.M., Ramiro, A., González, J., Sabio, E., Gañán, J., Rodríguez, M.A., 2004. Combustion optimisation of biomass residue pellets for domestic heating with a mural boiler. Biomass Bioenergy 27, 145–154. http://dx.doi.org/10.1016/j.biombioe.2004.01.004.

Grantz, D.A., Garner, J.H.B., Johnson, D.W., 2003. Ecological effects of particulate matter. Environ. Int. 29, 213–239. http://dx.doi.org/10.1016/S0160-4120(02)00181-2.

Grieshop, A.P., Donahue, N.M., Robinson, A.L., 2009a. Laboratory investigation of photochemical oxidation of organic aerosol from wood fires 2: analysis of aerosol mass spectrometer data. Atmos. Chem. Phys. 9, 2227–2240. http://dx.doi.org/10.5194/acp-9-2227-2009.

Grieshop, A.P., Logue, J.M., Donahue, N.M., Robinson, A.L., 2009b. Laboratory investigation of photochemical oxidation of organic aerosol from wood fires 1: measurement and simulation of organic aerosol evolution. Atmos. Chem. Phys. 9, 1263–1277. http://dx.doi.org/10.5194/acp-9-1263-2009.

Grigonyte, J., Nuutinen, I., Koponen, T., Lamberg, H., Tissari, J., Jokiniemi, J., Sippula, O., 2014. Evaluation of a heat exchanger designed for efficient fine particle precipitation in small scale wood combustion. Energy Fuel 28, 6058–6065. http://dx.doi.org/10.1021/ef500958x.

Gu, J., Pitz, M., Schnelle-Kreis, J., Diemer, J., Reller, A., Zimmermann, R., Soentgen, J., Stoelzel, M., Wichmann, H.-E., Peters, A., Cyrys, J., 2011. Source apportionment of ambient particles: comparison of positive matrix factorization analysis applied to particle size distribution and chemical composition data. Atmos. Environ. 45, 1849–1857. http://dx.doi.org/10.1016/j.atmosenv.2011.01.009.

Happo, M.S., Uski, O., Jalava, P.I., Kelz, J., Brunner, T., Hakulinen, P., Mäki-Paakkanen, J., Kosma, V.M., Jokiniemi, J., Obernberger, I., Hirvonen, M.R., 2013. Pulmonary inflammation and tissue damage in the mouse lung after exposure to PM samples from biomass heating appliances of old and modern technologies. Sci. Total Environ. 443, 256–266. http://dx.doi.org/10.1016/j.scitotenv.2012.11.004.

Hays, M.D., Geron, C.D., Linna, K.J., Smith, N.D., Schauer, J.J., 2002. Speciation of gasphase and fine particle emissions from burning of foliar fuels. Environ. Sci. Technol. 36, 2281–2295. http://dx.doi.org/10.1021/es0111683.

Hedberg, E., Johansson, C., Johansson, L., Swietlicki, E., Brorström-Lundén, E., 2006. Is levoglucosan a suitable quantitative tracer for wood burning? Comparison with receptor modeling on trace elements in Lycksele, Sweden. J. Air Waste Manage. Assoc. 56, 1669–1678. http://dx.doi.org/10.1080/10473289.2006.10464572.

Hennigan, C.J., Sullivan, A.P., Collett, J.L., Robinson, A.L., 2010. Levoglucosan stability in biomass burning particles exposed to hydroxyl radicals. Geophys. Res. Lett. 37, 2–5. http://dx.doi.org/10.1029/2010GL043088.

Hennigan, C.J., Miracolo, M.A., Engelhart, G.J., May, A.A., Presto, A.A., Lee, T., Sullivan, A.P., McMeeking, G.R., Coe, H., Wold, C.E., Hao, W. M., Gilman, J.B., Kuster, W.C., de Gouw, J., Schichtel, B.A., Collett Jr., J.L., Kreidenweis, S.M., Robinson, A.L., 2011. Chemical and physical transformations of organic aerosol from the photo-oxidation of open biomass burning emissions in an environmental chamber. Atmos. Chem. Phys. 11, 7669–7686. http://dx.doi.org/10.5194/acp-11-7669-2011.

Herich, H., Hueglin, C., Buchmann, B., 2011. A 2.5 year's source apportionment study of black carbon from wood burning and fossil fuel combustion at urban and rural sites in Switzerland. Atmos. Meas. Tech. 4, 1409–1420. http://dx.doi.org/10.5194/amt-4-1409-2011.

Hildemann, L.M., Cass, G.R., Markowski, G.R., 1989. A dilution stack sampler for collection of organic aerosol emissions: design, characterization and field tests. Aerosol Sci. Technol. 10, 193–204. http://dx.doi.org/10.1080/02786828908959234.

Hinwood, A.L., Trout, M., Murby, J., Barton, C., Symons, B., 2008. Assessing urinary levoglucosan and methoxyphenols as biomarkers for use in woodsmoke exposure studies. Sci. Total Environ. 402, 139–146. http://dx.doi.org/10.1016/j.scitotenv.2008.04.012.

Hodzic, A., Madronich, S., Bohn, B., Massie, S., Menut, L., Wiedinmyer, C., 2007. Wildfire particulate matter in Europe during summer 2003: meso-scale modeling of smoke emissions, transport and radiative effects. Atmos. Chem. Phys. Discuss. 7, 4705–4760. http://dx.doi.org/10.5194/acpd-7-4705-2007.

Hoffmann, D., Tilgner, A., Iinuma, Y., Herrmann, H., 2010. Atmospheric stability of levoglucosan: a detailed laboratory and modeling study. Environ. Sci. Technol. 44, 694–699. http://dx.doi.org/10.1021/es902476f.

Hukkanen, A., Kaivosoja, T., Sippula, O., Nuutinen, K., Jokiniemi, J., Tissari, J., 2012. Reduction of gaseous and particulate emissions from small-scale wood combustion with a catalytic combustor. Atmos. Environ. 50, 16–23. http://dx.doi.org/10.1016/j.atmosenv.2012.01.016.

Iinuma, Y., Boge, O., Grafe, R., Herrmann, H., 2010. Methyl-nitrocatechols: atmospheric tracer compounds for biomass burning secondary organic aerosols. Environ. Sci. Technol. 44, 8453–8459.

Jalava, P.I., Salonen, R.O., Nuutinen, K., Pennanen, A.S., Happo, M.S., Tissari, J., Frey, A., Hillamo, R., Jokiniemi, J., Hirvonen, M.R., 2010. Effect of combustion condition on cytotoxic and inflammatory activity of residential wood combustion particles. Atmos. Environ. 44, 1691–1698. http://dx.doi.org/10.1016/j.atmosenv.2009.12.034.

Jalava, P.I., Happo, M.S., Kelz, J., Brunner, T., Hakulinen, P., Mäki-Paakkanen, J., Hukkanen, A., Jokiniemi, J., Obernberger, I., Hirvonen, M.R., 2012. *In vitro* toxicological characterization of particulate emissions from residential biomass heating systems based on old and new technologies. Atmos. Environ. 50, 24–35. http://dx.doi.org/10.1016/j.atmosenv.2012.01.009.

Jang, E., Alam, M.S., Harrison, R.M., 2013. Source apportionment of polycyclic aromatic hydrocarbons in urban air using positive matrix factorization and spatial distribution analysis. Atmos. Environ. 79, 217–285. http://dx.doi.org/10.1016/j.atmosenv.2013.06.056.

Johansson, L.S., Leckner, B., Gustavsson, L., Cooper, D., Tullin, C., Potter, A., 2004. Emission characteristics of modern and old-type residential boilers fired with wood logs and wood pellets. Atmos. Environ. 38, 4183–4195. http://dx.doi.org/10.1016/j.atmosenv.2004.04.020.

Jordan, T.B., Seen, A.J., 2005. Effect of airflow setting on the organic composition of woodheater emissions. Environ. Sci. Technol. 39, 3601–3610.

Kaivosoja, T., Jalava, P.I., Lamberg, H., Virén, A., Tapanainen, M., Torvela, T., Tapper, U., Sippula, O., Tissari, J., Hillamo, R., Hirvonen, M.R., Jokiniemi, J., 2013. Comparison of emissions and toxicological properties of fine particles from wood and oil boilers in small (20–25 kW) and medium (5–10 MW) scale. Atmos. Environ. 77, 193–201. http://dx.doi.org/10.1016/j.atmosenv.2013.05.014.

Karagulian, F., Belis, C.A., Dora, C.F.C., Prüss-Ustün, A.M., Bonjour, S., Adair-Rohani, H., Amann, M., 2015. Contributions to cities' ambient particulate matter (PM): a systematic review of local source contributions at global level. Atmos. Environ. 120, 475–483. http://dx.doi.org/10.1016/j.atmosenv.2015.08.087.

Karanasiou, A.A., Siskos, P.A., Eleftheriadis, K., 2009. Assessment of source apportionment by positive matrix factorization analysis on fine and coarse urban aerosol size fractions. Atmos. Environ. 43, 3385–3395. http://dx.doi.org/10.1016/j.atmosenv.2009.03.051.

Karanasiou, A., Minguillón, M.C., Viana, M., Alastuey, A., Putaud, J.-P., Maenhaut, W., Panteliadis, P., Močnik, G., Favez, O., Kuhlbusch, T.A.J., 2015. Thermal-optical analysis for the measurement of elemental carbon (EC) and organic carbon (OC) in ambient air a literature review. Atmos. Meas. Tech. Discuss. 8, 9649–9712. http://dx.doi.org/10.5194/amtd-8-9649-2015.

Karvosenoja, N., Klimont, Z., Tohka, A., Johansson, M., 2007. Cost-effective reduction of fine primary particulate matter emissions in Finland. Environ. Res. Lett. 2, 044002. http://dx.doi.org/10.1088/1748-9326/2/4/044002.

Kato, M., Loomis, D., Brooks, L.M., Gattas, G.F.J., Gomes, L., Carvalho, A.B., Rego, M.A.V., DeMarini, D.M., 2004. Urinary biomarkers in charcoal workers exposed to wood smoke in Bahia state, Brazil. Cancer Epidemiol. Biomark. Prev. 13, 1005–1012.

Kelz, J., Brunner, T., Obernberger, I., Jalava, P., Hirvonen, M.-R., 2010. PM emissions from old and modern biomass combustion systems. In: ETA Florence Renewable Energies (Ed.), Proc. of the 18th European Biomass Conference and Exhibition. Lyon, France, pp. 1231–1243.

Kessler, S.H., Smith, J.D., Che, D.L., Worsnop, D.R., Wilson, K.R., Kroll, J.H., 2010. Chemical sinks of organic aerosol: kinetics and products of the heterogeneous oxidation of erythritol and levoglucosan. Environ. Sci. Technol. 44, 7005–7010. http://dx.doi.org/10.1021/es101465m.

Khalil, M.A., Rasmussen, R., 2003. Tracers of wood smoke. Atmos. Environ. 37, 1211 1222. http://dx.doi.org/10.1016/S1352-2310(02)01014-2.

Khelfa, A., Finqueneisel, G., Auber, M., Weber, J.V., 2008. Influence of some minerals on the cellulose thermal degradation mechanisms: thermogravimetic and pyrolysis-mass spectrometry studies. J. Therm. Anal. Calorim. 92, 795–799. http://dx.doi.org/10.1007/s10973-007-8649-8.

Kim, E., Larson, T.V., Hopke, P.K., Slaughter, C., Sheppard, L.E., Claiborn, C., 2003. Source identification of $PM_{2.5}$ in an arid northwest U.S. City by positive matrix factorization. Atmos. Res. 66, 291–305. http://dx.doi.org/10.1016/S0169-8095(03)00025-5.

Kim, Y.J., Kim, K.W., Kim, S.D., Lee, B.K., Han, J.S., 2006. Fine particulate matter characteristics and its impact on visibility impairment at two urban sites in Korea: Seoul and Incheon. Atmos. Environ. 40, 593–605. http://dx.doi.org/10.1016/j.atmosenv.2005.11.076.

Kistler, M., 2012. Particulate matter and odor emission factors from small scale biomass combustion units. In: PhD Dissertation. Vienna University of Technology.

Kistler, M., Schmidl, C., Padouvas, E., Giebl, H., Lohninger, J., Ellinger, R., Bauer, H., Puxbaum, H., 2012. Odor, gaseous and PM_{10} emissions from small scale combustion of wood types indigenous to Central Europe. Atmos. Environ. 51, 86–93. http://dx.doi.org/10.1016/j.atmosenv.2012.01.044.

Kjällstrand, J., Olsson, M., 2004. Chimney emissions from small-scale burning of pellets and fuelwood-examples referring to different combustion appliances. Biomass Bioenergy 27, 557–561. http://dx.doi.org/10.1016/j.biombioe.2003.08.014.

Kjällstrand, J., Petersson, G., 2001. Phenolic antioxidants in wood smoke. Sci. Total Environ. 277, 69–75. http://dx.doi.org/10.1016/S00489697(00)00863-9.

Krecl, P., Hedberg Larsson, E., Ström, J., Johansson, C., 2008. Contribution of residential wood combustion to hourly winter aerosol in northern Sweden determined by positive matrix factorization. Atmos. Chem. Phys. Discuss. 8, 5725–5760. http://dx.doi.org/10.5194/acpd-8-5725-2008.

Křůmal, K., Mikuška, P., Vojtěšek, M., Večeřa, Z., 2010. Seasonal variations of monosaccharide anhydrides in PM_1 and $PM_{2.5}$ aerosol in urban areas. Atmos. Environ. 44, 5148–5155. http://dx.doi.org/10.1016/j.atmosenv.2010.08.057.

Kuo, L.J., Herbert, B.E., Louchouarn, P., 2008. Can levoglucosan be used to characterize and quantify char/charcoal black carbon in environmental media? Org. Geochem. 39, 1466–1478. http://dx.doi.org/10.1016/j.orggeochem.2008.04.026.

Lai, C., Liu, Y., Ma, J., Ma, Q., He, H., 2014. Degradation kinetics of levoglucosan initiated by hydroxyl radical under different environmental conditions. Atmos. Environ. 91, 32–39. http://dx.doi.org/10.1016/j.atmosenv.2014.03.054.

Lamberg, H., Nuutinen, K., Tissari, J., Ruusunen, J., Yli-Pirilä, P., Sippula, O., Tapanainen, M., Jalava, P., Makkonen, U., Teinilä, K., Saarnio, K., Hillamo, R., Hirvonen, M.R., Jokiniemi, J., 2011a. Physicochemical characterization of fine particles from small-scale wood combustion. Atmos. Environ. 45, 7635–7643. http://dx.doi.org/10.1016/j.atmosenv.2011.02.072.

Lamberg, H., Sippula, O., Tissari, J., Jokiniemi, J., 2011b. Effects of air-staging and load on fine particle and gaseous emissions from a small-scale pellet boiler. Energ. Fuel. 25, 4952–4960. http://dx.doi.org/10.1021/ef2010578.

Lamberg, H., Tissari, J., Jokiniemi, J., Sippula, O., 2013. Fine particle and gaseous emissions from a small-scale boiler fueled by pellets of various raw materials. Energ. Fuel. 27, 7044–7053. http://dx.doi.org/10.1021/ef401267t.

Lauraguais, A., Coeur-Tourneur, C., Cassez, A., Seydi, A., 2012. Rate constant and secondary organic aerosol yields for the gas-phase reaction of hydroxyl radicals with syringol (2,6-dimethoxyphenol). Atmos. Environ. 55, 43–48. http://dx.doi.org/10.1016/j.atmosenv.2012.02.027.

Lauraguais, A., Coeur-Tourneur, C., Cassez, A., Deboudt, K., Fourmentin, M., Choël, M., 2014. Atmospheric reactivity of hydroxyl radicals with guaiacol (2-methoxyphenol), a biomass burning emitted compound: secondary organic aerosol formation and gasphase oxidation products. Atmos. Environ. 86, 155–163. http://dx.doi.org/10.1016/j.atmosenv.2013.11.074.

Lee, S., Liu, W., Wang, Y., Russell, A.G., Edgerton, E.S., 2008. Source apportionment of $PM_{2.5}$: comparing PMF and CMB results for four ambient monitoring sites in the southeastern United States. Atmos. Environ. 42, 4126–4137. http://dx.doi.org/10.1016/j.atmosenv.2008.01.025.

Leskinen, J., Tissari, J., Uski, O., Virén, A., Torvela, T., Kaivosoja, T., Lamberg, H., Nuutinen, I., Kettunen, T., Joutsensaari, J., Jalava, P.I., Sippula, O., Hirvonen, M.R., Jokiniemi, J., 2014. Fine particle emissions in three different combustion conditions of a wood chip fired appliance-particulate physico-chemical properties and induced cell death. Atmos. Environ. 86, 129–139. http://dx.doi.org/10.1016/j.atmosenv.2013.12.012.

Li, C.K., Kamens, R.M., 1993. The use of polycyclic aromatic hydrocarbons as source signatures in receptor modeling. Atmos. Environ. A. Gen. Top. 27, 523–532. http://dx.doi.org/10.1016/0960-1686(93)90209.

Li, Z., Trinidad, D., Pittman, E.N., Riley, E.A., Sjodin, A., Dills, R.L., Paulsen, M., Simpson, C.D., 2016. Urinary polycyclic aromatic hydrocarbon metabolites as biomarkers to woodsmoke exposure-results from a controlled exposure study. J. Expo. Sci. Environ. Epidemiol. 26, 241–248. http://dx.doi.org/10.1038/jes.2014.94-H.

Limousy, L., Jeguirim, M., Dutournié, P., Kraiem, N., Lajili, M., Said, R., 2013. Gaseous products and particulate matter emissions of biomass residential boiler fired with spent coffee grounds pellets. Fuel 107, 323–329. http://dx.doi.org/10.1016/j.fuel.2012.10.019.

Lipsky, E.M., Robinson, A.L., 2005. Design and evaluation of a portable dilution sampling system for measuring fine particle emissions. Aerosol Sci. Technol. 39, 542–553. http://dx.doi.org/10.1080/027868291004850.

Lipsky, E.M., Robinson, A.L., 2006. Effects of dilution on fine particle mass and partitioning of semivolatile organics in diesel exhaust and wood smoke. Environ. Sci. Technol. 40, 155–162. http://dx.doi.org/10.1021/es050319p.

Löndahl, J., Pagels, J., Boman, C., Swietlicki, E., Massling, A., Rissler, J., Blomberg, A., Bohgard, M., Sandström, T., 2008. Deposition of biomass combustion aerosol particles in the human respiratory tract. Inhal. Toxicol. 20, 923–933. http://dx.doi.org/10.1080/08958370802087124.

Louchouarn, P., Kuo, L.J., Wade, T.L., Schantz, M., 2009. Determination of levoglucosan and its isomers in size fractions of aerosol standard reference materials. Atmos. Environ. 43, 5630–5636. http://dx.doi.org/10.1016/j.atmosenv.2009.07.040.

Maenhaut, W., Vermeylen, R., Claeys, M., Vercauteren, J., Matheeussen, C., Roekens, E., 2012. Assessment of the contribution from wood burning to the PM_{10} aerosol in Flanders, Belgium. Sci. Total Environ. 437, 226–236. http://dx.doi.org/10.1016/j.scitotenv.2016.04.074.

Maenhaut, W., Vermeylen, R., Claeys, M., Vercauteren, J., Roekens, E., 2016. Sources of the PM_{10} aerosol in Flanders, Belgium, and re-assessment of the contribution from wood burning. Sci. Total Environ. 562, 550–560. http://dx.doi.org/10.1016/j.scitotenv.2016.04.074.

Martinsson, J., Abdul Azeem, H., Sporre, M.K., Bergström, R., Ahlberg, E., Öström, E., Kristensson, A., Swietlicki, E., Eriksson Stenström, K., 2016. Carbonaceous aerosol source apportionment using the aethalometer model-evaluation by radiocarbon and levoglucosan analysis at a rural background site in southern Sweden. Atmos. Chem. Phys. Discuss. 1–32. http://dx.doi.org/10.5194/acp-2016-1005.

Mazzoleni, L.R., Zielinska, B., Moosmüller, H., 2007. Emissions of levoglucosan, methoxy phenols, and organic acids from prescribed burns, laboratory combustion of wildland fuels, and residential wood combustion. Environ. Sci. Technol. 41, 2115–2122. http://dx.doi.org/10.1021/es061702c.

McCracken, J.P., Smith, K.R., Díaz, A., Mittleman, M.A., Schwartz, J., 2007. Chimney stove intervention to reduce long-term wood smoke exposure lowers blood pressure among Guatemalan women. Environ. Health Perspect. 115, 996–1001. http://dx.doi.org/10.1289/ehp.9888.

McDonald, J.D., Zielinska, B., Fujita, E.M., Sagebiel, J.C., Chow, J.C., Watson, J.G., 2000. Fine particle and gaseous emission rates from residential wood combustion. Environ. Sci. Technol. 34, 2080–2091. http://dx.doi.org/10.1021/es9909632.

Migliavacca, G., Morreale, C., Hugony, F., Tombolato, I., Pession, G., 2014. Reduction of PM emissions from biomass combustion appliances: evaluation of efficiency of electrostatic precipitators. Chem. Eng. Trans. 37, 25–30. http://dx.doi.org/10.3303/CET1437005.

Milic, A., Miljevic, B., Alroe, J., Mallet, M., Canonaco, F., Prevot, A.S.H., Ristovski, Z.D., 2016. The ambient aerosol characterization during the prescribed bushfire season in Brisbane 2013. Sci. Total Environ. 560–561, 225–232. http://dx.doi.org/10.1016/j.scitotenv.2016.04.036.

Minguillón, M.C., Perron, N., Querol, X., Szidat, S., Fahrni, S.M., Alastuey, A., Jimenez, J.L., Mohr, C., Ortega, A.M., Day, D.A., Lanz, V.A., Wacker, L., Reche, C., Cusack, M., Amato, F., Kiss, G., Hoffer, A., Decesari, S., Moretti, F., Hillamo, R., Teinilä, K., Seco, R., Peñuelas, J., Metzger, A., Schallhart, S., Müller, M., Hansel, A., Burkhart, J.F., Baltensperger, U., Prévót, A.S.H., 2011. Fossil versus contemporary sources of fine elemental and organic carbonaceous particulate matter during the DAURE campaign in Northeast Spain. Atmos. Chem. Phys. 11, 12067–12084. http://dx.doi.org/10.5194/acp-11-12067-2011.

Miranda, T., Montero, I., Sepúlveda, F.J., Arranz, J.I., Rojas, C.V., Nogales, S., 2015. A review of pellets from different sources. Materials (Basel) 8, 1413–1427. http://dx.doi.org/10.3390/ma8041413.

Mitchell, E.J.S., Lea-Langton, A.R., Jones, J.M., Williams, A., Layden, P., Johnson, R., 2016. The impact of fuel properties on the emissions from the combustion of biomass and other solid fuels in a fixed bed domestic stove. Fuel Process. Technol. 142, 115–123. http://dx.doi.org/10.1016/j.fuproc.2015.09.031.

Mochida, M., Kawamura, K., Fu, P., Takemura, T., 2010. Seasonal variation of levoglucosan in aerosols over the western North Pacific and its assessment as a biomass burning tracer. Atmos. Environ. 44, 3511-3518. http://dx.doi.org/10.1016/j.atmosenv.2010.06.017.

Mohr, C., DeCarlo, P.F., Heringa, M.F., Chirico, R., Slowik, J.G., Richter, R., Reche, C., Alastuey, A., Querol, X., Seco, R., Peñuelas, J., Jiménez, J.L., Crippa, M., Zimmermann, R., Baltensperger, U., Prévôt, A.S.H., 2012. Identification and quantification of organic aerosol from cooking and other sources in Barcelona using aerosol mass spectrometer data. Atmos. Chem. Phys. 12, 1649–1665. http://dx.doi.org/10.5194/acp-12-1649-2012.

Mohr, C., Lopez-Hilfiker, F.D., Zotter, P., Prévôt, A.S.H., Xu, L., Ng, N.L., Herndon, S.C., Williams, L.R., Franklin, J.P., Zahniser, M.S., Worsnop, D.R., Knighton, W.B., Aiken, A.C., Gorkowski, K.J., Dubey, M.K., Allan, J.D., Thornton, J.A., 2013. Contribution of nitrated phenols to wood burning brown carbon light absorption in Detling, United Kingdom during winter time. Environ. Sci. Technol. 47, 6316–6324.

Molnár, P., Sallsten, G., 2013. Contribution to $PM_{2.5}$ from domestic wood burning in a small community in Sweden. Environ. Sci.: Processes Impacts 15, 833. http://dx.doi.org/10.1039/c3em30864b.

Monteiro, E., Mantha, V., Rouboa, A., 2012. Portuguese pellets market: analysis of the production and utilization constrains. Energ. Policy 42, 129 135. http://dx.doi.org/10.1016/j.enpol.2011.11.056.

Moon, K.J., Han, J.S., Ghim, Y.S., Kim, Y.J., 2008. Source apportionment of fine carbonaceous particles by positive matrix factorization at Gosan background site in East Asia. Environ. Int. 34, 654–664. http://dx.doi.org/10.1016/j.envint.2007.12.021.

Naeher, L.P., Brauer, M., Lipsett, M., Zelikoff, J.T., Simpson, C.D., Koenig, J.Q., Smith, K.R., 2007. Woodsmoke health effects: a review. Inhal. Toxicol. 19, 67–106. http://dx.doi.org/10.1080/08958370600985875.

Naeher, L.P., Barr, D.B., Adetona, O., Simpson, C.D., 2013. Urinary levoglucosan as a biomarker for woodsmoke exposure in wildland firefighters. Int. J. Occup. Environ. Health 19, 304–310. http://dx.doi.org/10.1179/2049396713Y.0000000037.

Nava, S., Lucarelli, F., Amato, F., Becagli, S., Calzolai, G., Chiari, M., Giannoni, M., Traversi, R., Udisti, R., 2015. Biomass burning contributions estimated by synergistic coupling of daily and hourly aerosol composition records. Sci. Total Environ. 511, 11–20. http://dx.doi.org/10.1016/j.scitotenv.2014.11.034.

Net, S., Alvarez, E.G., Gligorovski, S., Wortham, H., 2011. Heterogeneous reactions of ozone with methoxyphenols, in presence and absence of light. Atmos. Environ. 45, 3007–3014. http://dx.doi.org/10.1016/j.atmosenv.2011.03.026.

NILU, 2011. Deliverable D2.2.1: source apportionment using receptor modelling: intercomparison across cities and between methodologies. In: TRANSPHORM - Transport related Air Pollution and Health impacts – Integrated Methodologies for Assessing Particulate Matter. 7th Framework Programme. ENV.2009.1.2.2.1. ISBN: 978-82- 425.

Nolte, C.G., Schauer, J.J., Cass, G.R., Simoneit, B.R.T., 2001. Highly polar organic compounds present in wood smoke and in the ambient atmosphere. Environ. Sci. Technol. 35, 1912–1919. http://dx.doi.org/10.1021/es001420r.

Nussbaumer, T., Lauber, A., 2010. Formation mechanisms and physical properties of particles from wood combustion for design and operation of electrostatic precipitators. In: 18th European Biomass Conference and Exhibition, 3–7 May, Lyon, France.

Nussbaumer, T., Czasch, C., Klippel, N., Johansson, L., Tullin, C., 2008a. Particulate emissions from biomass combustion in IEA countries survey on measurements and emission factors. In: International Energy Agency Bioenergy Task 32, Zürich, Switzerland. ISBN 3-908705-18-5.

Nussbaumer, T., Doberer, A., Klippel, N., Bühler, R., Vock, W., 2008. Influence of ignition and operation type on particle emissions from residential wood combustion. In: 16th European Biomass Conference and Exhibition. Valencia, Spain, pp. 2–6.

Nuutinen, K., Jokiniemi, J., Sippula, O., Lamberg, H., Sutinen, J., Horttanainen, P., Tissari, J., 2014. Effect of air staging on fine particle, dust and gaseous emissions from masonry heaters. Biomass Bioenergy 67, 167–178. http://dx.doi.org/10.1016/j.biombioe.2014.04.033.

Oanh, N.T.K., Nghiem, L.H., Phyu, Y.L., 2002. Emission of polycyclic aromatic hydrocarbons, toxicity, and mutagenicity from domestic cooking using sawdust briquettes, wood, and kerosene. Environ. Sci. Technol. 36, 833–839. http://dx.doi.org/10.1021/es011060n.

Obaidullah, M., Bram, S., Verma, V.K., Ruyck, J. De, 2012. A review on particle emissions from small scale biomass combustion. Int. J. Renew. Energy Res. 2, 147–159.

Obernberger, I., Thek, G., 2004. Physical characterisation and chemical composition of densified biomass fuels with regard to their combustion behaviour. Biomass Bioenergy 27, 653–669. http://dx.doi.org/10.1016/j.biombioe.2003.07.006.

Öhman, M., Boström, D., Nordin, A., Hedman, H., 2004. Effect of kaolin and limestone addition on slag formation during combustion of wood fuels. Energ. Fuel. 18, 1370–1376. http://dx.doi.org/10.1021/ef040025+.

Olsson, M., 2006. Wheat straw and peat for fuel pellets-organic compounds from combustion. Biomass Bioenergy 30, 555–564. http://dx.doi.org/10.1016/j.biombioe.2006.01.005.

Orasche, J., Seidel, T., Hartmann, H., Schnelle-Kreis, J., Chow, J.C., Ruppert, H., Zimmermann, R., 2012. Comparison of emissions from wood combustion. Part 1: emission factors and characteristics from different small-scale residential heating appliances considering particulate matter and polycyclic aromatic hydrocarbon (PAH)-related toxicological potential. Energ. Fuel. 26, 6695–6704. http://dx.doi.org/10.1021/ef301295k.

Orasche, J., Schnelle-Kreis, J., Schön, C., Hartmann, H., Ruppert, H., Arteaga-Salas, J.M., Zimmermann, R., 2013. Comparison of emissions from wood combustion. Part 2: impact of combustion conditions on emission factors and characteristics of particlebound organic species and polycyclic aromatic hydrocarbon (PAH)-related toxicological potential. Energ. Fuel. 27, 1482–1491. http://dx.doi.org/10.1021/ef301506h.

Ortega, A.M., Day, D.A., Cubison, M.J., Brune, W.H., Bon, D., de Gouw, J.A., Jimenez, J.L., 2013. Secondary organic aerosol formation and primary organic aerosol oxidation from biomass-burning smoke in a flow reactor during FLAME-3. Atmos. Chem. Phys. 13, 11551–11571. http://dx.doi.org/10.5194/acp-13-11551-2013.

Ozgen, S., Cernuschi, S., Giugliano, M., 2013. Experimental evaluation of particle number emissions from wood combustion in a closed fireplace. Biomass Bioenergy 50, 65–74. http://dx.doi.org/10.1016/j.biombioe.2013.01.015.

Ozgen, S., Caserini, S., Galante, S., Giugliano, M., Angelino, E., Marongiu, A., Hugony, F., Migliavacca, G., Morreale, C., 2014. Emission factors from small scale appliances burning wood and pellets. Atmos. Environ. 94, 144–153. http://dx.doi.org/10.1016/j.atmosenv.2014.05.032.

Pagels, J., Dutcher, D.D., Stolzenburg, M.R., Mcmurry, P.H., Gälli, M.E., Gross, D.S., 2013. Fine-particle emissions from solid biofuel combustion studied with single particle mass spectrometry: identification of markers for organics, soot, and ash components. J. Geophys. Res. Atmos. 118, 859–870. http://dx.doi.org/10.1029/2012JD018389.

Pashynska, V., Vermeylen, R., Vas, G., Maenhaut, W., Claeys, M., 2002. Development of a gas chromatographic/ion trap mass spectrometric method for the determination of levoglucosan and saccharidic compounds in atmospheric aerosols. Application to urban aerosols. J. Mass Spectrom. 37, 1249–1257. http://dx.doi.org/10.1002/jms.391.

Pedersen, D.U., Durant, J.L., Penman, B.W., Crespi, C.L., Hemond, H.F., Lafleur, A.L., Cass, G.R., 2004. Human-cell mutagens in respirable airborne particles in the northeastern United States. 1. Mutagenicity of fractionated samples. Environ. Sci. Technol. 38, 682–689. http://dx.doi.org/10.1021/es0347282.

Peng, G., Roberts, J.C., 2000. Solubility and toxicity of resin acids. Water Res. 34, 2779 2785. http://dx.doi.org/10.1016/S0043-1354(99)00406-6.

Perrone, M.G., Larsen, B.R., Ferrero, L., Sangiorgi, G., De Gennaro, G., Udisti, R., Zangrando, R., Gambaro, A., Bolzacchini, E., 2012. Sources of high $PM_{2.5}$ concentrations in Milan, northern Italy: molecular marker data and CMB modelling. Sci. Total Environ. 414, 343–355. http://dx.doi.org/10.1016/j.scitotenv.2011.11.026.

Pettersson, E., Boman, C., Westerholm, R., Boström, D., Nordin, A., 2011. Stove performance and emission characteristics in residential wood log and pellet combustion, Part 2: wood stove. Energ. Fuel. 25, 315–323. http://dx.doi.org/10.1021/ef1007787.

Petzold, A., Ogren, J.A., Fiebig, M., Laj, P., Li, S.-M., Baltensperger, U., Holzer-Popp, T., Kinne, S., Pappalardo, G., Sugimoto, N., Wehrli, C., Wiedensohler, A., Zhang, X.-Y., 2013. Recommendations for reporting “black carbon” measurements. Atmos. Chem. Phys. 13, 8365–8379. http://dx.doi.org/10.5194/acp-13-8365-2013.

Piazzalunga, A., Fermo, P., Bernardoni, V., Vecchi, R., Valli, G., De Gregorio, M.A., 2010. A simplified method for levoglucosan quantification in winter time atmospheric particulate matter by high performance anion-exchange chromatography coupled with pulsed amperometric detection. Int. J. Environ. Anal. Chem. 90, 934–947. http://dx.doi.org/10.1080/03067310903023619.

Pietrogrande, M.C., Bacco, D., Ferrari, S., Kaipainen, J., Ricciardelli, I., Riekkola, M.L., Trentini, A., Visentin, M., 2015. Characterization of atmospheric aerosols in the Po Valley during the supersite campaigns – part 3: contribution of wood combustion to wintertime atmospheric aerosols in Emilia Romagna región (northern Italy). Atmos. Environ. 122, 291–305.

Pio, C.A., Legrand, M., Oliveira, T., Afonso, J., Santos, C., Caseiro, A., Fialho, P., Barata, F., Puxbaum, H., Sanchez-Ochoa, A., Kasper-Giebl, A., Gelencsér, A., Preunkert, S., Schock, M., 2007. Climatology of aerosol composition (organic versus inorganic) at nonurban sites on a west-east transect across Europe. J. Geophys. Res. Atmos. 112, 1–15. http://dx.doi.org/10.1029/2006JD008038.

Pöschl, U., 2005. Atmospheric aerosols: composition, transformation, climate and health effects. Angew. Chem. Int. Ed. 44, 7520–7540. http://dx.doi.org/10.1002/anie.200501122.

Purvis, C.R., McCrillis, R.C., Kariher, P.H., 2000. Fine Particulate Matter (PM) and organic speciation of fireplace emissions. Environ. Sci. Technol. 34, 1653–1658. http://dx.doi.org/10.1021/ES981006F.

Puxbaum, H., Caseiro, A., Sánchez-Ochoa, A., Kasper-Giebl, A., Claeys, M., Gelencsér, A., Legrand, M., Preunkert, S., Pio, C.A., 2007. Levoglucosan levels at background sites in Europe for assessing the impact of biomass combustion on the European aerosol background. J. Geophys. Res. Atmos. 112, 1–11. http://dx.doi.org/10.1029/2006JD008114.

Querol, X., 2014. El problema de la cadidad del aire urbano. ASGECO, Madrid, Spain 13 Feb.

Querol, X., Alastuey, A., Moreno, T., Viana, M.M., Castillo, S., Pey, J., Rodríguez, S., Artiñano, B., Salvador, P., Sánchez, M., Garcia Dos Santos, S., Herce Garraleta, M.D., Fernandez Patier, R., Moreno-Grau, S., Negral, L., Minguillón, M.C., Monfort, E., Sanz, M.J., Palomo-Marín, R., Pinilla-Gil, E., Cuevas, E., de la Rosa, J., Sánchez de la Campa, A., 2008. Spatial and temporal variations in airborne particulate matter (PM_{10} and $PM_{2.5}$) across Spain 1999-2005. Atmos. Environ. 42, 3964–3979. http://dx.doi.org/10.1016/j.atmosenv.2006.10.071.

Querol, X., Alastuey, A., Viana, M., Moreno, T., Reche, C., Minguillón, M.C., Ripoll, A., Pandolfi, M., Amato, F., Karanasiou, A., Pérez, N., Pey, J., Cusack, M., Vázquez, R., Plana, F., Dall'Osto, M., de la Rosa, J., Sánchez de la Campa, A., Fernández-Camacho, R., Rodríguez, S., Pio, C., Alados-Arboledas, L., Titos, G., Artíñano, B., Salvador, P., García Dos Santos, S., Fernández Patier, R., 2013. Variability of carbonaceous aerosols in remote, rural, urban and industrial environments in Spain: implications for air quality policy. Atmos. Chem. Phys. 13, 6185–6206.http://dx.doi.org/10.5194/acp-13-6185-2013.

Ramdahl, T., 1983. Retene - a molecular marker of wood combustion in ambient air. Nature 306, 580–582. http://dx.doi.org/10.1038/306580a0.

Reche, C., Viana, M., Amato, F., Alastuey, A., Moreno, T., Hillamo, R., Teinilä, K., Saarnio, K., Seco, R., Peñuelas, J., Mohr, C., Prévôt, A.S.H., Querol, X., 2012. Biomass burning contributions to urban aerosols in a coastal Mediterranean City. Sci. Total Environ. 427-428, 175–190. http://dx.doi.org/10.1016/j.scitotenv.2012.04.012.

Reisen, F., Meyer, C.P. (Mick), Keywood, M.D., 2013. Impact of biomass burning sources on seasonal aerosol air quality. Atmos. Environ. 67, 437 447. http://dx.doi.org/10.1016/j.atmosenv.2012.11.004.

Ricard, V., Jaffrezo, J.-L., Kerminen, V.-M., Hillamo, R.E., Sillanpaa, M., Ruellan, S., Liousse, C., Cachier, H., 2002. Two years of continuous aerosol measurements in northern Finland. J. Geophys. Res. 107, 1–17. http://dx.doi.org/10.1029/2001JD000952.

Rigol, A., Lacorte, S., Barceló, D., 2003. Sample handling and analytical protocols for analysis of resin acids in process waters and effluents from pulp and paper mills. TrAC Trends Anal. Chem. 22, 738–749. http://dx.doi.org/10.1016/S0165-9936(03)01011-2.

Riva, G., Pedretti, E.F., Toscano, G., Duca, D., Pizzi, A., 2011. Determination of polycyclic aromatic hydrocarbons in domestic pellet stove emissions. Biomass Bioenergy 35, 4261–4267. http://dx.doi.org/10.1016/j.biombioe.2011.07.014.

Rogge, W.F., Hildemann, L.M., Mazurek, M.a., Cass, G.R., 1998. Sources of fine organic aerosol. 9. Pine, oak, and synthetic log combustion in residential fireplaces. Environ. Sci. Technol. 32, 13–22. http://dx.doi.org/10.1021/es960930b.

Rohr, A.C., Habre, R., Godbold, J., Moshier, E., Schachter, N., Kattan, M., Grunin, A., Nath, A., Coull, B., Koutrakis, P., 2014. Asthma exacerbation is associated with particulate matter source factors in children in New York City. Air Qual. Atmos. Health 7, 239–250. http://dx.doi.org/10.1007/s11869-0130230-y.

Roy, A., Hu, W., Wei, F., Korn, L., Chapman, R.S., Zhang, J., 2012. Ambient particulate matter and lung function growth in Chinese children. Epidemiology 23, 464–472. http://dx.doi.org/10.1016/j.pestbp.2011.02.012.Investigations.

Rylance, J., Gordon, S.B., Naeher, L.P., Patel, A., Balmes, J.R., Adetona, O., Rogalsky, D.K., Martin, W.J., 2013. Household air pollution: a call for studies into biomarkers of exposure and predictors of respiratory disease. AJP Lung Cell. Mol. Physiol. 304, L571–L578. http://dx.doi.org/10.1152/ajplung.00416.2012.

Saarikoski, S., Timonen, H., Saarnio, K., Aurela, M., Järvi, L., Keronen, P., Kerminen, V.- M., Hillamo, R., 2008. Sources of organic carbon in fine particulate matter in northern European urban air. Atmos. Chem. Phys. 8, 6281–6295. http://dx.doi.org/10.5194/acp-8-6281-2008.

Saarnio, K., Teinilä, K., Aurela, M., Timonen, H., Hillamo, R., 2010. High-performance anion exchange chromatography-mass spectrometry method for determination of levoglucosan, mannosan, and galactosan in atmospheric fine particulate matter. Anal. Bioanal. Chem. 398, 2253–2264. http://dx.doi.org/10.1007/s00216-010-4151-4.

Saffari, A., Daher, N., Samara, C., Voutsa, D., Kouras, A., Manoli, E., Karagkiozidou, O., Vlachokostas, C., Moussiopoulos, N., Shafer, M.M., Schauer, J.J., Sioutas, C., 2013. Increased biomass burning due to the economic crisis in Greece and its adverse impact on wintertime air quality in Thessaloniki. Environ. Sci. Technol. 47, 13313–13320. http://dx.doi.org/10.1021/es403847h.

Saint-Jalm, Y., 1981. Qualitative analysis of the hydroxyl fraction of cigarette smoke. Ann Tabac. Sect. 18, 41–48.

Saleh, R., Hennigan, C.J., McMeeking, G.R., Chuang, W.K., Robinson, E.S., Coe, H., Donahue, N.M., Robinson, A.L., 2013. Absorptivity of brown carbon in fresh and photo-chemically aged biomass-burning emissions. Atmos. Chem. Phys. 13, 7683–7693. http://dx.doi.org/10.5194/acp-13-7683-2013.

Saleh, R., Robinson, E.S., Tkacik, D.S., Ahern, A.T., Liu, S., Aiken, A.C., Sullivan, R.C., Presto, A.A., Dubey, M.K., Yokelson, R.J., Donahue, N.M., Robinson, A.L., 2014. Brownness of organics in aerosols from biomass burning linked to their black carbon content. Nat. Geosci. 7, 647–650. http://dx.doi.org/10.1038/ngeo2220.

Salvador, P., Artíñano, B., Viana, M.M., Querol, X., Alastuey, A., González-Fernández, I., Alonsoa, R., 2011. Spatial and temporal variations in PM_{10} and $PM_{2.5}$ across Madrid metropolitan area in 1999–2008. Procedia Environ. Sci. 4, 198–208. http://dx.doi.org/10.1016/j.proenv.2011.03.024.

Samet, J.M., Dominici, F., Curriero, F.C., Coursac, I., Zeger, S.L., 2000. Fine particulate air pollution and mortality in 20 U.S. cities, 1987–1994. N. Engl. J. Med. 343, 1742–1749. http://dx.doi.org/10.1056/NEJMoa012295.

Sankaranarayanan, L., Semmens, E.O., Noonan, C.W., Ward, T.J., 2016. Urinary levoglucosan as a biomarker for residential wood smoke exposure. Int. J. Environ. Anal. Chem. 96, 137–147. http://dx.doi.org/10.1080/03067319.2015.1137906.

Santoso, M., Hopke, P.K., Hidayat, A., Diah, Dwiana L., 2008. Sources identification of the atmospheric aerosol at urban and suburban sites in Indonesia by positive matrix factorization. Sci. Total Environ. 397, 229–237. http://dx.doi.org/10.1016/j.scitotenv.2008.01.057.

Schauer, J.J., Kleeman, M.J., Cass, G.R., Simoneit, B.R.T., 2001. Measurement of emissions from air organic compounds from fireplace combustion of wood. Environ. Sci. Technol. 35, 1716–1728.

Schkolnik, G., Rudich, Y., 2006. Detection and quantification of levoglucosan in atmospheric aerosols: a review. Anal. Bioanal. Chem. 385, 26–33. http://dx.doi.org/10.1007/s00216-005-0168-5.

Schmidl, C., Marra, I.L., Caseiroa, A., Kotianová, P., Berner, A., Bauer, H., Kasper Giebl, A., Puxbaum, H., 2008. Chemical characterisation of fine particle emissions from wood stove combustion of common woods growing in mid-European Alpine regions. Atmos. Environ. 42, 126–141.

Schmidl, C., Luisser, M., Padouvas, E., Lasselsberger, L., Rzaca, M., Ramirez-Santa Cruz, C., Handler, M., Peng, G., Bauer, H., Puxbaum, H., 2011. Particulate and gaseous emissions from manually and automatically fired small scale combustion systems. Atmos. Environ. 45, 7443–7454. http://dx.doi.org/10.1016/j.atmosenv.2011.05.006.

Schwarz, J., Cusack, M., Karban, J., Chalupnícková, E., Havránek, V., Smolík, J., Zdímal, V., 2016. $PM_{2.5}$ chemical composition at a rural background site in Central Europe, including correlation and air mass trajectory analysis. Atmos. Res. 176–177, 108–120.

Shen, G., Yang, Y., Wang, B.I.N., Wang, R., Russell, A.G., 2010. Emission factors of particulate matter and elemental carbon for crop residues and coals burned in typical household stoves in China. Environ. Sci. Technol. 44, 7157–7162.

Shen, G., Tao, S., Wei, S., Zhang, Y., Wang, R., Wang, B., Li, W., Shen, H., Huang, Y., Yang, Y., Wang, W., Wang, X., Simonich, S.L.M., 2012. Retene emission from residential solid fuels in China and evaluation of retene as a unique marker for soft wood combustion. Environ. Sci. Technol. 46, 4666-4672. http://dx.doi.org/10.1021/es300144m.

Shen, G., Xue, M., Wei, S., Chen, Y., Wang, B., Wang, R., Lv, Y., Shen, H., Li, W., Zhang, Y., Huang, Y., Chen, H., Wei, W., Zhao, Q., Li, B., Wu, H., TAO, S., 2013a. The influence of fuel moisture, charge size, burning rate and air ventilation conditions on emissions of PM, OC, EC, parent PAHs, and their derivatives from residential wood combustion. J. Environ. Sci. 25, 1808–1816. http://dx.doi.org/10.1124/dmd.107.016501.CYP3A4-Mediated.

Shen, G., Xue, M., Wei, S., Chen, Y., Wang, B., Wang, R., Shen, H., Li, W., Zhang, Y., Huang, Y., Chen, H., Wei, W., Zhao, Q., Li, B., Wu, H., Tao, S., 2013b. Influence of fuel mass load, oxygen supply and burning rate on emission factor and size distribution of carbonaceous particulate matter from indoor corn straw burning. J. Environ. Sci. 25, 511–519. http://dx.doi.org/10.1016/S1001-0742(12)60191-0.

Sigsgaard, T., Forsberg, B., Annesi-Maesano, I., Blomberg, A., Bølling, A., Boman, C., Bønløkke, J., Brauer, M., Bruce, N., Héroux, M.-E., Hirvonen, M.-R., Kelly, F., Künzli, N., Lundbäck, B., Moshammer, H., Noonan, C., Pagels, J., Sallsten, G., Sculier, J.-P., Brunekreef, B., 2015. Health impacts of anthropogenic biomass burning in the developed world. Eur. Respir. J. 46, 1577–1588. http://dx.doi.org/10.1183/13993003.01865-2014.

Sillanpää, M., Frey, A., Hillamo, R., Pennanen, A.S., Salonen, R.O., 2005. Organic, elemental and inorganic carbon in particulate matter of six urban environments in Europe. Atmos. Chem. Phys. 5, 2869–2879. http://dx.doi.org/10.5194/acpd-5-2719-2005.

Simoneit, B.R., 2002. Biomass burning — a review of organic tracers for smoke from incomplete combustion. Appl. Geochem. http://dx.doi.org/10.1016/S0883-2927(01)00061-0.

Simoneit, B.R.T., Schauer, J.J., Nolte, C.G., Oros, D.R., Elias, V.O., Fraser, M.P., Rogge, W.F., Cass, G.R., 1999. Levoglucosan, a tracer for cellulose in biomass burning and atmospheric particles. Atmos. Environ. 33, 173–182. http://dx.doi.org/10.1016/S1352-2310(98)00145-9.

Simpson, C.D., Paulsen, M., Dills, R.L., Liu, L.J.S., Kalman, D.A., 2005. Determination of methoxyphenols in ambient atmospheric particulate matter: tracers for wood combustion. Environ. Sci. Technol. 39, 631–637. http://dx.doi.org/10.1021/es0486871.

Sippula, O., Hytönen, K., Tissari, J., Raunemaa, T., Jokiniemi, J., 2007. Effect of wood fuel on the emissions from a top-feed pellet stove. Energ. Fuel. 21, 1151–1160. http://dx.doi.org/10.1021/ef060286e.

Sippula, O., Hokkinen, J., Puustinen, H., Yli-Pirilä, P., Jokiniemi, J., 2009a. Particle emissions from small wood-fired district heating units. Energy Fuel 23, 2974–2982. http://dx.doi.org/10.1021/ef900098v.

Sippula, O., Hokkinen, J., Puustinen, H., Yli-Pirilä, P., Jokiniemi, J., 2009b. Comparison of particle emissions from small heavy fuel oil and wood-fired boilers. Atmos. Environ. 43, 4855–4864. http://dx.doi.org/10.1016/j.atmosenv.2009.07.022.

Slade, J.H., Knopf, D.A., 2014. Multiphase OH oxidation kinetics of organic aerosol: the role of particle phase state and relative humidity. Geophys. Res. Lett. 41, 5297–5306. http://dx.doi.org/10.1002/2014GL060582.

Song, Y., Zhang, Y., Xie, S., Zeng, L., Zheng, M., Salmon, L.G., Shao, M., Slanina, S., 2006. Source apportionment of $PM_{2.5}$ in Beijing by positive matrix factorization. Atmos. Environ. 40, 1526–1537. http://dx.doi.org/10.1016/j.atmosenv.2005.10.039.

Srimuruganandam, B., Nagendra, S.M.S., 2012. Application of positive matrix factorization in characterization of PM_{10} and $PM_{2.5}$ emission sources at urban roadside. Chemosphere 88, 120–130. http://dx.doi.org/10.1016/j.chemosphere.2012.02.083.

Szidat, S., Jenk, T.M., Synal, H.A., Kalberer, M., Wacker, L., Hajdas, I., Kasper-Giebl, A., Baltensperger, U., 2006. Contributions of fossil fuel, biomass-burning, and biogenic emissions to carbonaceous aerosols in Zurich as traced by ^{14}C. J. Geophys. Res. Atmos. 111, 1–12. http://dx.doi.org/10.1029/2005JD006590.

Szidat, S., Prévôt, A.S.H., Sandradewi, J., Alfarra, M.R., Synal, H.A., Wacker, L., Baltensperger, U., 2007. Dominant impact of residential wood burning on particulate matter in Alpine valleys during winter. Geophys. Res. Lett. 34, 1–6. http://dx.doi.org/10.1029/2006GL028325.

Szidat, S., Ruff, M., Perron, N., Wacker, L., Synal, H.-A., Hallquist, M., Shannigrahi, A.S., Yttri, K.E., Dye, C., Simpson, D., 2009. Fossil and non-fossil sources of organic carbon (OC) and elemental carbon (EC) in Göteborg, Sweden. Atmos. Chem. Phys. 9, 1521–1535. http://dx.doi.org/10.5194/acp-9-15212009.

Tao, J., Gao, J., Zhang, L., Zhang, R., Che, H., Zhang, Z., Lin, Z., Jing, J., Cao, J., Hsu, S.- C., 2014. $PM_{2.5}$ pollution in a megacity of southwest China: source apportionment and implication. Atmos. Chem. Phys. 14, 8679–8699. http://dx.doi.org/10.5194/acp-14-8679-2014.

Tissari, J., Hytönen, K., Lyyränen, J., Jokiniemi, J., 2007. A novel field measurement method for determining fine particle and gas emissions from residential wood combustion. Atmos. Environ. 41, 8330–8344. http://dx.doi.org/10.1016/j.atmosenv.2007.06.018.

Tissari, J., Lyyränen, J., Hytönen, K., Sippula, O., Tapper, U., Frey, A., Saarnio, K., Pennanen, A.S., Hillamo, R., Salonen, R.O., Hirvonen, M.-R., Jokiniemi, J., 2008a. Fine particle and gaseous emissions from normal and smouldering wood combustion in a conventional masonry heater. Atmos. Environ. 42, 7862–7873. http://dx.doi.org/10.1016/j.atmosenv.2008.07.019.

Tissari, J., Sippula, O., Kouki, J., Vuorio, K., Jokiniemi, J., 2008b. Fine particle and gas emissions from the combustion of agricultural fuels fired in a 20 kW burner. Energ. Fuel. 22, 2033–2042. http://dx.doi.org/10.1021/ef700766y.

Tissari, J., Hytönen, K., Sippula, O., Jokiniemi, J., 2009. The effects of operating conditions on emissions from masonry heaters and sauna stoves. Biomass Bioenergy 33, 513–520. http://dx.doi.org/10.1016/j.biombioe.2008.08.009.

Titos, G., del Águila, A., Cazorla, A., Lyamani, H., Casquero-Vera, J.A., Colombi, C., Cuccia, E., Gianelle, V., Mo, G., Alastuey, A., Olmo, F.J., Alados-Arboledas, L., 2017. Spatial and temporal variability of carbonaceous aerosols: assessing the impact of biomass burning in the urban environment. Sci. Total Environ. 578, 613–625.

Torvela, T., Tissari, J., Sippula, O., Kaivosoja, T., Leskinen, J., Virén, A., Lähde, A., Jokiniemi, J., 2014. Effect of wood combustion conditions on the morphology of freshly emitted fine particles. Atmos. Environ. 87, 65–76. http://dx.doi.org/10.1016/j.atmosenv.2014.01.028.

Toscano, G., Duca, D., Amato, A., Pizzi, A., 2014. Emission from realistic utilization of wood pellet stove. Energy 68, 644–650. http://dx.doi.org/10.1016/j.energy.2014.01.108.

Vassura, I., Venturini, E., Marchetti, S., Piazzalunga, A., Bernardi, E., Fermo, P., Passarini, F., 2014. Markers and influence of open biomass burning on atmospheric particulate size and composition during a major bonfire event. Atmos. Environ. 82, 218–225.

Verma, V.K., Bram, S., Gauthier, G., De Ruyck, J., 2011. Performance of a domestic pellet boiler as a function of operational loads: Part-2. Biomass Bioenergy 35, 272–279. http://dx.doi.org/10.1016/j.biombioe.2010.08.043.

Verma, V.K., Bram, S., Delattin, F., Laha, P., Vandendael, I., Hubin, A., De Ruyck, J., 2012. Agro-pellets for domestic heating boilers: standard laboratory and real life performance. Appl. Energy 90, 17–23. http://dx.doi.org/10.1016/j.apenergy.2010.12.079.

Verma, V.K., Bram, S., Delattin, F., De Ruyck, J., 2013. Real life performance of domestic pellet boiler technologies as a function of operational loads: a case study of Belgium. Appl. Energy 101, 357–362. http://dx.doi.org/10.1016/j.apenergy.2012.02.017.

Viana, M., Reche, C., Amato, F., Alastuey, A., Querol, X., Moreno, T., Lucarelli, F., Nava, S., Calzolai, G., Chiari, M., Rico, M., 2013. Evidence of biomass burning aerosols in the Barcelona urban environment during winter time. Atmos. Environ. 72, 81–88. http://dx.doi.org/10.1016/j.atmosenv.2013.02.031.

Vicente, E.D., Duarte, M.A., Calvo, A.I., Nunes, T.F., Tarelho, L.A.C., Custódio, D., Colombi, C., Gianelle, V., Sanchez de la Campa, A., Alves, C.A., 2015a. Influence of operating conditions on chemical composition of particulate matter emissions from residential combustion. Atmos. Res. 166, 92–100. http://dx.doi.org/10.1016/j.atmosres.2015.06.016.

Vicente, E.D., Duarte, M.A., Calvo, A.I., Nunes, T.F., Tarelho, L., Alves, C.A., 2015b. Emission of carbon monoxide, total hydrocarbons and particulate matter during wood combustion in a stove operating under distinct conditions. Fuel Process. Technol. 131, 182–192. http://dx.doi.org/10.1016/j.fuproc.2014.11.021.

Vicente, E.D., Duarte, M.A., Tarelho, L.A.C., Nunes, T.F., Amato, F., Querol, X., Colombi, C., Gianelle, V., Alves, C.A., 2015c. Particulate and gaseous emissions from the combustion of different biofuels in a pellet stove. Atmos. Environ. 120, 15–27. http://dx.doi.org/10.1016/j.atmosenv.2015.08.067.

Vicente, E.D., Vicente, A.M., Musa Bandowe, B.A., Alves, C.A., 2016. Particulate phase emission of parent polycyclic aromatic hydrocarbons (PAHs) and their derivatives (alkyl PAHs, oxygenated-PAHs, azaarenes and nitrated PAHs) from manually and automatically fired combustion appliances. Air Qual. Atmos. Health 9, 653–668. http://dx.doi.org/10.1007/s11869-015-0364-1.

Viidanoja, J., Kerminen, V.M., Hillamo, R., 2002. Measuring the size distribution of atmospheric organic and black carbon using impactor sampling coupled with thermal carbon analysis: method development and uncertainties. Aerosol Sci. Technol. 36, 607–616. http://dx.doi.org/10.1080/02786820252883847.

Vu, B., Alves, C.A., Gonçalves, C., Pio, C., Gonçalves, F., Pereira, R., 2012. Mutagenicity assessment of aerosols in emissions from wood combustion in Portugal. Environ. Pollut. 166, 172–181. http://dx.doi.org/10.1016/j.envpol.2012.03.005.

Wagener, S., Langner, M., Hansen, U., Moriske, H.J., Endlicher, W.R., 2012. Source apportionment of organic compounds in Berlin using positive matrix factorization-assessing the impact of biogenic aerosol and biomass burning on urban particulate matter. Sci. Total Environ. 435-436, 392–401. http://dx.doi.org/10.1016/j.scitotenv.2012.07.039.

Waked, A., Favez, O., Alleman, L.Y., Piot, C., Petit, J.-E., Delaunay, T., Verlinden, E., Golly, B., Besombes, J.-L., Jaffrezo, J.-L., Leoz-Garziandia, E., 2014. Source apportionment of PM_{10} in a north-western Europe regional urban background site (Lens, France) using positive matrix factorization and including primary biogenic emissions. Atmos. Chem. Phys. 14, 3325–3346. http://dx.doi.org/10.5194/acp-14-3325-2014.

Wallner, P., Kundi, M., Moshammer, H., Scharf, S., Schmutzer, M., Weiss, S., Hohenblum, P., Hutter, H.-P., 2013. Urinary levoglucosan levels in Austrian communities differing in agrarian quota. Int. J. Hyg. Environ. Health 216, 280–283. http://dx.doi.org/10.1016/j.ijheh.2012.05.001.

Wang, Y., Hopke, P.K., 2013. A ten–year source apportionment study of ambient fine particulate matter in San Jose, California. Atmos. Pollut. Res. 4, 398–404. http://dx.doi.org/10.5094/APR.2013.045.

Ward, T.J., Hamilton, R.F., Dixon, R.W., Paulsen, M., Simpson, C.D., 2006. Characterization and evaluation of smoke tracers in PM: results from the 2003 Montana wildfire season. Atmos. Environ. 40, 7005–7017. http://dx.doi.org/10.1016/j.atmosenv.2006.06.034.

Weimer, S., Alfarra, M.R., Schreiber, D., Mohr, M., Prévôt, A.S.H., Baltensperger, U., 2008. Organic aerosol mass spectral signatures from wood-burning emissions: influence of burning conditions and type. J. Geophys. Res. Atmos. 113, 1–10. http://dx.doi.org/10.1029/2007JD009309.

WHO, 2014. Burden of Disease from the Joint Effects of Household and Ambient Air Pollution for 2012. World Health Organization, Geneva, Switzerland.

WHO, 2015. Residential Heating with Wood and Coal: Health Impacts and Policy Options in Europe and North America. World Health Organization, Copenhagen, Denmark.

Wiinikka, H., 2005. High temperature aerosol formation and emission minimization during combustion of wood pellets. Dep. Appl. Phys. Mech. Eng. 196. http://dx.doi.org/10.1016/j.combustflame.2006.08.009.

Wiinikka, H., Grönberg, C., Boman, C., 2013. Emissions of heavy metals during fixed bed combustion of six biomass fuels. Energ. Fuel. 27, 1073-1080. http://dx.doi.org/10.1021/ef3011146.

Williams, P.T., Horne, P.A., 1994. The role of metal salts in the pyrolysis of biomass. Renew. Energy 4, 1–13. http://dx.doi.org/10.1016/09601481(94)90058-2.

Win, K.M., Persson, T., 2014. Emissions from residential wood pellet boilers and stove characterized into start-up, steady operation, and stop emissions. Energ. Fuel. 28, 2496–2505. http://dx.doi.org/10.1021/ef4016894.

Win, K.M., Persson, T., Bales, C., 2012. Particles and gaseous emissions from realistic operation of residential wood pellet heating systems. Atmos. Environ. 59, 320–327. http://dx.doi.org/10.1016/j.atmosenv.2012.05.016.

Wöhler, M., Jaeger, D., Reichert, G., Schmidl, C., Pelz, S.K., 2017. Influence of pellet length on performance of pellet room heaters under real life operation conditions. Renew. Energy 105, 66–75. http://dx.doi.org/10.1016/j.renene.2016.12.047.

Yatkin, S., Bayram, A., 2008. Source apportionment of PM_{10} and $PM_{2.5}$ using positive matrix factorization and chemical mass balance in Izmir, Turkey. Sci. Total Environ. 390, 109–123. http://dx.doi.org/10.1016/j.scitotenv.2007.08.059.

Yin, J., Harrison, R.M., Chen, Q., Rutter, A., Schauer, J.J., 2010. Source apportionment of fine particles at urban background and rural sites in the UK atmosphere. Atmos. Environ. 44, 841–851. http://dx.doi.org/10.1016/j.atmosenv.2009.11.026.

Yttri, K.E., Dye, C., Håvard Slørdal, L., Braathen, O.-A., 2005. Quantification of monosaccharide anhydrides by liquid chromatography combined with mass spectrometry: application to aerosol samples from an uand a suburban site influenced by small-scale wood burning. J. Air Waste Manage. Assoc. 55, 1169–1177. http://dx.doi.org/10.1080/10473289.2005.10464720.

Yttri, K.E., Aas, W., Bjerke, A., Cape, J.N., Cavalli, F., Ceburnis, D., Dye, C., Emblico, L., Facchini, M.C., Forster, C., Hanssen, J.E., Hansson, H.C., Jennings, S.G., Maenhaut, W., Putaud, J.P., Tørseth, K., 2007. Elemental and organic carbon in PM_{10}: a one year measurement campaign within the European Monitoring and Evaluation Programme EMEP. Atmos. Chem. Phys. 7, 5711–5725. http://dx.doi.org/10.5194/acp-7-5711-2007.

Yttri, K.E., Dye, C., Braathen, O.-A., Simpson, D., Steinnes, E., 2009. Carbonaceous aerosols in Norwegian urban areas. Atmos. Chem. Phys. 9, 2007–2020. http://dx.doi.org/10.5194/acp-9-2007-2009.

Yttri, K.E., Schnelle-Kreis, J., Maenhaut, W., Abbaszade, G., Alves, C., Bjerke, A., Bonnier, N., Bossi, R., Claeys, M., Dye, C., Evtyugina, M., García-Gacio, D., Hillamo, R., Hoffer, A., Hyder, M., Iinuma, Y., Jaffrezo, J.L., Kasper-Giebl, A., Kiss, G., López-Mahia, P.L., Pio, C., Piot, C., Ramirez-Santa-Cruz, C., Sciare, J., Teinilä, K., Vermeylen, R., Vicente, A., Zimmermann, R., 2015. An intercomparison study of analytical methods used for quantification of levoglucosan in ambient aerosol filter samples. Atmos. Meas. Tech. 8, 125–147. http://dx.doi.org/10.5194/amt-8-125-2015.

Yu, H.T., 2002. Environmental carcinogenic polycyclic aromatic hydrocarbons: photochemistry and phototoxicity. J. Environ. Sci. Heal. C 20, 149 183.

Yu, H., 2013. Environmental carcinogenic polycyclic aromatic hydrocarbons: photochemistry and phototoxicity. J. Environ. Sci. Health C Environ. Carcinog. Ecotoxicol. Rev. 20, 149–183. http://dx.doi.org/10.1081/GNC-120016203.

Zappoli, S., Andracchio, A., Fuzzi, S., Facchini, M.C., Gelencsér, A., Kiss, G., Krivácsy, Z., Molnár, A., Mészáros, E., Hansson, H.C., Rosman, K., Zebühr, Y., 1999. Inorganic, organic and macromolecular components of fine aerosol in different areas of Europe in relation to their water solubility. Atmos. Environ. 33, 2733–2743. http://dx.doi.org/10.1016/S1352-2310(98)00362-8.

Zdráhal, Z., Oliveira, J., Vermeylen, R., Claeys, M., Maenhaut, W., 2002. Improved method for quantifying levoglucosan and related monosaccharide anhydrides in atmospheric aerosols and application to samples from urban and tropical locations. Environ. Sci. Technol. 36, 747–753. http://dx.doi.org/10.1021/ES015619V.

Zhang, J., Smith, K.R., Ma, Y., Ye, S., Jiang, F., Qi, W., Liu, P., Khalil, M.A.K., Rasmussen, R.A., Thorneloe, S.A., 2000. Greenhouse gases and other airborne pollutants from household stoves in China: a database for emission factors. Atmos. Environ. 34, 4537–4549.

Zhang, X.L., Tao, S., Liu, W.X., Yang, Y., Zuo, Q., Liu, S.Z., 2005. Source diagnostics of polycyclic aromatic hydrocarbons based on species ratios: a multimedia approach. Environ. Sci. Technol. 39, 9109–9114. http://dx.doi.org/10.1021/es0513741.

Zhang, Y., Obrist, D., Zielinska, B., Gertler, A., 2013. Particulate emissions from different types of biomass burning. Atmos. Environ. 72, 27–35. http://dx.doi.org/10.1016/j.atmosenv.2013.02.026.

Zhang, Y.L., Schnelle-Kreis, J., Abbaszade, G., Zimmermann, R., Zotter, P., Shen, R.R., Schafer, K., Shao, L., Prévôt, A.S.H., Szidat, S., 2015. Source apportionment of elemental carbon in Beijing, China: insights from radiocarbon and organic marker measurements. Environ. Sci. Technol. 49, 8408–8415. http://dx.doi.org/10.1021/acs.est.5b01944.

CHAPTER 3

Chapter 3. Emissions from residential combustion of certified and uncertified pellets

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Abstract

The aim of the present study was to evaluate the relationship between fuel certification and gaseous and PM_{10} emissions and their composition. Two pellets labelled as ENplus A1 (certified pellets R and P) and a non-certified brand of pellets were tested in a pellet stove. The impact of operating conditions on emissions was also evaluated. The highest carbon monoxide (CO, 2.7-6.1-fold) and total organic carbon (TOC, 1.9-11-fold) emissions were observed for certified pellets R. Nitrogen oxide (NO) emissions were higher for non-certified pellets (2.5-3.2-fold). The compliance of gaseous emissions with the Ecodesign thresholds was not ensured by certification. Certified pellets P generated significantly lower PM_{10} emissions than the other two types of pellets at medium and nominal loads. Water soluble ions represented from 36 to 68 %wt. of the PM_{10} mass. The combustion of certified pellets P and non-certified pellets generated total carbon PM_{10} mass fractions ranging from 23 to 50 %wt., whereas pellets R resulted in lower mass fractions (7-14 %wt. PM_{10}). The chromatographically resolved organic compounds were dominated by anhydrosugars and alkanols. Pyrene and retene were the most abundant among polyaromatic hydrocarbons.

Keywords: Certified pellets; Chemical composition; Gaseous emissions; Non-certified pellets; Pellet stove; PM_{10} emissions

3.1. Introduction

Increasing environmental concerns associated with fossil fuel consumption and EU bioenergy targets led to an increase in renewable energy production and utilization (European Union, 2019). Woody biomass meets an important share of Europe's renewable-energy demand (AEBIOM, 2017). Among wood-based fuels, pellets offer numerous advantages and are particularly attractive (Obernberger and Thek, 2010), as evidenced by the strong growth of the pellet market over the years. In 2017, EU28 countries consumed around 24.1 million tonnes of wood pellets with nine million tonnes used for residential heating (Bioenergy Europe, 2018).

Key drivers behind the household's heating system choice are the fuel price (Martinopoulos et al., 2018; Sandro et al., 2019; Thomson and Liddell, 2015) and also the environmental benefits (Thomson and Liddell, 2015). Despite the fact that pellet combustion heating devices allow achieving lower emissions compared with traditional firewood combustion in batch mode operated appliances (Vicente and Alves, 2018), this technology is strongly dependent on stove/boiler design (e.g. fuel feeding system: bottom, horizontal or top fed, burner pot configuration) (Polonini et al., 2019; Verma et al., 2013; Win and Persson, 2014) and fuel physical (e.g. pellet length, particle density, durability, bulk density) (Garcia-Maraver et al., 2014; Wöhler et al., 2017) and chemical properties (e.g. fuel ash content, S, Cl and K contents) (Lamberg et al., 2013; Schmidt et al., 2018; Tissari et al., 2008) for optimal performance. Furthermore, the user can still affect the emissions by adjusting the stove or boiler to operate at different heat output levels (nominal load or partial load). Generally, researchers found higher gaseous and particulate emissions when the pellet appliance is operated under partial loads (Schmidl et al., 2011; Venturini et al., 2018, 2015; Verma et al., 2013).

The fuel quality is directly interconnected to consumer's satisfaction with respect to pellet based residential heating (Sandro et al., 2019). In fact, besides its impact on emissions, the use of lower quality raw materials for pellet production, with high content of ash and critical inorganic elements (e.g. alkali metals, Cl, S and Si), can result in ash related problems (e.g. corrosion, slagging and fouling) (Carvalho et al., 2013; Fournel et al., 2015a; Öhman et al., 2004; Rabaçal et al., 2013; Zeng et al., 2016). Taking into account the importance of ensuring the quality of pellet fuels, many European countries, such as Germany, Austria, Sweden and Switzerland, developed their own standards (Verma et al., 2011). In order to harmonise the European pellet market, the EN 14961-2 introduced a common standard for residential pellet fuels, which displaced all other national standards across the EU (e.g. DIN-52731, DIN plus, Ö-Norm M-7135, SS-187120). The European standard for wood pellets was followed a few years later by the international standard (ISO 17225-2). The ENplus certification scheme ensures consumers that the standard requirements are met (EPC, 2013). Worldwide, the number of countries with ENplus certified producers increased from 7 to 44 between 2011 and 2017. The share of ENplus certified pellets on the European market was 70% in 2017 (Bioenergy Europe, 2018). Over the years, several studies focused on assessing how the fuel labelling ensures compliance with the European standard requirements for a specific quality class (Duca et al., 2014; Pollex et al., 2018; Sandro et al., 2019). Duca et al. (2014) analysed chemical and physical parameters of commercial bagged pellets during a three-year period. The research results revealed that certification is useful to guarantee a high pellet quality. More recently, Pollex et al. (2018) evaluated 249 high quality pellet samples to assess the potassium content. The authors reported huge variation in this ash forming element among the tested samples and highlighted that the current limitation of fuel ash content is not enough to ensure low ash forming elements, such as potassium, in the pellets. Several studies have reported linear relationships between PM emissions and fuel K content (Lamberg et al., 2013; Zeng et al., 2016). Fine particles are mainly formed by vaporisation of ash forming elements (e.g. K, Na, S, Cl and easily volatile heavy metals, such as Zn and Pb) and subsequent nucleation and condensation due to flue gas cooling (Obernberger et al., 2006; Obernberger and Thek, 2006; Tissari et al., 2008).

Several studies have focused on emissions from certified pellets. The main goal of most of them was to compare emissions from pellets manufactured from alternative raw materials with those obtained from the combustion of a high quality fuel (Mack et al., 2019; Schmidt et al., 2018; Verma et al., 2012). Other studies reporting the performance of certified pellets aimed to evaluate the effect of combustion appliance operation on emissions (Schmidl et al., 2011; Verma et al., 2013; Win and Persson, 2014). More recently, Venturini et al. (2018) investigated the emissions from the combustion of three wood pellets of distinct quality classes. The combustion of pellets with similar quality in the same combustion appliance and under similar combustion conditions was performed by Arranz et al. (2015) and Fachinger et al. (2017). While the study of Arranz et al. (2015) focused mainly on the gaseous emissions, the latter entails a more detailed characterisation, including PM emissions and chemical speciation. Fachinger et al. (2017) reported slight differences in the gaseous emissions and PM chemical composition from the combustion of two types of pellets both complying with the threshold values defined for class A1 pellets (EN plus A1).

Despite the valuable data provided by the mentioned studies, the emissions from combustion of pellets sold in the Portuguese market are still poorly typified. The aim of this work was to evaluate the emissions (gaseous compounds and particulate matter) and the PM chemical composition from the combustion of two different brands of pellets with certification ENplus A1 and one brand of pellets without certification, all of them manufactured in Portugal. The effect of stove operation on emissions and PM chemical composition from the combustion of each type of pellets was also evaluated.

3.2. Methodology

3.2.1. Combustion experiments

The experimental infrastructure and main features of the combustion appliance used in the present work are described in detail in previous publications (Vicente et al., 2019, 2015). Combustion tests were performed using a commercially available residential stove equipped with top feed burner and with a rated nominal power output of 9.6 kW. Pellets are automatically fed from the stove internal storage tank to the combustion chamber by an auger screw feeding system and ignited by an electrical resistance. The combustion air is driven by an electric fan through an intake at the back of the stove and supplied under the pellet bed through holes in the burner pot. Another internal fan is responsible for circulating air through a heat exchanger and directing it back to the room. The stove power output can be set at five different levels through a control panel on the top of the stove. The combustion air and fuel feed rate are regulated automatically depending upon the chosen load setting. To investigate the influence of biofuel quality on emissions, three types of pellets were tested: two different brands of commercial pellets labelled as ENplus A1 certified pellets (certified pellets R and P) and non-certified pellets. For each pellet, three operation conditions were tested including nominal load and partial load (lowest and medium settings). The fuel feed rate for each fuel was determined by prior calibration of the screw feeding system for the three levels of power output under analysis. The measurements were performed in triplicate by recording the time spent to empty a known amount of pellets from the storage tank as a function of the load setting selected. In addition, the fuel was weighed before pouring it into the storage tank and after the combustion test in order to verify the fuel consumption rate. The fuel properties were determined according to international CEN/TS standards and are listed in Table 3.1. The threshold for the moisture content (≤10 %wt.) (EPC, 2013) was met for all the pellet brands. As regards ash content, pellets R satisfied the requirements for the A1 class (≤0.7 %wt.), while the other two pellet types had a slightly higher ash content. The carbon, hydrogen, and sulphur contents of the pellets under analysis in the present study are similar to those reported in the literature for wood and woody biomass pellets (Obernberger and Thek, 2004). However, the nitrogen contents of the certified pellets are higher than the maximum values allowed for the highest quality class (≤0.3), whereas the non-certified pellets show a N-content higher than that allowed for the lowest quality class (≤1.0) (EPC, 2013).

Table 3.1. Proximate and ultimate analysis of pellet types used in the combustion experiments.

Proximate analysis	Unit	Certified pellets R	Certified pellets P	Non-certified pellets
Moisture[a]	wt.%, as received	7.2 ± 0.04	8.0 ± 0.03	7.3 ± 0.03
Ash[b]	wt.%, dry basis	0.43 ± 0.03	0.77 ± 0.01	0.84 ± 0.01
Ultimate analysis[c]				
C	wt.%, dry basis	49.7	48.7	49.4
H		6.3	6.1	6.2
N		0.71	0.78	1.02
S		< 0.01 (Lq)	< 0.01 (Lq)	< 0.01 (Lq)
O (by difference)		42.9	43.7	42.5
Lower heating value[d]	MJ kg^{-1}	18.47	18.50	18.53

Lq – limit of quantification; [a] CEN/TS 14774; [b] CEN/TS 14775; [c] CEN/TS 15104; [d] CEN/TS 14918

The flue gas temperature was monitored at several points along the combustion and exhaust system (combustion chamber, at the pellet stove exit and at the exit of the chimney) using K-type thermocouples (Table 3.2). The flue gas composition was monitored continuously using a Fourier transform infrared spectrometer (FTIR, Gasmet, CX4000). The determination of the O_2 concentrations was made by a paramagnetic analyser (ADC, O2-700 model) after flue gas drying. The operational parameters for each pellet type are presented in Table 3.2.

Particulate matter sampling was carried out in a dilution tunnel, under isokinetic and steady state conditions, through a stainless-steel probe positioned centrally in the dilution tunnel cross section using a low volume sampler.

Table 3.2. Operating parameters of the stove for the combustion of certified and non-certified pellets.

Pellet type	Operation mode	Temperature in the combustion chamber (°C)	Temperature at the exit of the chimney (°C)	Fuel mass rate (kg h^{-1})	Power output (kW)	O_2 (%)
Certified pellets R	Low power	548 ± 17.7	68.3 ± 0.31	0.92 ± 0.12	4.7	15.3 ± 0.23
	Medium power	540 ± 15.9	70.5 ± 9.3	1.05 ± 0.04	5.4	15.5 ± 0.56
	High power	617 ± 9.9	85.6 ± 0.45	1.19 ± 0.10	6.1	14.3 ± 0.34
Certified pellets P	Low power	744 ± 5.0	94.2 ± 2.43	1.26 ± 0.08	6.5	14.0 ± 0.21
	Medium power	718 ± 24.2	99.6 ± 0.65	1.48 ± 0.03	7.6	14.4 ± 0.28
	High power	740 ± 21.4	112 ± 1.31	1.74 ± 0.11	8.9	13.8 ± 0.31
Non-certified pellets	Low power	648 ± 61.9	67.6 ± 2.00	1.32 ± 0.05	6.8	11.2 ± 0.31
	Medium power	717 ± 9.6	85.0 ± 1.79	1.55 ± 0.03	8.0	11.3 ± 0.32
	High power	775 ± 4.8	89.3 ± 10.2	1.84 ± 0.09	9.5	10.9 ± 0.16

The sampler (TECORA, model 2.004.01) encompasses the PM_{10} sampling head, a pump operating at 2.3 m^3 h^{-1}, and a control and data storage unit. The mean gas velocity and temperature, in the dilution tunnel and chimney exit, were monitored by a Pitot tube (Testo AG 808) and K-type thermocouple, respectively. PM_{10} samples were collected on pre-baked (6 h, 500 $^{\circ}C$) quartz fibre filters (Pallflex®) and weighted with a microbalance (RADWAG 5/2Y/F).

3.2.2. Analytical techniques

Organic and elemental carbon: The carbonaceous particulate fractions were quantified by a thermal optical method. Organic carbon (OC) was measured in a nitrogen atmosphere and elemental carbon (EC) in a 4% oxygen 96% nitrogen atmosphere at controlled heating. Correction of pyrolytic conversion of OC to EC was achieved by monitoring the transmission of light through the filter with a laser beam and a photodetector. A non-dispersive infrared (NDIR) CO_2 analyser quantifies continuously the CO_2 released from the thermal volatilisation and oxidation of different carbon fractions.

Water soluble ions: Ion chromatography analysis was performed by means of an ICS-5000 instrument (Thermo Scientific) equipped with an auto sampler and ion-exchange columns. For the analysis of anions, the instrument was equipped with Ionpac AS11-HC-4 μm (2 × 250 mm), mobile phase: 30 mM potassium hydroxide. For analysis of cations, the instrument was equipped with a DIONEX Ionpac CS16 analytical (3 × 250 mm), mobile phase: 30 mM methanesulfonic acid. After electrochemical suppression (AERS 500 (4 mm) and CERS 500 (4 mm) suppressors), quantification was performed with a conductivity detector. Calibration was performed using external standards diluted from a stock solution supplied by Thermo Scientific. A portion of each sample (2 punches 9 mm) was extracted with Milli-Q water (1.5 ml) under ultrasonic agitation (30 min).

Organic compounds: Portions of the filter replicate samples were combined and firstly extracted by refluxing dichloromethane (300 ml) for 24 h. After filtration, the pieces of filter were subsequently extracted by sonication with methanol (75 ml, 30 min). The total organic extract, obtained from the two extraction procedures, was dried and then fractionated by vacuum flash chromatography with silica gel into different classes of organic compounds. The different organic extracts were subsequently dried before the analysis by gas chromatography-mass spectrometry (GC-MS). Before the analysis, fractions that included more polar compounds (alcohols, acids and sugars) were silylated in sealed vials with N,O-bis(trimethylsilyl)-trifluoroacetamide (BSTFA).

3.2.3. Statistical analysis

The significance of differences between emissions under distinct operational loads and types of pellets was evaluated by one-way ANOVA, followed by Bonferroni's post hoc test. Three measurements were performed for each pellet type under each operational condition. In the absence of normality or homogeneity of variances, as assessed with Shapiro-Wilk and Levene's tests, respectively, the transformation of the variable was performed. Pearson correlations were computed and the respective coefficient were presented as r. A value of $p < 0.05$ was considered statistically significant. All the statistical analyses were performed with IBM SPSS Statistics Version 24.

3.3. Results and discussion

3.3.1. Gaseous emission factors

CO emission factors (EFs) varied according to fuel and stove operation mode (Table 3.3). The highest CO EFs were recorded during the combustion of certified pellets R (2.7-6.1-fold) under the three operational conditions tested ($p < 0.05$) and were inversely correlated with the temperature in the combustion chamber ($r = -0.849$, $p = 0.004$). The temperatures recorded in the combustion chamber were significantly lower during the combustion of this type of pellets in comparison with the temperatures reached during the combustion of pellets P and non-certified pellets ($p < 0.05$). Temperature is an important factor on the fuel reaction rates, hampering an efficient fuel conversion if too low (Brunner et al., 2009). The physical characteristics of pellets (pellet durability, proportion of fines, pellet length and diameter) can affect the combustion performance and consequently the emissions (Garcia-Maraver et al., 2014; Obernberger and Thek, 2004; Wöhler et al., 2017). In fact, Wöhler et al. (2017) burned three softwood pellet samples, differing only in length, and reported a decrease in the fuel mass flow into the combustion chamber for longer pellets. The authors argued that this reduction led to an increase in the level of residual oxygen, which decreased the combustion temperature, resulting in higher CO emissions for the combustion of long pellets compared to short pellets.

The influence of stove operation on CO EFs was only significant for the certified pellets. The trend observed for these two pellet types was distinct. While the combustion of pellets P generated lower CO EFs under minimum load operation in comparison with both medium and nominal load ($p < 0.05$), CO EFs from pellets R were significantly lower at nominal load than under medium power output ($p < 0.05$). Venturini et al. (2015) reported 1.4 times higher CO emissions for the combustion of wood pellets in a stove at partial load than those at nominal load. More recently, a similar trend was observed by the same researchers for three different quality pellets (Venturini et al., 2018). A more accentuated difference in CO emissions under different load operations was reported by Tissari et al. (2008) (10-fold) and by Schmidl et al. (2011) (15-fold) for the combustion of wood pellets. CO emissions can be highly variable, even using automatically fired stoves and high quality pellets (Table 3.3).

In small scale combustion systems, nitrogen oxides are mainly formed from the fuel nitrogen since the temperatures necessary to activate the other two mechanisms (thermal and prompt NO_x formation) are not reached (Brunner et al., 2009; Nussbaumer, 2003). In the present study, NO EFs were similar for both certified pellet brands at all operation modes and similar to the EFs reported by Win and Persson (2014) (Table 3.3). On the other hand, the combustion of non-certified pellets resulted in NO EFs 2.5-3.2-fold higher ($p < 0.05$) in comparison with certified pellets, which might be related to the fuel N content (Table 3.1).

The main compounds contributing to the TOC emissions were formaldehyde (CH_2O), propane (C_3H_8) and ethane (C_2H_6) for the combustion of certified pellets R and P, and non-certified pellets, respectively. The TOC and individual hydrocarbon EFs are displayed in Fig. 3.1. Under the minimum operation mode, certified pellets R generated significantly higher TOC emissions (4.6-6.1-fold) than the other two types of pellets ($p < 0.05$). When operating the stove at medium power output, certified pellets R and P generated the highest and the lowest TOC emissions, respectively ($p < 0.05$). Nominal load operation led to 2.5-4.8-fold significantly lower emissions from pellets P in comparison with the other pellet types ($p < 0.05$).

The release of SO_2 varies as a function of the fuel sulphur content (Carvalho et al., 2013), which is generally low in woody biomass fuels (Vassilev et al., 2010). In the present study, the sulphur content of pellet fuels was below the quantification limit. Thus, the SO_2 EFs were low, ranging from 0.59 ± 0.46 to 6.4 ± 2.8 mg MJ^{-1} (Fig. 3.2). A significant difference between the medium and nominal loads was only registered for certified pellets R. Under nominal loads, no significant differences were observed in the SO_2 EFs from the combustion of different pellet types. Partial loads led to significantly lower emissions from the combustion of non-certified compared with the certified pellets P (lower load) and R (medium load). The SO_2 EFs obtained in the present study are comparable with those previously obtained for the combustion of wood pellets (Brassard et al., 2014; Fachinger et al., 2017). Higher SO_2 emissions were reported by Orasche et al. (2012) for the combustion of certified pellets (20-87 mg MJ^{-1}) in a pellet stove under different operation conditions.

Table 3.3. CO, NO, NO_x and PM EFs (mg MJ^{-1}) found in the present study and comparison with data from the literature.

Fuel Certification	PM fraction	Operation mode	CO	NO	NO_X	PM	Reference
Certified pellets R (ENplus A1)	PM_{10}	Low power	589 ± 111	66.1 ± 1.34	105 ± 0.502[b]	37.7 ± 1.60	This study
		Medium power	710 ± 44.1	62.0 ± 2.81	101 ± 4.89[b]	40.5 ± 1.48	
		High power	407 ± 135	65.0 ± 2.94	101 ± 5.96[b]	44.5 ± 1.04	
Certified pellets P (ENplus A1)		Low power	122 ± 11.4	64.1 ± 0.578	98.4 ± 0.887[b]	36.2 ± 6.19	
		Medium power	149 ± 2.34	68.9 ± 3.78	106 ± 5.79[b]	21.9 ± 1.61	
		High power	151 ± 5.30	70.1 ± 2.55	107 ± 3.91[b]	23.2 ± 2.59	
Non-certified pellets		Low power	182 ± 56.3	179 ± 12.9	276 ± 19.0[b]	29.8 ± 9.68	
		Medium power	117 ± 38.3	198 ± 8.64	303 ± 13.5[b]	43.5 ± 4.83	
		High power	108 ± 23.2	172 ± 6.19	264 ± 9.49[b]	46.2 ± 1.01	
DIN+ pellets	TSP	Partial load	259 ± 7.53	79 ± 1.53	N/A	78 ± 9.5[c]	Venturini et al. (2018)
		Nominal load	176 ± 5.13	83 ± 1.53	N/A	46 ± 9.3[c]	
EN 14961-2	N/A	Cold start	1390	N/A	256	110[c]	Orasche et al. (2012)
		Nominal load	413	N/A	165	36[c]	
ENplus A1 pellets (1)	PM_1	Full cycle[a]	400 ± 60	N/A	N/A	11 ± 3[d]	Fachinger et al. (2017)
ENplus A1 pellets (2)			430 ± 60	N/A	N/A	17 ± 5[d]	
DIN+ pellets	PM	Nominal load	66 - 78	N/A	N/A	56 – 77[c]	Ozgen et al. (2014)
DIN+ pellets	TSP	Nominal load	193 ± 12	N/A	80 ± 20	23 ± 3[e]	Schmidt et al. (2018)
SS 187120	$PM_{2.5}$	High power	16 ± 2	63 ± 1	N/A	55 ± 3[c]	Win and Persson (2014)
		Medium power	23 ± 2	63 ± 1	N/A	43 ± 6[c]	
		Low power	48 ± 5	60 ± 1	N/A	55 ± 5[c]	
ÖNORM M7135/ DIN+ pellets	PM_{10}	Start-up phase	116	N/A	81.2	8.5[c]	Schmidl et al. (2011)
		Full load	33.2	N/A	83.2	7.9[c]	
		Partial load	488	N/A	78.6	3.0[c]	

[a]Full and partial load operation, start-up, load change and shut down procedures; [b]NO_X as NO_2; N/A - information not available; [c]dilution tunnel; [d]consecutive ejector diluters; [e]chimney

Hydrogen fluoride (HF) EFs were low (Fig. 3.2) and similar to the EFs reported in the literature for the combustion of wood pellets (Vicente et al., 2019). Although no significant differences among operational loads for each pellet type was recorded ($p < 0.05$), EFs were significantly higher for non-certified pellets in comparison with the certified biofuels ($p < 0.05$) for all operating conditions. Hydrogen chloride (HCl) emissions also showed the influence of the burnt fuel, being higher for certified pellets P than for the other two pellet fuels ($p < 0.05$) for all operating conditions, which might indicate higher Cl content in this type of pellets. The HCl EFs obtained in the present study (Fig. 3.2) are comparable to those documented in previous studies for the combustion of wood pellets (Brassard et al., 2014; Lamberg et al., 2013; Tissari et al., 2008; Vicente et al., 2019).

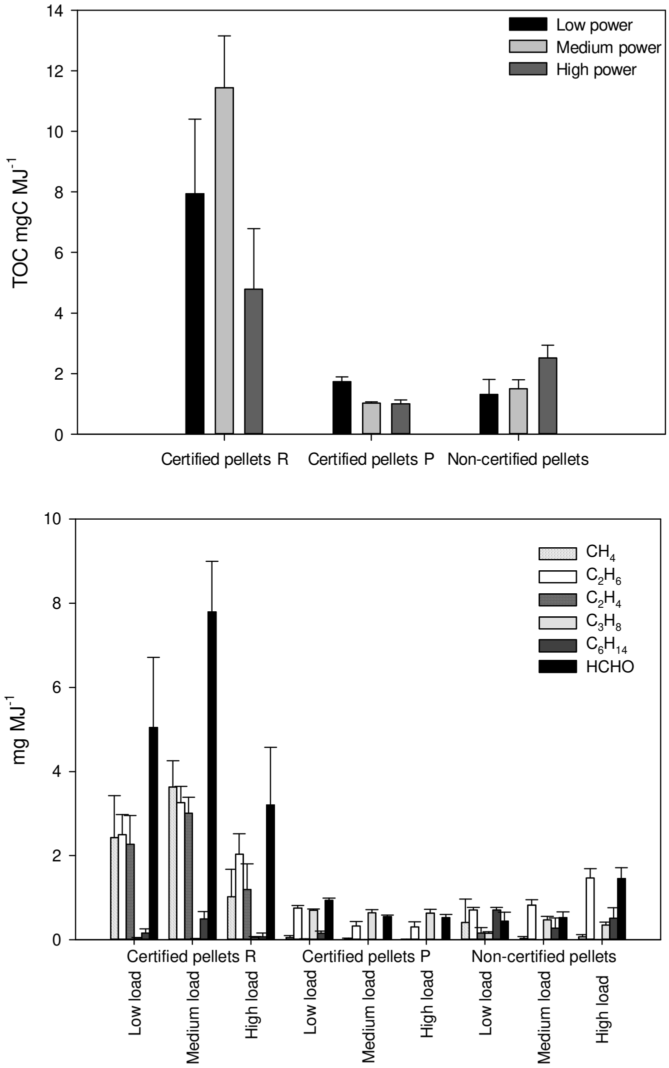

Figure 3.1. Emission factors of TOC and individual hydrocarbons (CH_4, C_2H_6, C_2H_4, C_3H_8, C_6H_{14} and HCHO) from pellet combustion.

In the present work, NH_3 was produced in small amounts, which is in agreement with studies reporting emissions from woody pelletised fuels (Brassard et al., 2014; Fournel et al., 2015b; Vicente et al., 2019). The EFs obtained for the combustion of certified pellets were significantly lower than for non-certified pellets at nominal and medium load operation ($p < 0.05$). However, the lowest level of power output generated significantly higher emissions for certified pellets P in comparison with the other two pellet types ($p < 0.05$). A positive correlation was found between the power output and NH_3 emissions for the combustion of certified pellets R ($r = 0.797$, $p = 0.010$) and non-certified pellets ($r = 0.767$, $p = 0.016$).

The Commission Regulation 2015/1185 (European Commission, 2015) (implementing Directive 2009/125/EC - Ecodesign requirements for energy-related products) establishes the emission requirements for 2022. The CO emissions of the pellet stove were below the regulated limit (300 mg Nm^{-3} at 13% O_2, nominal load) for certified pellets P and non-certified pellets. However, during the combustion of pellets R, CO emissions (575 ± 125 mg Nm^{-3} at 13% O_2) exceeded that limit. Non-optimal combustion conditions, such as low combustion temperatures, can increase CO emissions, even in automated combustion appliances.

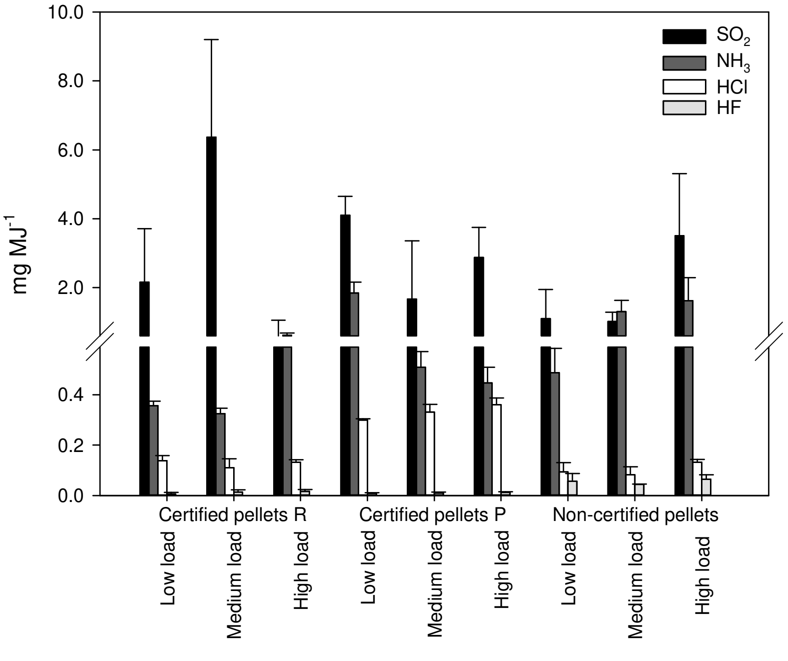

Figure 3.2. Emission factors of SO_2, NH_3, HCl and HF from pellet combustion.

As discussed above, NO_X emissions from residential combustion are closely related to the fuel N content rather than the combustion technology employed. In the present study, NO_X emissions were below the Ecodesign limit (200 mg m^{-3} expressed as NO_2 at 13% O_2, nominal load) for the combustion of certified pellets but above this value for non-certified pellets (337 ± 31.1 mg Nm^{-3} of NO_X expressed as NO_2 at 13% O_2).

3.3.2. Particulate emission factors

Regardless of type of pellet burned, PM_{10} average EFs ranged from 23.2 ± 2.59 to 46.2 ± 1.01 mg MJ^{-1} when operating at nominal load. These results are similar to the ones reported in the literature for the combustion of certified pellets under full load operation (Table 3.3).

The PM_{10} emissions from the combustion of the three pellet types under different loads presented substantial variations. Pellets P generated the highest PM_{10} EFs at the lowest power output, which were significantly different from those recorded at the other two operational loads ($p < 0.05$). No significant differences were found between the EFs for the operation of the pellet stove at medium and nominal loads. Contrasting with that, pellets R generated significantly higher PM_{10} emissions at nominal load than under the minimum and medium level of power output ($p < 0.05$). Similarly, for the combustion of non-certified pellets, significantly higher PM emissions were recorded at nominal load compared with the operation under the lowest level of power output ($p < 0.05$). Most researchers found a decrease in PM_{10} emissions when operating pellet stoves at nominal loads (Boman et al., 2011; Riva et al., 2011; Venturini et al., 2018, 2015). However, Win and Persson (2014) evaluated different combustion appliances at different loads and reported that for the majority of the units tested, no linear correlation between particle emission and combustion power was observed. The authors pointed out that PM emissions may be influenced by the change in fuel load, due to the fact that the O_2 level and combustor temperature may vary with fuel load and excess air.

Under the minimum power output, PM_{10} EFs were similar, regardless the type of pellets, while increasing the load led to significant differences, ranging from 1.8 to 2.0-fold, between the EFs of certified pellets P and the other two types ($p < 0.05$) (Table 3.3). PM emissions were significantly lower at increased loads for certified pellets P, whereas no significant differences were recorded between certified pellets R and non-certified pellets. The PM_{10} emissions were below the Ecodesign emission limit for all types of pellets. PM_{10} EFs from the combustion of certified pellets R and non-certified pellets were significantly correlated with the temperature in the combustion chamber ($r = 0.733$, $p = 0.025$ and $r = 0.799$, $p = 0.010$ for pellets R and non-certified pellets, respectively).

3.3.3. Inorganic ions

The dominant water soluble species in particles resulting from combustion of certified pellets were sulphate, potassium, chloride and nitrate, which globally represented from 35 to 66 %wt. of the PM_{10} mass (92-98% of the total ionic content). The major ions in particles generated from non-certified pellets were chloride, potassium, sulphate and sodium. These ionic species accounted for 43 to 49 %wt. of the PM_{10} mass (92-97% of the total ionic content) (Fig. 3.3). Venturini et al. (2015) reported a contribution of inorganic ions to total PM in the range from 20 %wt. (partial load) to 37.5 %wt. (nominal load) during the combustion of pellets in a top fed stove. In the present study, the contribution of inorganic ions to the PM_{10} mass was higher.

The significant correlation between potassium and sulphate EFs for both certified pellets ($r = 0.791$, $p = 0.011$ and $r = 0.744$, $p = 0.022$ for pellets R and P, respectively) leads to suppose that particles consisted mainly of K_2SO_4. These results are in line with those reported by Sippula et al. (2007). The authors tested 11 different pellet fuels in a top-fed pellet stove and reported that for the majority of the fuels, 60-80% of potassium was in the form of K_2SO_4. The predominance of potassium, sulphate and chloride for the combustion of woody pellets in automatic appliances has been reported in other previous studies (Boman et al., 2011, 2004; Lamberg et al., 2011; Tissari et al., 2008; Venturini et al., 2018, 2015). Despite the lower contributions to PM_{10} mass, ammonium, lithium, calcium and magnesium were also detected.

The combustion of certified pellets was the only one that made it possible to observe significant differences in the emission of ionic species. The combustion of pellets R under nominal loads generated significantly higher potassium emissions ($p < 0.05$) than the operation at medium and lower loads.

At the lowest level of power output, no significant differences in the EFs of the ionic species was recorded for the combustion of the different pellets. However, for increased operation loads, the ionic composition of particles varied with the type of biofuel, specially the emissions of chloride, which were significantly higher for non-certified pellets ($p < 0.05$). During the operation at nominal load significantly higher emissions of sulphate were recorded for certified pellets R in comparison with pellets P and non-certified pellets ($p < 0.05$), while potassium emissions were significantly different between biofuels ($p < 0.05$). Also, significantly higher nitrate EFs were recorded for pellets R compared with pellets P for both medium and nominal loads ($p < 0.05$).

Several key factors affect the emission of inorganic compounds during biomass combustion, such as the elemental composition of the fuel, the temperature in the combustion chamber, as well as the volatility of the element (Czech et al., 2018; Jeguirim et al., 2017; Knudsen et al., 2004; Van

Lith et al., 2006). In the present study, a positive correlation was recorded between potassium EFs and the combustion chamber temperature for non-certified and certified pellets R ($r = 0.841$, $p = 0.004$ and $r = 0.701$, $p = 0.036$ for pellets R and non-certified pellets, respectively).

3.3.4. Carbonaceous content

The OC and EC emissions, in the range from 0.188 to 3.31 mg MJ^{-1} and from 2.22 to 14.9 mg MJ^{-1}, respectively, were affected by both operating conditions of the stove and pellet type burned. The importance of fuel quality on carbonaceous emissions has been also highlighted in previous studies. Vicente et al. (2015) reported OC EFs ranging from 7.40 ± 1.86 (wood pellets) to 48.7 ± 30.9 (agro fuels) mg MJ^{-1}, whereas the EC EFs ranged from 1.77 ± 0.44 (wood pellets) to 54.5 ± 23.5 (agro fuels) mg MJ^{-1}. More recently, the combustion of laboratory made acacia pellets under partial load conditions generated EFs of 22.9 ± 9.28 mg MJ^{-1} and 6.82 ± 2.47 mg MJ^{-1} for OC and EC, respectively (Vicente et al., 2019). The carbonaceous emissions obtained in the present study for certified pellets are comparable with those reported by Orasche et al. (2012) and Schmidl et al. (2011) for the combustion of certified pellets in small scale stoves.

The OC and EC EFs from certified pellets P were significantly higher ($p < 0.05$) under the lowest operational setting compared to medium and nominal loads. The differences in the carbonaceous EFs from pellets R combustion were only substantial for OC, which was significantly lower under nominal load operation. No significant differences were recorded between the operational loads tested for the combustion of non-certified pellets. The effect of operating conditions on the PM carbonaceous content was reported in previous studies. Venturini et al. (2015) documented a 2.7-fold decrease in TC EFs from nominal to partial pellet stove operation. Tissari et al. (2008) compared the OC and EC EFs from the combustion of wood pellets under nominal and partial loads, reporting a 90-fold and a 3-fold increase in EC and OC EFs, respectively, under partial load operation.

The combustion of certified pellets P and non-certified pellets generated total carbon (TC) mass fractions in PM_{10} ranging from 23 to 50 %wt., while pellets R resulted in lower TC contributions to the PM_{10} mass (7-14 %wt. PM_{10}). For the combustion of wood pellets, Venturi et al. (2015) observed higher TC contributions to PM mass compared to the values of the present study (45-65% nominal and partial load, respectively). Under minimum and medium operational loads, pellets R generated 2 to 6-fold significantly ($p < 0.05$) lower EC emissions in comparison with the other two pellet types. Under the lowest fuel load operation, no significant differences were recorded for OC EFs, while under medium loads the emissions were significantly ($p < 0.05$) lower for certified pellets

P. Nominal load resulted in significantly higher emissions of both OC and EC for non-certified pellets. OC EFs from the combustion of certified pellets R were found to correlate negatively with the potassium EFs (r = - 0.780, p = 0.013), while for certified pellets P potassium EFs correlated with EC instead (r = - 0.760, p = 0.017). OC EFs from both certified pellets correlated with the TOC EFs (r = 0.741, p = 0.022 and r = 0.861, p = 0.003 for pellets R and P, respectively).

The OC to EC ratios have been widely used in atmospheric sciences for the apportionment of emission sources. For wildfires in Southern Europe, OC/EC ratios ranging from 7 to 69 were reported in $PM_{2.5}$ samples (Vicente et al., 2012). In Chinese temples, where incense is burned intensely, OC/EC ratios were in the range from 2.6 to 17 in PM_{10} samples (Wang et al., 2007). OC/EC values in the range 1.1-14.1 have been reported in emissions from residential coal combustion (Chen et al., 2006). OC/EC ratios below 1 have been described in road tunnel studies where fresh vehicle exhaust emissions represented the dominant source of carbonaceous aerosol (Alves et al., 2016; Cheng et al., 2010; Pio et al., 2011). In the present study, the OC/EC ratios varied widely, ranging from 0.04 (certified pellets P, highest power output) to 1.4 (certified pellets R, medium power output). Thus, the characteristic OC/EC ratios for identifying biomass combustion are not valid for certified pellets in advanced combustion technology.

For mass balance calculations (Fig. 3.3), the analysed OC was converted into organic matter (OM), considering an OM/OC ratio of 1.6. The contribution of OM was low, never exceeding 20 %wt. of the PM_{10} mass (Fig. 3.3).

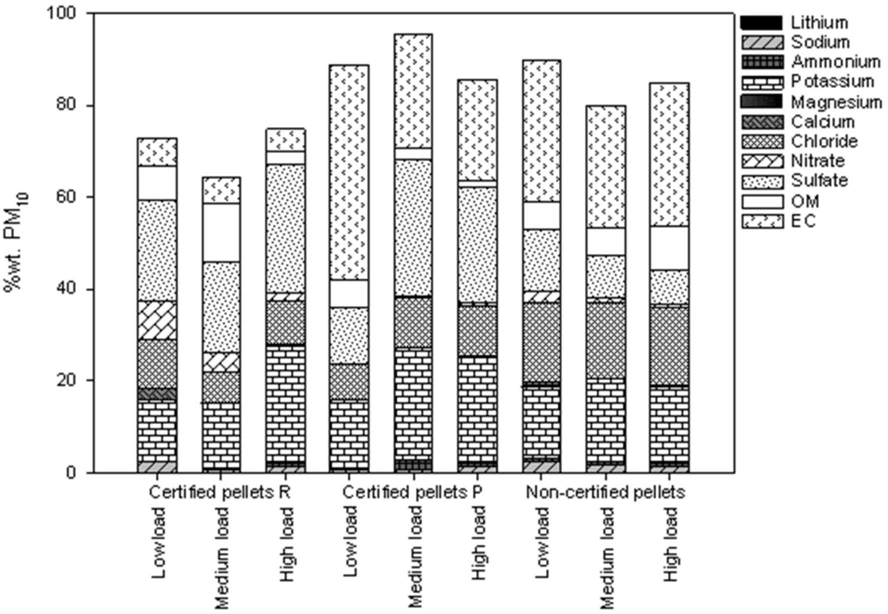

Figure 3.3. Chemical composition of PM_{10} (Σ chemical constituents = OC × 1.6 + EC + inorganic ions) for the combustion of the distinct pellets under different operating conditions.

3.3.5. Organic speciation

A large variety of PM-bound organic species were emitted during the combustion of pellets, namely saccharides, resin acids, polycyclic aromatic hydrocarbons (PAHs), alkanes, sterols, n-alkanols, phenolic compounds, among others (Tables 3.4 and 3.5). Organic compounds were dominated by alkanols (non-certified pellets) and saccharides (certified pellets P and R).

Numerous sources contribute to atmospheric n-alkanes, such as higher plant waxes (emitted from leaf abrasion or from biomass combustion), open burning of plastics, fossil fuel combustion and biogenic detritus, including microbial sources (Alves, 2008). The relative source input of PM-bound n-alkanes can be identified by diagnostic parameters, such as the carbon preference index (CPI), defined as the sum of odd-over even-carbon numbered n-alkanes from C_{11} to C_{35}, and by the carbon number of the compound with maximum concentration in the homologous series (C_{max}). Natural vegetation waxes consist of longer chain ($> C_{20}$) n-alkanes. Oros and Simoneit (2001b) reported an odd to even carbon number predominance (CPI from 0.5 to 3.4) in conifer wood smoke particles and C_{max} highly variable in the range from C_{20} to C_{33}. Higher CPIs ranging from 2.1 to 11.8 (Oros et al., 2006) and from 2.6 to 6.8 (Oros and Simoneit, 2001a) were reported for the combustion of grass and deciduous trees, respectively. In the present study, the n-alkane series comprised homologues from C_{11} to C_{35}. The C_{max} was observed for C_{11} for non-certified pellets and certified pellets R, while for certified pellets P the maximum was recorded for C_{25}. For non-certified pellets and certified pellets R, it was not possible to calculate a CPI value due to the absence of even carbon numbered n-alkanes. For certified pellets P, the CPI was 1.8. Globally, this organic class represented a PM_{10} mass fraction of 1.25, 7.96 and 596 $\mu g\ g^{-1}$ for non-certified pellets and certified pellets R and P, respectively. The dominant alkenes in PM_{10} emitted during the combustion of certified pellets were octadecene (certified pellets P, 103 $\mu g\ g^{-1}$ PM_{10}) and tricosene (certified pellets R, 13.5 $\mu g\ g^{-1}$ PM_{10}), while non-certified pellets generated a higher PM mass fraction of squalene (12.1 $\mu g\ g^{-1}$ PM_{10}).

n-Alkanoic acids were identified as a major compound class in samples from the combustion of deciduous and conifer trees, as well from grasses (Oros et al., 2006; Oros and Simoneit, 2001a, 2001b). These compounds are a major class in conifer smoke samples as they are the units of plant fats, oils and phospholipids (Oros and Simoneit, 2001b). In the present study, n-alkanoic acids showed a strong even to odd C number predominance, with CPI (even-to-odd homologues) of 4.7, 6.0 and 6.3 for PM from non-certified pellets, and certified pellets R and P, respectively. For the combustion of pellets P, C_{max} was observed at C_{16} (palmitic acid), which is in good agreement with literature data on biomass combustion emissions (Oros et al., 2006; Oros and Simoneit, 2001a, 2001b). For pellets R and non-certified pellets, the C_{max} was observed at C_{18} (stearic acid). This organic class represented a PM_{10} mass fraction ranging from 4.31 (certified pellets R) to 1011 μg g^{-1} (certified pellets P). Unsaturated fatty acids were also detected in PM_{10} from pellet combustion. The highest mass fractions were recorded for 9-octadecenoic acid (oleic acid) for non-certified and certified pellets R and 9-cis-hexadecenoic (linoleic acid) for pellets P.

Numerous sources, such as biomass combustion, vehicular exhausts, cooking and marine bacteria, have been pointed out as contributors to dicarboxylic acids (Kawamura and Bikkina, 2016, and references therein). In the present study, the most abundant n-alkanedioic acids in PM_{10} samples were malic, adipic and thapsic acids for non-certified and certified pellets P and R, respectively. Dicarboxylic acids accounted for PM_{10} mass fractions ranging from 0.255 (certified pellets R) to 110 μg g^{-1} (certified pellets P).

Alkanols from C_{10} to C_{30}, maximising at C_{15} (certified pellets P and non-certified pellets) and C_{16} (certified pellets R), were detected in the organic extracts obtained from pellet combustion. In PM samples from the combustion of deciduous and conifer trees, n-alkanols maximised at C_{22}, C_{24}, C_{28} and C_{29} (Oros et al., 2006; Oros and Simoneit, 2001a, 2001b). This class of organic compounds was dominant for non-certified pellets (23,847 μg g^{-1} PM_{10}). The contribution of alkanols to the PM_{10} mass emitted during the combustion of certified pellets P was also noticeable (21,040 μg g^{-1} PM_{10}), while certified pellets R generated a lower content of these compounds (2.19 μg g^{-1} PM_{10}).

The dominant PAHs in PM_{10} from the combustion of certified pellets P was pyrene, where as higher mass fractions of retene were observed in emissions from non-certified and certified pellets R (Table 3.5). Pyrene has been identified amongst the three most abundant PAHs from biomass combustion (Nyström et al., 2017; Orasche et al., 2013; Pettersson et al., 2011). Retene has also been found as an abundant polyaromatic hydrocarbon from conifer wood combustion in traditional and improved combustion appliances (Ramdahl, 1983; Shen et al., 2012; Vicente et al., 2016). Globally, 4-ring congeners encompassed from 73.3 (certified pellets R) to 220 (certified pellets P) μg g^{-1} PM_{10}, representing more than half of total PAHs from the combustion of certified pellets P and non-certified pellets.

Monosaccharide derivatives from the breakdown of cellulose have been described as the major organic components in particles from biomass combustion (Simoneit et al., 1999). However, the temperature range within which these compounds are formed (150-350 °C) (Kuo et al., 2008) is surpassed in automatically controlled combustion appliances, such as pellet stoves. In fact, these combustion appliances emit low or undetectable amounts of anhydrosugars (Alves et al., 2017; Schmidl et al., 2011; Vicente et al., 2015). In the current study, these compounds were present in samples from the three pellet fuels with levoglucosan encompassing 0.01 to 0.02 %wt. of the particle mass.

The levoglucosan to mannosan (L/M) ratio can be employed to distinguish biomass categories. Lower ratios have been described for softwood (1.3-6.0) and higher ratios (10.9-83.4) for hardwood combustion (Fine et al., 2001; Orasche et al., 2012; Schmidl et al., 2011, 2008), since the latter has larger amounts of cellulose than hemicellulose. In the present study, L/M ratios of 6.8, 7.0 and 8.6 were recorded for non-certified pellets and certified pellets P and R, respectively. These values are higher than the ones (around 2) reported by Alves et al. (2017) for pellet combustion in the same stove, indicating that characteristic ratios usually employed to trace biomass types are not suitable for automatically fired combustion appliances.

Other saccharidic constituents have been detected and identified in the smoke plume from a wildfire, comprising monosaccharides (e.g. erythrose, arabinose, ribose, galactose, glucose, mannose, fructose and rhamnose), disaccharides (sucrose and maltose) and polyols (glycerol, erythritol, arabitol, mannitol and inositol) (Vicente et al., 2011). Zhang et al. (2013) reported significant inositol levels in aerosols from broadleaf shrub combustion, suggesting its potential use as tracer for green foliage. In the present study, three polyols were detected (glycerol, erythritol and quebrachitol). Although many other saccharides were present in the samples, its quantification was not possible due to similar fragmentation patterns and isomerism among many compounds.

Table 3.4. Oxygenated compounds mass fraction (µg g^{-1} PM_{10}) detected in particles emitted in the flue gases during the combustion of the three pellet types in the stove.

Compounds	Non-certified pellets	Certified pellets P	Certified pellets R
Saccharides and polyols			
Levoglucosan	90.3	68.9	153
Mannosan	13.3	9.88	17.8
Galactosan	8.57	5.68	57.0
Meso-Erythritol	1.34	19.3	0.016
Glycerol	193	211	1.314
Quebrachitol	0.218	nd	0.001
Other saccharides and polyols	6.57	20947	40.6
Total saccharides and polyols	313	21262	269
Phenolic compounds			
Benzyl alcohol	37.3	305	30.9
Coniferyl alcohol	nd	nd	0.148
Vanillin	2.75	3.20	2.54
Vanillic acid	bdl	0.481	2.97
Syringic acid	0.051	bdl	0.204
Sinapyl alcohol	nd	nd	nd

Cinnamic acid	1.503	1.16	10.4
Hydrocinnamic (coumaric) acid	nd	nd	8.15
3-Methoxy-4-hydroxycinnamic (ferulic) acid	nd	nd	0.155
Benzoic acid	22.0	32.0	0.845
4-Hydroxybenzaldehyde	26.4	23.6	3.98
4-Hydroxybenzoic acid	1.71	2.33	0.596
4-Phenylphenol	nd	nd	0.163
2,4-Di-tert-butylphenol	104	1.64	14.7
Resorcinol	0.141	0.343	0.729
4-Hydroxyphenylethanol (tyrosol)	28.3	132	nd
5-Isopropyl-3-methylphenol	0.236	1.67	nd
2-Isopropyl-5-methylphenol (thymol)	nd	nd	1.63
Isoeugenol	1.06	1.19	nd
2-Methoxy-4-propylphenol	1.56	0.979	nd
2,6-Di-tert-butyl-1,4-benzoquinone	32.3	38.6	0.965
Hydroxyacetophenone	3.30	11.8	1.35
Total phenolic compounds	263	556	80.4
Resin acids			
Abietic acid	2.84	nd	bdl
Dehydroabietic acid	7.08	bdl	54.1
Isopimaric acid	1.06	0.744	1.19
Total resin acids	*11.0*	*0.744*	*55.3*
n-Alkenoic acids			
9-Hexadecenoic (palmitoleic) acid	3.14	bdl	0.238
9-12-Octadecadienoic (linoleic) acid	2.85	0.773	0.060
9-Octadecenoic (oleic) acid	22.3	bdl	3.64
Total n-alkenoic acids	28.3	0.773	3.94
n-Alkanoic acids			
Octanoic (caprylic) acid	bdl	bdl	0.765
Nonanoic (pelargonic) acid	34.5	11.2	0.619
Decanoic (capric) acid	12.8	bdl	0.774
Undecanoic acid	2.47	1.54	bdl
Dodecanoic (lauric) acid	12.1	10.6	0.133
Tridecanoic	10.1	32.1	nd
Tetradecanoic (myristic) acid	80.6	139	bdl
Pentadecanoic acid	57.5	60.4	bdl
Hexadecanoic (palmitic) acid	129	363	bdl
Heptadecanoic acid	12.0	27.1	bdl

Octadecanoic (stearic) acid	296	300	1.42
Nonadecanoic acid	1.81	5.91	bdl
Eicosanoic acid	10.4	10.2	bdl
Docosanoic acid	9.95	8.93	0.362
Tetracosanoic acid	bdl	37.3	bdl
Hexacosanoic acid	3.24	3.36	0.237
Total n-alkanoic acids	*673*	*1011*	*4.31*
n-Alkanedioic acids			
Butanedioic (succinic) acid	3.972	28.8	bdl
Octanedioic (suberic) acid	bdl	19.0	bdl
1,5-Pentanedioic (glutaric) acid	3.876	9.16	bdl
Butanedioic (malic) acid	84.9	3.82	bdl
Hexanedioic (adipic) acid	2.707	43.7	bdl
Nonanedioic (azelaic) acid	0.964	bdl	bdl
Decanedioic (sebacic) acid	0.866	2.43	bdl
Hexadecanedioic (thapsic) acid	2.34	3.57	0.255
Total alkanedioic acids	*100*	*110*	*0.255*
Other acids			
Glycolic acid	32.6	bdl	bdl
Levulinic acid	4.70	28.9	bdl
3-Hydroxypropionic (hydracrylic) acid	27.8	31.1	bdl
Glyceric acid	72.5	145	bdl
3-Hydroxybutanoic acid	4.44	6.83	bdl
3,4-Dihydroxybutanoic acid	bdl	15.4	bdl
Pinic acid	bdl	bdl	10.5
Citric acid	0.850	2.53	nd
Podocarpic acid	0.014	nd	bdl
Lactic (2-Hydroxypropanoic) acid	nd	nd	14.5
Pyruvic (2-oxopropenoic) acid	nd	nd	0.653
2-Furoic (2-furanocarboxylic) acid	nd	nd	1.75
Total other acids	*143*	*230*	*27.4*
Alkanols			
Decanol	nd	0.910	0.026
Dodecanol	928	564	0.658
Tridecanol	564	1335	nd
Tetradecanol	9306	7953	bdl
Pentadecanol	12822	10815	0.012
Hexadecanol	129	156	0.920
Heptadecanol	24.1	40.4	nd
Octadecanol	20.6	108	bdl
Docosanol	22.4	48.1	bdl
Tricosanol	6.24	13.6	0.004

Tetracosanol	nd	nd	0.567
Pentacosanol	3.74	1.01	0.005
Heptacosanol	0.541	0.591	bdl
Octacosanol	20.0	3.15	bdl
Tricontanol	1.22	1.97	bdl
Total alkanols	*23847*	*21040*	*2.19*
Sterols			
Cholesterol	13.0	15.8	bdl
β-Sitosterol	6.03	10.5	bdl
Stigmasterol	nd	nd	bdl
5-Cholestan-3-ol (dehydrocholesterol)	nd	nd	bdl
Total sterols	*19.1*	*26.3*	bdl
Phthalates			
Bis(2-ethylhexyl)phthalate	bdl	bdl	bdl
Benzyl butyl phthalate	2.12	1.09	1.55
Bis(2-ethylhexyl)adipate	1.11	2.77	1.18
Di-n-butyl phthalate	bdl	5.74	85.25
Diethyl phthalate	bdl	bdl	bdl
Dimethyl phthalate	nd	nd	0.01
Total phthalates	3.23	9.59	88.0
Other hydroxyl compounds			
2-Methylcyclohexanol	1.15	nd	bdl
2,3-Pinanediol	nd	nd	0.026
1-Monopalmitin	149	172	1.70
1-Monostearin	177	191	13.1
1-Monolauroyl-rac-glycerol	0.448	0.476	nd
(-)-Isopulegol	nd	nd	0.016
Total other hydroxyl compounds	*328*	*363*	*14.8*

bdl- below detection limit; nd- not detected

The alkylphenol 2,4-di-tert-butylphenol was the most abundant (104 µg g^{-1} PM_{10}) phenolic compound in PM_{10} from the combustion of non-certified pellets, whereas certified pellets yielded higher particulate mass fractions of benzyl alcohol (305 and 30.9 µg g^{-1} PM_{10} for certified pellets P and R, respectively). These two phenolic compounds have been reported in particles from wildfires (Alves et al., 2011) and combustion of acacia pellets (Vicente et al., 2019). Lignin, a large and complex polymer in wood tissues, is mainly derived from the polymerisation of p-coumaryl, coniferyl and sinapyl alcohols. The relative proportions of biomonomers are specific to the class of plants (Gelencsér, 2004; Simoneit, 2002). In the present study, the methoxyphenols vanillin and vanillic acid, with a guaiacyl structure, were always present in the particulate samples from certified pellets combustion. The presence of products from coniferyl-type lignin pyrolysis and the low mass fractions of syringic acid indicate combustion of softwood pellets (Gelencsér, 2004; Simoneit, 2002). Pflieger and Kroflič (2017) evaluated the toxicity of guaiacol and its nitro derivatives generated during its aging in the tropospheric aqueous phase. The authors used the *Vibrio fischeri* bioluminescence assay to assess the toxicity and concluded that, according to the European legislation, all the studied compounds are harmful.

Sterols are constituents of plant lipid membranes and waxes (Oros and Simoneit, 2001a). β-Sitosterol has been described as the most abundant sterol in wood smoke from wildfires (Vicente et al., 2011), charcoal combustion in barbecue grills (Vicente et al., 2018) and Chinese cooking, which is characterised by the high consumption of vegetables (Zhao et al., 2007). In the present study, β-Sitosterol was found at mass concentrations from 6.03 (non-certified pellets) to 10.5 (certified pellets P) µg g^{-1} PM_{10}, whereas it was below de detection limit for pellets R.

Table 3.5. PAH mass fractions (µg g^{-1} PM_{10}) in the particulate matter emitted in the flue gases during the combustion of the three pellet types in the stove.

Compounds	Non-certified pellets	Certified pellets P	Certified pellets R
Acenaphthene	bdl	bdl	bdl
Fluorene	7.22	bdl	bdl
Phenanthrene	bdl	4.28	1.72
Anthracene	0.067	0.790	0.120
Acenaphthylene	nd	bdl	bdl
Retene	105	88.9	177
Fluoranthene	45.7	96.5	26.9
Pyrene	51.1	101	23.5
Chrysene	33.1	15.7	13.9
Benzo[a]anthracene	12.8	6.90	9.00
Benzo[b]fluoranthene	5.50	bdl	6.91
Benzo[k]fluoranthene	6.18	bdl	5.55
Benzo[e]pyrene	6.52	0.150	5.99
Benzo[a]pyrene	3.58	0.261	6.11
Perylene	bdl	0.906	0.157
Dibenzo[a,h]anthracene	bdl	bdl	0.625
Indeno[1,2,3-cd]pyrene	bdl	bdl	4.89
Benzo[g,h,i]perylene	0.369	bdl	5.77
Total PAHs	277	315	288

bdl- below detection limit; nd- not detected

Resin acids are biosynthesised mainly by conifers and their major biomarkers are diterpenoids that, upon combustion, are released as natural or thermally altered compounds (Gelencsér, 2004; Oros and Simoneit, 2001b). In the present study, the major natural product in the PM samples was isopimaric acid, with mass fractions ranging from 0.744 to 1.19 µg g^{-1} PM$_{10}$. Dehydroabietic acid has been described as one of the major oxidation products of resin acids (Oros and Simoneit, 2001b). In the present study, this compound has been detected at mass fractions ranging from 7.08 (non-certified pellets) to 54.1 (certified pellets R) µg g^{-1} PM$_{10}$, whereas it was below de detection limit for pellets P. Dehydroabietic acid has been pointed out as suitable biomarker for distinguishing combustion emissions of softwood from hardwood (Fine et al., 2004, 2001; Gelencsér, 2004). However, under atmospheric conditions, this compound may be unstable, suffering degradation by OH radicals (Lai et al., 2015). Thus, its concentrations may not fully represent the impact from softwood burning when used as a tracer in source apportionment studies.

3.4. Conclusions

The effects of pellet quality, based on certification criteria, on gaseous and PM emissions and chemical composition were studied in a top fed pellet stove. Three pellet brands were used, including two certified pellets (EN plus A1) and one brand without certification. The combustion of these pellets was studied in the stove under three levels of power output (lowest, medium and highest).

The chemical properties of the three pellets were compared with the ENplus certification requirements. Both brands of certified pellets did not fulfil the ENplus A1 standards regarding the nitrogen content, while one of the certified brands revealed a slightly higher ash content than the quality criterion. Although the ENplus certification scheme includes audits of certified companies, it should be mandatory to producers periodically and randomly analyse samples of biofuels since the quality of the raw material may not be reproducible, compromising the quality of the final product.

The main conclusion that can be withdrawn from this study is that fuel certification does not totally ensure high combustion performance and low emissions. The combustion of two brands of ENplus certified pellets, with identical quality class (A1), resulted in distinct emissions and different behaviour under different operating conditions. Generally, certified pellets P performed better than the other two pellet types. While the combustion of certified pellets R generated the highest CO and TOC emissions, noncertified pellets yielded the highest NO emissions and, under nominal load operation, NH_3 and carbonaceous compounds bound to PM. In fact, both pellets generated emissions surpassing the thresholds set by the Ecodesign directive. Despite the high emissions, the highest power output and lowest excess of air were observed for the combustion of non-certified pellets. On the other hand, the lowest temperatures in the combustion chamber were recorded for certified pellets R. Considering the distinct behavior recorded for each fuel under different loads, it is not possible to point out the optimal operation condition. The pellet stove employed in this study, like most in-use stoves across Europe, is not equipped with a complete control system to measure the fuel supply into the combustion chamber, temperature or flue gas oxygen. The improvement of small-scale technologies for wood pellet combustion might prevent such high variability in emissions due to fluctuations in fuel quality. Further research work should also focus on the physical characteristics of wood pellets and how these parameters affect the combustion conditions and emissions. This information can be valuable to propose stricter thresholds in European legislation to reduce emissions from residential biomass combustion.

Substantial differences were observed in the composition of PM_{10}, depending on the biofuel burned and operating conditions. The combustion of certified pellets P and non-certified pellets generated higher carbonaceous mass fractions in PM_{10} than certified pellets R. PM_{10} was mainly composed of inorganic constituents, which differed quantitatively with the type of pellet and stove operating conditions. Potassium, one of the most abundant water soluble ions, was positively correlated with the combustion chamber temperature for two of the tested fuels. Retene and pyrene were the dominant PAHs in PM_{10} from pellet combustion. Levoglucosan was detected in all samples and the highest mass fraction was recorded for certified pellets R (1.7-2.2 times than non-certified pellets and certified pellets P, respectively). Phenolic compounds were dominated by coniferyl-type lignin pyrolysis products, in accordance with the composition of softwood lignin. Several other polar constituents were quantified in PM_{10} samples also including various types of acids, sterols, and polyols. The contribution of these compounds to the PM_{10} mass varied with the pellet type used.

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References

AEBIOM, 2017. European Bioenergy Outlook. AEBIOM Statistical Report. Brussels.

Alves, C.A., 2008. Characterisation of solvent extractable organic constituents in atmospheric particulate matter: An overview. An. Acad. Bras. Cienc. 80, 21–82. https://doi.org/10.1590/S0001-37652008000100003

Alves, C.A., Oliveira, César, Martins, N., Mirante, F., Caseiro, A., Pio, C., Matos, M., Silva, H.F., Oliveira, Cristina, Camões, F., 2016. Road tunnel, roadside, and urban background measurements of aliphatic compounds in size-segregated particulate matter. Atmos. Res. 168, 139–148. https://doi.org/10.1016/j.atmosres.2015.09.007

Alves, C.A., Vicente, A., Monteiro, C., Gonçalves, C., Evtyugina, M., Pio, C., 2011. Emission of trace gases and organic components in smoke particles from a wildfire in a mixed-evergreen forest in Portugal. Sci. Total Environ. 409, 1466–1475. https://doi.org/10.1016/j.scitotenv.2010.12.025

Alves, C.A., Vicente, E.D., Rocha, S., Vicente, A.M., 2017. Organic tracers in aerosols from the residential combustion of pellets and agro-fuels. Air Qual. Atmos. Health 10, 37–45. https://doi.org/10.1007/s11869-016-0406-3

Arranz, J.I., Miranda, M.T., Montero, I., Sepúlveda, F.J., Rojas, C. V., 2015. Characterization and combustion behaviour of commercial and experimental wood pellets in South West Europe. Fuel 142, 199–207. https://doi.org/10.1016/j.fuel.2014.10.059

Bioenergy Europe, 2018. Bioenergy Europe Statistical Report 2018 - Pellet Report. Brussels.

Boman, C., Nordin, A., Bostro, D., Marcus, O., 2004. Characterization of inorganic particulate matter from residential combustion of pelletized biomass fuels. Energ. Fuel. 18, 338–348.

Boman, C., Pettersson, E., Westerholm, R., Boström, D., Nordin, A., 2011. Stove performance and emission characteristics in residential wood log and pellet combustion, part 1: Pellet stoves. Energ. Fuel. 25, 307–314. https://doi.org/10.1021/ef100774x

Brassard, P., Palacios, J.H., Godbout, S., Bussières, D., Lagacé, R., Larouche, J.P., Pelletier, F., 2014. Comparison of the gaseous and particulate matter emissions from the combustion of agricultural and forest biomasses. Bioresour. Technol. 155, 300–306. https://doi.org/10.1016/j.biortech.2013.12.027

Brunner, T., Obernberger, I., Scharler, R., 2009. Primary measures for low-emission residential wood combustion – Comparison of old with optimised modern systems, in: ETA-Renewable Energies (Ed.), 17th European Biomass Conference & Exhibition. Hamburg.

Carvalho, L., Wopienka, E., Pointner, C., Lundgren, J., Verma, V.K., Haslinger, W., Schmidl, C., 2013. Performance of a pellet boiler fired with agricultural fuels. Appl. Energy 104, 286–296. https://doi.org/10.1016/j.apenergy.2012.10.058

Chen, Y., Zhi, G., Feng, Y., Fu, J., Feng, J., Sheng, G., Simoneit, B.R.T., 2006. Measurements of emission factors for primary carbonaceous particles from residential raw-coal combustion in China. Geophys. Res. Lett. 33, 2–5. https://doi.org/10.1029/2006GL026966

Cheng, Y., Lee, S.C., Ho, K.F., Chow, J.C., Watson, J.G., Louie, P.K.K., Cao, J.J., Hai, X., 2010. Chemically-speciated on-road $PM_{2.5}$ motor vehicle emission factors in Hong Kong. Sci. Total Environ. 408, 1621–1627. https://doi.org/10.1016/j.scitotenv.2009.11.061

Czech, H., Miersch, T., Orasche, J., Abbaszade, G., Sippula, O., Tissari, J., Michalke, B., Schnelle-Kreis, J., Streibel, T., Jokiniemi, J., Zimmermann, R., 2018. Chemical composition and speciation of particulate organic matter from modern residential small-scale wood combustion appliances. Sci. Total Environ. 612, 636–648. https://doi.org/10.1016/j.scitotenv.2017.08.263

Directive 2009/125/EC, 2009. Directive 2009/125/EC of the European Parliament and of the Council of 21 October 2009 establishing a framework for the setting of ecodesign requirements for energy-related products. Official Journal of the European Communities. L 285/10.

Duca, D., Riva, G., Foppa Pedretti, E., Toscano, G., 2014. Wood pellet quality with respect to EN 14961-2 standard and certifications. Fuel 135, 9–14. https://doi.org/10.1016/j.fuel.2014.06.042

EPC, 2013. Handbook for the Certification of Wood Pellets for Heating Purposes, Version 2.0. European Pellet Council (EPC), Brussels, Belgium.

European Commission, 2015. Commission Regulation (EU) 2015/1185 implementing Directive 2009/125/EC of the European Parliament and of the Council with regard to ecodesign requirements for solid fuel local space heaters. Official Journal of the European Union. https://doi.org/http://eur-lex.europa.eu/pri/en/oj/dat/2003/l_285/l_28520031101en00330037.pdf

European Union, 2019. Energy balance sheets - 2017 Data. Publications Office of the European Union, Luxembourg.

Fachinger, F., Drewnick, F., Gieré, R., Borrmann, S., 2017. How the user can influence particulate emissions from residential wood and pellet stoves: Emission factors for different fuels and burning conditions. Atmos. Environ. 158, 216–226. https://doi.org/10.1016/j.atmosenv.2017.03.027

Fine, P.M., Cass, G.R., Simoneit, B.R.T., 2004. Chemical characterization of fine particle emissions from the wood stove combustion of prevalent United States tree species. Environ. Eng. Sci. 21, 387–409. https://doi.org/10.1089/109287504323067021

Fine, P.M., Cass, G.R., Simoneit, B.R.T., 2001. Chemical characterization of fine particle emissions from fireplace combustion of woods grown in the northeastern United States. Environ. Sci. Technol. 35, 2665–2675. https://doi.org/10.1021/es001466k

Fournel, S., Palacios, J., Godbout, S., Heitz, M., 2015a. Effect of additives and fuel blending on emissions and ash-related problems from small-scale combustion of reed canary grass. Agriculture 5, 561–576. https://doi.org/10.3390/agriculture5030561

Fournel, S., Palacios, J.H., Morissette, R., Villeneuve, J., Godbout, S., Heitz, M., Savoie, P., 2015b. Influence of biomass properties on technical and environmental performance of a multi-fuel boiler during on-farm combustion of energy crops. Appl. Energy 141, 247–259. https://doi.org/10.1016/j.apenergy.2014.12.022

Garcia-Maraver, A., Zamorano, M., Fernandes, U., Rabaçal, M., Costa, M., 2014. Relationship between fuel quality and gaseous and particulate matter emissions in a domestic pellet-fired boiler. Fuel 119, 141–152. https://doi.org/10.1016/j.fuel.2013.11.037

Gelencsér, A., 2004. Carbonaceous Aerosol. Springer, Dordrecht, The Netherlands.

Jeguirim, M., Kraiem, N., Lajili, M., Guizani, C., Zorpas, A., Leva, Y., Michelin, L., Josien, L., Limousy, L., 2017. The relationship between mineral contents, particle matter and bottom ash distribution during pellet combustion: molar balance and chemometric analysis. Environ. Sci. Pollut. Res. 24, 9927–9939. https://doi.org/10.1007/s11356-017-8781-3

Kawamura, K., Bikkina, S., 2016. A review of dicarboxylic acids and related compounds in atmospheric aerosols: Molecular distributions, sources and transformation. Atmos. Res. 170, 140–160. https://doi.org/10.1016/j.atmosres.2015.11.018

Knudsen, J.N., Jensen, P.A., Dam-Johansen, K., 2004. Transformation and Release to the Gas Phase of Cl, K, and S during Combustion of Annual Biomass. Energ. Fuel. 18, 1385–1399. https://doi.org/10.1021/ef049944q

Kuo, L.J., Herbert, B.E., Louchouarn, P., 2008. Can levoglucosan be used to characterize and quantify char/charcoal black carbon in environmental media? Org. Geochem. 39, 1466–1478. https://doi.org/10.1016/j.orggeochem.2008.04.026

Lai, C., Liu, Y., Ma, J., Ma, Q., He, H., 2015. Laboratory study on OH-initiated degradation kinetics of dehydroabietic acid. Phys. Chem. Chem. Phys. 17, 10953–10962. https://doi.org/10.1039/c5cp00268k

Lamberg, H., Nuutinen, K., Tissari, J., Ruusunen, J., Yli-Pirilä, P., Sippula, O., Tapanainen, M., Jalava, P., Makkonen, U., Teinilä, K., Saarnio, K., Hillamo, R., Hirvonen, M.R., Jokiniemi, J., 2011. Physicochemical characterization of fine particles from small-scale wood combustion. Atmos. Environ. 45, 7635–7643. https://doi.org/10.1016/j.atmosenv.2011.02.072

Lamberg, H., Tissari, J., Jokiniemi, J., Sippula, O., 2013. Fine particle and gaseous emissions from a small-scale boiler fueled by pellets of various raw materials. Energ. Fuel. 27, 7044–7053. https://doi.org/10.1021/ef401267t

Mack, R., Kuptz, D., Schön, C., Hartmann, H., 2019. Combustion behavior and slagging tendencies of kaolin additivated agricultural pellets and of wood-straw pellet blends in a small-scale boiler. Biomass Bioenergy 125, 50–62. https://doi.org/10.1016/j.biombioe.2019.04.003

Martinopoulos, G., Papakostas, K.T., Papadopoulos, A.M., 2018. A comparative review of heating systems in EU countries, based on efficiency and fuel cost. Renew. Sustain. Energy Rev. 90, 687–699. https://doi.org/10.1016/j.rser.2018.03.060

Nussbaumer, T., 2003. Combustion and co-combustion of biomass: Fundamentals, technologies, and primary measures for emission reduction. Energ. Fuel. 17, 1510–1521. https://doi.org/10.1021/ef030031q

Nyström, R., Lindgren, R., Avagyan, R., Westerholm, R., Lundstedt, S., Boman, C., 2017. Influence of wood species and burning conditions on particle emission characteristics in a residential wood stove. Energ. Fuel. 31, 5514–5524. https://doi.org/10.1021/acs.energyfuels.6b02751

Obernberger, I., Brunner, T., Bärnthaler, G., 2006. Chemical properties of solid biofuels-significance and impact. Biomass Bioenergy 30, 973–982. https://doi.org/10.1016/j.biombioe.2006.06.011

Obernberger, I., Thek, G., 2010. The Pellet Handbook. The production and thermal utilisation of biomass pellets. Earthscan, London, Washington, DC.

Obernberger, I., Thek, G., 2006. Recent developments concerning pellet combustion technologies – a review of Austrian developments, in: Proceedings of the 2nd World Conference on Pellets. Stockholm, Sweden, pp. 31–40.

Obernberger, I., Thek, G., 2004. Physical characterisation and chemical composition of densified biomass fuels with regard to their combustion behaviour. Biomass Bioenergy 27, 653–669. https://doi.org/10.1016/j.biombioe.2003.07.006

Öhman, M., Boman, C., Hedman, H., Nordin, A., Boström, D., 2004. Slagging tendencies of wood pellet ash during combustion in residential pellet burners. Biomass Bioenergy 27, 585–596. https://doi.org/10.1016/j.biombioe.2003.08.016

Orasche, J., Schnelle-Kreis, J., Schön, C., Hartmann, H., Ruppert, H., Arteaga-Salas, J.M., Zimmermann, R., 2013. Comparison of emissions from wood combustion. Part 2: Impact of combustion conditions on emission factors and characteristics of particle-bound organic species and polycyclic aromatic hydrocarbon (PAH)-related toxicological potential. Energ. Fuel. 27, 1482–1491. https://doi.org/10.1021/ef301506h

Orasche, J., Seidel, T., Hartmann, H., Schnelle-Kreis, J., Chow, J.C., Ruppert, H., Zimmermann, R., 2012. Comparison of emissions from wood combustion. Part 1: Emission factors and characteristics from different small-scale residential heating appliances considering particulate matter and polycyclic aromatic hydrocarbon (PAH)-related toxicological potential of particle-bound organic species. Energ. Fuel. 26, 6695–6704. https://doi.org/10.1021/ef301295k

Oros, D.R., Abas, M.R. bin, Omar, N.Y.M.J., Rahman, N.A., Simoneit, B.R.T., 2006. Identification and emission factors of molecular tracers in organic aerosols from biomass burning: Part 3. Grasses. Appl. Geochem. 21, 919–940. https://doi.org/10.1016/J.APGEOCHEM.2006.01.008

Oros, D.R., Simoneit, B.R., 2001a. Identification and emission factors of molecular tracers in organic aerosols from biomass burning Part 2. Deciduous trees. Appl. Geochem. 16, 1545–1565. https://doi.org/10.1016/S0883-2927(01)00022-1

Oros, D.R., Simoneit, B.R.T., 2001b. Identicfiation and emission factors of molecular tracers in organic aerosols from biomass burning Part 1. Temperate climate conifers, Appl. Geochem. https://doi.org/http://dx.doi.org/10.1016/S0883-2927(01)00021-X

Ozgen, S., Caserini, S., Galante, S., Giugliano, M., Angelino, E., Marongiu, A., Hugony, F., Migliavacca, G., Morreale, C., 2014. Emission factors from small scale appliances burning wood and pellets. Atmos. Environ. 94, 144–153. https://doi.org/10.1016/j.atmosenv.2014.05.032

Pettersson, E., Boman, C., Westerholm, R., Boström, D., Nordin, A., 2011. Stove performance and emission characteristics in residential wood log and pellet combustion, part 2: Wood stove. Energ. Fuel. 25, 315–323. https://doi.org/10.1021/ef1007787

Pflieger, M., Kroflič, A., 2017. Acute toxicity of emerging atmospheric pollutants from wood lignin due to biomass burning. J. Hazard. Mater. 338, 132–139. https://doi.org/10.1016/j.jhazmat.2017.05.023

Pio, C., Cerqueira, M., Harrison, R.M., Nunes, T., Mirante, F., Alves, C., Oliveira, C., Sanchez de la Campa, A., Artíñano, B., Matos, M., 2011. OC/EC ratio observations in Europe: Re-thinking the approach for apportionment between primary and secondary organic carbon. Atmos. Environ. 45, 6121–6132. https://doi.org/10.1016/j.atmosenv.2011.08.045

Pollex, A., Zeng, T., Khalsa, J., Erler, U., Schmersahl, R., Schön, C., Kuptz, D., Lenz, V., Nelles, M., 2018. Content of potassium and other aerosol forming elements in commercially available wood pellet batches. Fuel 232, 384–394. https://doi.org/10.1016/j.fuel.2018.06.001

Polonini, L.F., Petrocelli, D., Parmigiani, S.P., Lezzi, A.M., 2019. Influence on CO and PM emissions of an innovative burner pot for pellet stoves: An experimental study. Energies 12, 1–13. https://doi.org/10.3390/en12040590

Rabaçal, M., Fernandes, U., Costa, M., 2013. Combustion and emission characteristics of a domestic boiler fired with pellets of pine, industrial wood wastes and peach stones. Renew. Energy 51, 220–226. https://doi.org/10.1016/j.renene.2012.09.020

Ramdahl, T., 1983. Retene - a molecular marker of wood combustion in ambient air. Nature 306, 580–582. https://doi.org/10.1038/306580a0

Riva, G., Pedretti, E.F., Toscano, G., Duca, D., Pizzi, A., 2011. Determination of polycyclic aromatic hydrocarbons in domestic pellet stove emissions. Biomass Bioenergy 35, 4261–4267. https://doi.org/10.1016/j.biombioe.2011.07.014

Sandro, N., Agis, P., Gojmir, R., Vlasta, Z., Müslüm, A., 2019. Using pellet fuels for residential heating: A field study on its efficiency and the users' satisfaction. Energy Build. 184, 193–204. https://doi.org/10.1016/j.enbuild.2018.12.007

Schmidl, C., Luisser, M., Padouvas, E., Lasselsberger, L., Rzaca, M., Ramirez-Santa Cruz, C., Handler, M., Peng, G., Bauer, H., Puxbaum, H., 2011. Particulate and gaseous emissions from manually and automatically fired small scale combustion systems. Atmos. Environ. 45, 7443–7454. https://doi.org/10.1016/j.atmosenv.2011.05.006

Schmidl, C., Marra, I.L., Caseiroa, A., Kotianová, P., Berner, A., Bauer, H., Kasper-Giebl, A., Puxbaum, H., 2008. Chemical characterisation of fine particle emissions from wood stove combustion of common woods growing in mid-European Alpine regions. Atmos. Environ. 42, 126–141. https://doi.org/10.1016/j.atmosenv.2007.09.028

Schmidt, G., Trouvé, G., Leyssens, G., Schönnenbeck, C., Genevray, P., Cazier, F., Dewaele, D., Vandenbilcke, C., Faivre, E., Denance, Y., Le Dreff-Lorimier, C., 2018. Wood washing: Influence on gaseous and particulate emissions during wood combustion in a domestic pellet stove. Fuel Process. Technol. 174, 104–117. https://doi.org/10.1016/j.fuproc.2018.02.020

Shen, G., Tao, S., Wei, S., Zhang, Y., Wang, R., Wang, B., Li, W., Shen, H., Huang, Y., Yang, Y., Wang, W., Wang, X., Simonich, S.L.M., 2012. Retene emission from residential solid fuels in China and evaluation of retene as a unique marker for soft wood combustion. Environ. Sci. Technol. 46, 4666–4672. https://doi.org/10.1021/es300144m

Simoneit, B.R., 2002. Biomass burning - a review of organic tracers for smoke from incomplete combustion, Appl. Geochem. https://doi.org/10.1016/S0883-2927(01)00061-0

Simoneit, B.R.T., Schauer, J.J., Nolte, C.G., Oros, D.R., Elias, V.O., Fraser, M.P., Rogge, W.F., Cass, G.R., 1999. Levoglucosan, a tracer for cellulose in biomass burning and atmospheric particles. Atmos. Environ. 33, 173–182. https://doi.org/10.1016/S1352-2310(98)00145-9

Sippula, O., Hytönen, K., Tissari, J., Raunemaa, T., Jokiniemi, J., 2007. Effect of wood fuel on the emissions from a top-feed pellet stove. Energ. Fuel. 21, 1151–1160. https://doi.org/10.1021/ef060286e

Thomson, H., Liddell, C., 2015. The suitability of wood pellet heating for domestic households: A review of literature. Renew. Sustain. Energy Rev. 42, 1362–1369. https://doi.org/10.1016/j.rser.2014.11.009

Tissari, J., Sippula, O., Kouki, J., Vuorio, K., Jokiniemi, J., 2008. Fine particle and gas emissions from the combustion of agricultural fuels fired in a 20 kW burner. Energ. Fuel. 22, 2033–2042. https://doi.org/10.1021/ef700766y

Van Lith, S.C., Alonso-Ramírez, V., Jensen, P.A., Frandsen, F.J., Glarborg, P., 2006. Release to the gas phase of inorganic elements during wood combustion. Part 1: Development and evaluation of quantification methods. Energ. Fuel. 20, 964–978. https://doi.org/10.1021/ef050131r

Vassilev, S. V., Baxter, D., Andersen, L.K., Vassileva, C.G., 2010. An overview of the chemical composition of biomass. Fuel 89, 913–933. https://doi.org/10.1016/j.fuel.2009.10.022

Venturini, E., Vassura, I., Agostini, F., Pizzi, A., Toscano, G., Passarini, F., 2018. Effect of fuel quality classes on the emissions of a residential wood pellet stove. Fuel 211, 269–277. https://doi.org/10.1016/j.fuel.2017.09.017

Venturini, E., Vassura, I., Zanetti, C., Pizzi, A., Toscano, G., Passarini, F., 2015. Evaluation of non-steady state condition contribution to the total emissions of residential wood pellet stove. Energy 88, 650–657. https://doi.org/10.1016/j.energy.2015.05.105

Verma, V.K., Bram, S., Delattin, F., De Ruyck, J., 2013. Real life performance of domestic pellet boiler technologies as a function of operational loads: A case study of Belgium. Appl. Energy 101, 357–362. https://doi.org/10.1016/j.apenergy.2012.02.017

Verma, V.K., Bram, S., Delattin, F., Laha, P., Vandendael, I., Hubin, A., De Ruyck, J., 2012. Agro-pellets for domestic heating boilers: Standard laboratory and real life performance. Appl. Energy 90, 17–23. https://doi.org/10.1016/j.apenergy.2010.12.079

Verma, V.K., Bram, S., Vandendael, I., Laha, P., Hubin, A., De Ruyck, J., 2011. Residential pellet boilers in Belgium: Standard laboratory and real life performance with respect to European standard and quality labels. Appl. Energy 88, 2628–2634. https://doi.org/10.1016/j.apenergy.2011.02.004

Vicente, A., Alves, C., Monteiro, C., Nunes, T., Mirante, F., Cerqueira, M., Calvo, A., 2012. Organic speciation of aerosols from wild fi res in central Portugal during summer 2009. Atmos. Environ. 57, 186–196. https://doi.org/10.1016/j.atmosenv.2012.04.030

Vicente, A., Alves, C., Monteiro, C., Nunes, T., Mirante, F., Evtyugina, M., Cerqueira, M., Pio, C., 2011. Measurement of trace gases and organic compounds in the smoke plume from a wildfire in Penedono (central Portugal). Atmos. Environ. 45, 5172–5182. https://doi.org/10.1016/j.atmosenv.2011.06.021

Vicente, E.D., Alves, C.A., 2018. An overview of particulate emissions from residential biomass combustion. Atmos. Res. 199, 159–185. https://doi.org/10.1016/j.atmosres.2017.08.027

Vicente, E.D., Duarte, M.A., Tarelho, L.A.C., Nunes, T.F., Amato, F., Querol, X., Colombi, C., Gianelle, V., Alves, C.A., 2015. Particulate and gaseous emissions from the combustion of different biofuels in a pellet stove. Atmos. Environ. 120, 15–27. https://doi.org/10.1016/j.atmosenv.2015.08.067

Vicente, E.D., Vicente, A., Evtyugina, M., Carvalho, R., Tarelho, L.A.C., Oduber, F.I., Alves, C., 2018. Particulate and gaseous emissions from charcoal combustion in barbecue grills. Fuel Process. Technol. 176, 296–306. https://doi.org/10.1016/j.fuproc.2018.03.004

Vicente, E.D., Vicente, A.M., Evtyugina, M., Carvalho, R., Tarelho, L.A.C., Paniagua, S., Nunes, T., Otero, M., Calvo, L.F., Alves, C., 2019. Emissions from residential pellet combustion of an invasive acacia species. Renew. Energy 140, 319–329. https://doi.org/10.1016/j.renene.2019.03.057

Vicente, E.D., Vicente, A.M., Musa Bandowe, B.A., Alves, C.A., 2016. Particulate phase emission of parent polycyclic aromatic hydrocarbons (PAHs) and their derivatives (alkyl-PAHs, oxygenated-PAHs, azaarenes and nitrated PAHs) from manually and automatically fired combustion appliances. Air Qual. Atmos. Health 9, 653–668. https://doi.org/10.1007/s11869-015-0364-1

Wang, B., Lee, S.C., Ho, K.F., Kang, Y.M., 2007. Characteristics of emissions of air pollutants from burning of incense in temples, Hong Kong. Sci. Total Environ. 377, 52–60. https://doi.org/10.1016/j.scitotenv.2007.01.099

Win, K.M., Persson, T., 2014. Emissions from residential wood pellet boilers and stove characterized into start-up, steady operation, and stop emissions. Energ. Fuel. 28, 2496–2505. https://doi.org/10.1021/ef4016894

Wöhler, M., Jaeger, D., Reichert, G., Schmidl, C., Pelz, S.K., 2017. Influence of pellet length on performance of pellet room heaters under real life operation conditions. Renew. Energy 105, 66–75. https://doi.org/10.1016/j.renene.2016.12.047

Zeng, T., Weller, N., Pollex, A., Lenz, V., 2016. Blended biomass pellets as fuel for small scale combustion appliances: Influence on gaseous and total particulate matter emissions and applicability of fuel indices. Fuel 184, 689–700. https://doi.org/10.1016/j.fuel.2016.07.047

Zhang, Y., Obrist, D., Zielinska, B., Gertler, A., 2013. Particulate emissions from different types of biomass burning. Atmos. Environ. 72, 27–35. https://doi.org/10.1016/j.atmosenv.2013.02.026

Zhao, Y., Hu, M., Slanina, S., Zhang, Y., 2007. Chemical compositions of fine particulate organic matter emitted from Chinese cooking. Environ. Sci. Technol. 41, 99–105

CHAPTER 4

Chapter 4. Emissions from residential pellet combustion of an invasive acacia species

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Abstract

Currently, different types of raw materials are under investigation to fulfil the demand for pellet based renewable energy. The aim of this study was to experimentally quantify and characterise the gaseous and particulate matter (PM_{10}) emissions from the combustion of a pelletised invasive species growing in the Portuguese coastal areas. The combustion of acacia pellets in a stove used for domestic heating led to a noticeable production of environmentally relevant contaminants, such as carbon monoxide (CO, 2468 ± 485mgMJ^{-1}), sulphur dioxide (SO_2, 222 ± 115mg MJ^{-1}) and nitrogen oxides (NO_x, 478 ± 87 mg MJ^{-1}). Besides gaseous pollutant emissions, substantial particle emissions (118 ± 14 mg MJ^{-1}) were also generated. Particles consisted mostly of inorganic matter, mainly alkaline metals, sulphur and chlorine. About 25%wt. of the PM_{10} emitted had carbonaceous nature. The chromatographically resolved organic compounds were dominated by anhydrosugars, especially levoglucosan (284 µg g^{-1} PM_{10}), and several types of phenolic compounds. Retene (8.77 µg g^{-1} PM_{10}) was the chief compound among polyaromatic hydrocarbons.

Keywords: Acacia, Gaseous emissions, PM_{10}, OC/EC, Organic markers, Pellet stove

4.1. Introduction

Policies to increase the use of renewable energy are driving the demand and supply for wood pellets. Between 2015 and 2016, the production of wood pellets increased from 28 to 29 million tonnes and was concentrated almost entirely in Europe and North America (FAO, 2017). Europe is placed first worldwide in terms of wood pellet production and is even expected to further increase this advantage (Chrystelle and Ryckmans, 2012). Since 2007, pellet production in Portugal has also grown considerably with *Pinus pinaster* roundwood as the main raw material used in manufacturing (Nunes and Freitas, 2016). Apart from the recognised advantages of pelleting of biomass fuels, (Patzek and Pimentel, 2005) the wood pellet based bioenergy market has been causing economic and environmental concerns mainly due to its effect on forest ecosystems and their associated services (Dale et al., 2017; Parish et al., 2018). Despite this major emergent issue related to sustainability of the wood sourcing, the increasing demand for wood pellets is not expected to change in the near future (Goetzl, 2015). However, in certain countries of the European Union, it is highly compensatory to produce electric energy from biomass and the conversion of coal-fuelled power plants to solely biomass burning units is already a reality (Zakeri et al., 2015). The increasing use of such fuels in small units for domestic heating has instigated a wealth of publications focused on the characterisation of emissions from wood pellet combustion (Kistler et al., 2012; Vicente et al., 2015; Win and Persson, 2014). Additionally, the shortage of conventional raw materials and the availability of some unconventional pellet feedstocks prompted the investigation of alternatives including agricultural wastes, herbaceous biomass, waste paper, sludge, among others (Bernhardt et al., 2012; Miranda et al., 2015; Pizzi et al., 2018; Setiawan and Surachman, 2015; Wang et al., 2011). The main features affecting emissions from pellet combustion are related to the fuel physicochemical characteristics. Regarding the chemical composition, the raw materials selected for pellet production are of utmost importance (Arranz et al., 2015; Carvalho et al., 2013; Garcia-Maraver et al., 2014). Additionally, the pellets length and diameter, fine content and particle density are also of extreme importance since such physical aspects regulate the fuel feeding to the burner and, thus, can remarkably affect the emissions (Verma et al., 2012; Wöhler et al., 2017).

Invasive tree species could provide a bioenergy source and offer an opportunity to reduce the eradication costs of such species (Carneiro et al., 2014). Across the world, trees and shrubs have been introduced and have invaded many habitats causing impacts on the ecosystems (Wilson et al., 2011). Biomass pelletisation can increase the energy density of biomass, improve storability and reduce handling and transport costs. This process is a crucial factor in the transition from fossil fuels to refined renewable biofuels (Telmo and Lousada, 2011). In Portugal, exotic plants have increased during the last two centuries representing more than 15% of the country's flora (De Almeida and Freitas, 2001). The area occupied by acacia in this county significantly increased over the last decades almost doubling between 1995 and 2010 (ICNF, 2013). Acacias were introduced in Portugal over one hundred years ago in order to control coastal erosion. However, the species has spread and is now threating the native flora and becoming an environmental issue (Marchante et al., 2008). The clearance of long term invaded areas is a challenge since the accumulation of seeds allows the rapid reinvasion of the species after its control (Marchante et al., 2004). Carneiro et al. (2014) studied the potential of using acacias as bioenergy source and reported that one of the investigated species of the genus had a biomass production 1.8-3.4 times higher than that of eucalypt (*Eucalyptus globulus*) 1 year after planting, and almost 5 times in the second year.

The interest in using invasive acacia as source of bioenergy has been raised in previous studies. Ferreira et al. (2013) and Almeida and Pereira (2014) assessed the combustion and emission characteristics from acacia pellets in a pellet boiler and in a fluidised bed reactor, respectively. However, the PM emissions were overlooked, since these studies were focused on gaseous emissions and operating conditions of the combustion devices. Another previous study evaluated particulate emissions from the combustion of *Acacia longifolia* firewood in a residential appliance operated in batch mode, concluding that the emission characteristics are quite different from those recorded from the combustion of autochthonous species (Gonçalves et al., 2010). In fact, the gaseous emissions generated during combustion of pelletised fuels are quite different from those of uncompressed materials, as outlined by Fournel et al. (2015b) and Shen et al. (2012). Therefore, there is still a lack of knowledge concerning the combustion-related emissions from pellets of acacia, taking into account its potential as source of bioenergy. The aim of this study was to experimentally quantify and characterise the particulate and gaseous emissions from the combustion of acacia pellets in a residential stove in order to assess the suitability of this specific invasive species for pellet production.

4.2. Methodology

4.2.1. Combustion infrastructure, fuel and experimental procedure

The combustion experiments were carried out using a top-feed pellet stove manufactured by Solzaima (model Alpes). The pellets are filled into a storage tank through a hatch on the top of the pellet stove and supplied by means of an auger screw from the internal fuel storage to the burner pot. An electrical device allows the ignition of the pellets during the stove start-up phase. The activation phase was not included in the results. An intake at the back of the stove provides the combustion air to the combustion chamber, which is driven by an electric fan. The primary air is supplied through holes in the bottom of the grate, and secondary air is fed above the grate through three holes. The primary air flow rate was monitored continuously during the combustion process using a mass flow meter. The flue gas temperature was measured continuously using K-type thermocouples located at several points along the combustion and exhaust system, including in the combustion chamber, at the pellet stove exit (flue gas exhaust to chimney, after the exhaust gas fan) and at the exit of the chimney (Table 4.1).

Table 4.1. Flue gas temperature in the combustion chamber, at the pellet stove exit (flue gas exhaust to chimney) and at the exit of the chimney.

	Combustion chamber (°C)	Exhaust of the stove, after the exhaust gases fan (°C)	Exit of the chimney (°C)
Average	468 ± 82.2	144 ± 11.1	55.5 ± 1.66
Maximum	641 ± 51.7	158 ± 5.76	57.0 ± 1.12
Minimum	298 ± 134	123 ± 24.6	53.0 ± 4.41

The combustion flue gas flow rate through the chimney was calculated by monitoring the gas velocity with a Pitot tube (Testo AG 808). A schematic description of the combustion facility can be found elsewhere (Vicente et al., 2015).

The pellet stove used in the present study has automated loading process allowing the control of the heat output by adjusting the pellets feed rate. The power output, as well as the air flow from the heat exchanger, can be adjusted at five different levels. The average condition, fan level 3, was chosen to perform the combustion experiments. The fuel feed rate, determined by prior calibration of the screw feeding system, was 0.86 ± 0.05 kg h^{-1}.

The gaseous and particulate emission factors (EFs) are presented in milligrams of pollutant per MJ of fuel supplied to the burner. The fuel mass based emission factor, defined as the mass of pollutant emitted per unit fuel mass, was converted to energy based EF through the fuel heating value.

Samples of acacia (*Acacia longifolia*) were collected, processed and pelletised in a low duty machine. The whole tree (including bark, tree tops and branches) was used as raw material in this study. The feedstock was first ground and subsequently compressed to produce pellets of 6 mm in diameter without adding binders. The determination of fuel properties included moisture, ash content, volatile matter, C, H, N, and S and calorific value (Table 4.2).

Table 4.2. Proximate and ultimate analysis of the acacia pellets used as fuel in the combustion experiments.

Proximate analysis	Unit	Acacia pellets	Reference method
Moisture	wt.%, as received	10.4	ISO 18134-1:2015[a]
Ash	wt.%, dry basis	2.09	ISO 18122:2015[b]
Volatile matter		79.9	ISO 18123:2015[c]
Fixed carbon (by difference)		18.0~~1~~	
Ultimate analysis			
C	wt.%, dry basis	49.6	ISO 16948:2015[d]
H		5.81	
N		1.39	
S		0.09	ISO 16994:2016[e]
O (by difference)		41.0	
Lower heating value	MJ kg^{-1}	18.4	ISO 18125:2017[f]

[a] Solid biofuels - Determination of moisture content - Oven dry method - Part 1: Total moisture - Reference method.

[b] Solid biofuels - Determination of ash content.

[c] Solid biofuels - Determination of the content of volatile matter ash content.

[d] Solid biofuels - Determination of total content of carbon, hydrogen and nitrogen.

[e] Solid biofuels - Determination of total content of sulphur and chlorine.

[f] Solid biofuels - Determination of calorific value.

The properties of the acacia pellets produced in the present study were compared with the quality requirements for wood pellets for small scale use described in ISO 17225-2 (Solid biofuels - Fuel specifications and classes: Graded wood pellets). Regarding the moisture, ash, nitrogen and sulphur content, the acacia pellets used in the present study do not fit the standard requirements for any of the ISO 17225-2 quality classes.

4.2.2. Gas sampling and measurement techniques

A Fourier transform infrared spectrometer (FTIR, Gasmet, CX4000) was used for continuous monitoring of the flue gas composition. To carry out the flue gas sampling, a probe equipped with a mineral wool filter at the tip, to prevent the entrance of particles, was inserted at the chimney. The gas sampled was conducted to the emission monitoring system via a heated sampling line (at 180 °C) to prevent condensation of gaseous compounds in the flue gas.

4.2.3. Particulate matter sampling and analysis

Particulate matter collection was carried out in a dilution tunnel (hood dilution system), under isokinetic sampling conditions, using two TCR TECORA in parallel, each one operated at

2.3 m^3 h^{-1} (normal temperature and pressure conditions). The mean gas velocity in the dilution tunnel was monitored by a Pitot tube (Testo AG 808), whereas temperature was measured using a K-type thermocouple. After adjusting the stove heat level output, the flue gas composition was monitored in order to evaluate the steady state operating condition. Under steady conditions, two samples of particles were collected simultaneously for 20 min. This procedure was repeated four times.

The PM_{10} samples were collected on 47 mm diameter quartz fibre filters (Pallflex®) pre-baked at 500 °C for 6 h. The filters were conditioned for around 24 h in a room with controlled humidity and temperature before the gravimetric quantification. The filter weighing was performed with a microbalance (RADWAG 5/2Y/F) and obtained from the average of six measurements (relative standard deviation less than 0.02%).

Two filter punches of 9 mm were used to quantify the organic (OC) and elemental carbon (EC) content in each sampled filter by a thermal optical transmission technique. The filter punches were first subjected to a controlled heating in a non-oxidising nitrogen atmosphere in order to volatilise the OC. The second step consisted of the EC oxidation in a nitrogen and oxygen atmosphere. The filter light transmittance measurement allows separating the EC formed by OC pyrolysis during the first step from the one that was originally in the sample. The CO_2 released from the thermal volatilisation and oxidation of different carbon fractions was quantified by a non-dispersive infrared analyser.

Two filter punches of 9 mm from each filter were extracted with 1.5 ml of ultrapure Milli-Q water by ultrasonic agitation (15 + 15 min) and then filtered through a 13 mm PVDF syringe filter (Whatman™). The extracts were injected in a dual-system ion chromatograph (DIONEX, ICS-5000 + DC, USA) with conductance detector (ICS-5000). A DIONEX Ionpac AS11-HC-4 µm (2 × 250 mm) and a DIONEX Ionpac CS16 analytical (3 × 250 mm) column were used for the analysis of anions and cations, respectively. A detailed description of the method and the system can be found elsewhere (Vicente et al., 2018).

Portions of the filters were combined and extracted for 24 h with 300 ml of dichloromethane and then three times with methanol in an ultrasonic bath (25 ml for 10 min, each extraction). After each extraction, the extracts were combined and filtered. The total organic extract was concentrated and then separated into five different organic fractions on an activated (at 150 °C during 3 h) silica gel column using solvents of increasing polarity. After elution, the different organic fractions were vacuum concentrated and dried. The extracts were analysed by gas chromatography-mass spectrometry (GC-MS). Before the chromatographic analysis, the organic fractions corresponding to alcohols, sterols and sugars/acids, were subjected to a derivatisation process (silylation) using N,O-bis(trimethylsilyl)-trifluoroacetamide (BSTFA).

4.3. Results and discussion

4.3.1. Gaseous emission factors

The CO EF from the combustion of acacia pellets in the small-scale stove was, on average, 2468 ± 485 mg MJ^{-1}. In a previous study, performed with the same combustion appliance, CO EFs ranging from 90.9 to 740 mg MJ^{-1} were reported for four different types of wood pellets (Vicente et al., 2015), which were 3-26-fold lower than the EF generated from the acacia pellets of the present study. Under proper combustion conditions, on a well-designed combustion appliance, low CO emissions are expected from wood pellets, mainly due to the fuel homogeneity and low moisture content (Perez-Jimenez, 2015). However, large ranges are observed in the literature regarding the CO emitted from the combustion of pellets (Table 4.3). Wöhler et al. (2017) evaluated the effect of pellet length on the performance of pellet stoves under real life operation conditions and reported significant variation in gaseous and particulate emissions as a function of the studied physical parameter. Venturini et al. (2018) investigated the influence of pellet quality on pollutant emissions from a stove at partial and nominal load. The authors reported CO EFs ranging from 176 to 1117 mg MJ^{-1}, depending on stove operating condition and pellet quality. Aiming at studying the effect of fuel washing pre-treatment on emissions, Schmidt et al. (2018) burned pellets made of raw and washed woods (oak, beech and fir) on a pellet stove. The authors reported a reduction on CO emissions (between 31 and 51%) due to the washing process for all the pellets under analysis. The CO emissions observed here are much higher than those obtained in other studies for the combustion of wood pellets (Table 4.3). The average CO EF obtained in this study was similar to the one reported by Sippula et al. (2007) for the combustion of willow bark pellets in a top feed pellet burner and lower than the EFs reported by Gonçalves et al. (2012) for the combustion of acacia logs in batch operated combustion appliances (woodstove and fireplace). CO EFs, as well as other products from incomplete combustion, for the burning of pelletised biofuels are significantly lower than those recorded for the burning of their raw materials, as underlined by Shen et al. (2012) and Fournel et al. (2015b).

Table 4.3. Comparison between CO and NO_x EFs data from literature about residential biomass combustion and results of the present study.

Appliance	Fuel	CO (mg MJ^{-1})	NO_x (mg MJ^{-1})	Reference
Pellet stove	Acacia pellets	2468 ± 485	478 ± 87.3[a]	This study
	DIN+ pellets	193 ± 12	80 ± 20	Schmidt et al. (2018)
	Fir pellets	330 ± 15	73 ± 25	
	Washed fir pellets	225 ± 22	70 ± 34	
	Beech pellets	520 ± 16	130 ± 26	
	Washed beech pellets	396 ± 22	120 ± 35	
	Oak pellets	461 ± 18	147 ± 30	
	Washed oak pellets	239 ± 17	136 ± 28	
	Commercial pellets	142 ± 42	56 ± 16	Sippula et al. (2007)
	Birch bark pellets	604 ± 287	156 ± 74	
	Birch stem pellets	283 ± 68	78 ± 19	
	Spruce bark pellets	1926 ± 467	189 ± 46	
	Spruce stem pellets	194 ± 60	95 ± 28	
	Alder bark pellets	1013 ± 235	227 ± 53	
	Alder stem pellets	237 ± 60	123 ± 31	
	Pine bark pellets	444 ± 94	131 ± 28	
	Pine stem pellets	150 ± 29	82 ± 16	
	Willow bark pellets	2564 ± 675	282 ± 74	
	Willow stem pellets	339 ± 90	103 ± 28	
	EN plus A1 pellets	400 ± 60	55 ± 6[a]	Fachinger et al. (2017)
	70% softwood and 30% hardwood pellets	430 ± 60	75 ± 8[a]	
Hybrid stove	Birch wood logs	1200 - 4000	81 – 120[a]	Lamberg et al. (2017)
	Commercial softwood pellets	420 - 1430	42 – 60[a]	
Woodstove	Acacia wood logs	5361 ±1333	N/A	Gonçalves et al. (2012)
Fireplace		3433 ± 211	N/A	

[a] NO_x expressed as NO_2; N/A: information not available.

In the present study, the average NO_x EF (expressed as NO_2), was 478 ± 87.3 mg MJ^{-1}, which is far above the average EFs published by other authors for pellet combustion (Table 4.3). High NO_x emissions for the combustion of non-native *Acacia dealbata* pellets in a pellet boiler have been reported in a previous study (Ferreira et al., 2013). According to the same study, acacia pellets emitted 5 times higher NO_x than pine pellets. NO_x emissions from biomass combustion are mainly related to the fuel nitrogen content (Perez-Jimenez, 2015). It is worthy to note that the nitrogen content of the pellets used in the present study was 1.39 %wt (Table 4.2). Sippula et al. (2007) tested the combustion of pellets made of separate stem and bark materials of five different wood species and a commercial type of pellets. The lowest NO_x emissions were measured for commercial and stem pellets (56-123 mg MJ^{-1}). For bark pellets, the NO_x emissions were slightly higher, ranging from 131 to 282 mg MJ^{-1}. Fournel et al. (2015b) reported NO_x emissions ranging from 77 mg MJ^{-1} (wood pellets) to 299 mg MJ^{-1} (chopped miscanthus).

Regarding the total organic carbon (TOC) EF (71.96 ± 25.78 gC MJ^{-1}), the main compounds contributing to this emission were methane (25.7%), formaldehyde (24.5%) and ethane (24.0%). EFs of selected hydrocarbons are displayed in Fig. 4.1. In the present study, a good correlation was found between TOC and CO emissions ($r^2 = 0.98$). The CH_4 EF recorded in the present study was 25.39 ± 10.95 mg MJ^{-1}. Fournel et al. (2015b) reported CH_4 EF ranging from 0.7 to 2.9 mg MJ^{-1} for pelletised fuels and from 2.9 to 38.2 mg MJ^{-1} for the combustion of chopped biomass fuels in a multi-fuel boiler. CH_4 EFs ranging from 0.23 ± 0.03 (wood pellets) to 28.7 ± 5.7 (agricultural fuels) mg MJ^{-1} were reported by Vicente et al. (2015).

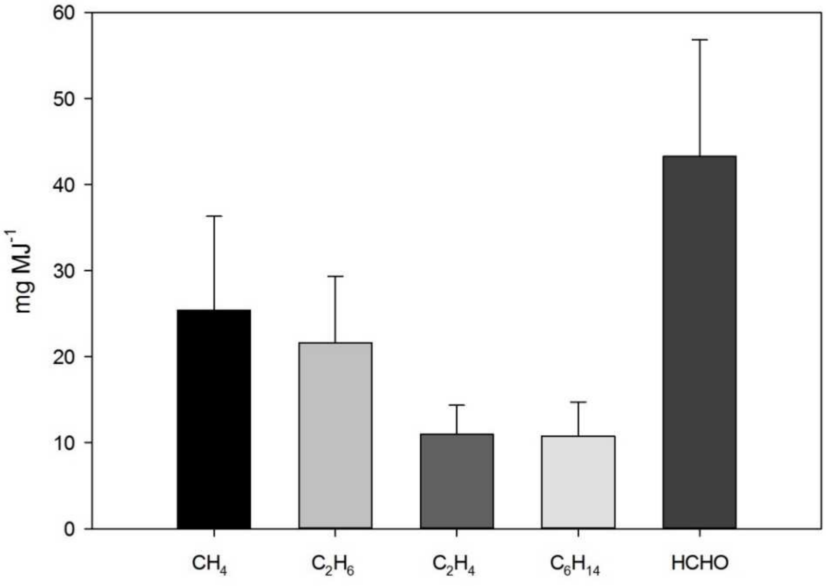

Figure 4.1. Emission factors of CH_4, C_2H_6, C_2H_4, C_6H_{14} and HCHO from the combustion of acacia pellets in the stove.

SO_2 emissions from biomass combustion are formed from the feedstock sulphur content. The elemental analysis of the pellets used in the present study revealed a sulphur content of 0.09 %wt., which resulted in an average SO_2 EF of 222 ± 115 mg MJ^{-1} (Fig. 4.2). The SO_2 EF is higher than those reported in the literature for the combustion of wood pellets in a residential combustion appliance (Lamberg et al., 2013). The SO_2 emissions from acacia pellets combustion were, however, comparable to those of Tissari et al. (2008) for the combustion of rape seed bark and rape seed in a residential cereal burner (224 and 284 mg MJ^{-1}, respectively) and to that of Carvalho et al. (2013) for wheat bran combustion in a pellet boiler (220 ± 2.7 mg MJ^{-1}). Blending calcium based additives with the fuel could be a strategy to address the high SO_2 emissions (Fournel et al., 2015a), preventing sulphate secondary aerosol formation in the atmosphere. The EFs of other acidic gases (Fig. 4.2), HCl and HF, were relatively low (0.41 ± 0.24 and 0.14 ± 0.04 mg MJ^{-1}, respectively). The HCl EF obtained in the present study is comparable to those obtained by Tissari et al. (2008) for the combustion of wood pellets in a pellet burner under different loads (0.27-1.07 mg MJ^{-1}) and slightly higher than those found by Lamberg et al. (2013) for the combustion of woody biomasses in a pellet boiler (0.02-0.27 mg MJ^{-1}). Fuel washing could reduce the acid gas emissions by removal of chloride and sulphur from the biomass fuel (Gudka et al., 2016). As regards the NH_3, the EF obtained for the combustion of acacia pellets was 1.81 ± 0.62 mg MJ^{-1} (Fig. 4.2), which is not far above the one reported by Fournel et al. (2015b), also for the combustion of wood pellets (1.20 mg MJ^{-1}).

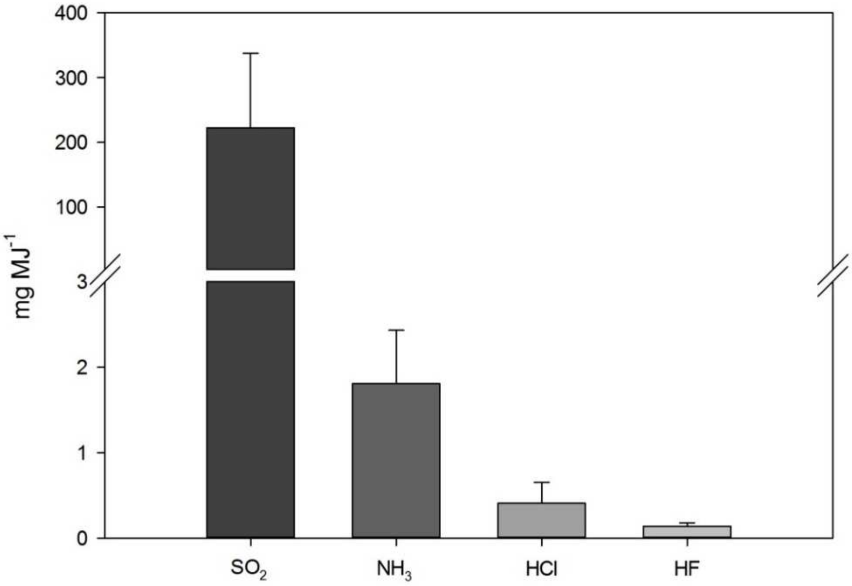

Figure 4.2. Emission factors of SO_2, NH_3, HCl and HF from the combustion of acacia pellets in the stove.

Detailed gaseous emissions from the combustion of alternative biofuels are of great research interest to support the adoption of quality control measures for biofuels in order to ensure a clean and efficient use in the future. The information obtained can also be useful in awareness-raising campaigns to avoid the manufacture of poor-quality biofuels in a loosely regulated and supervised market.

4.3.2. Particulate emission factors

The PM_{10} EF from combustion of acacia pellets was 118 ± 14.4 mg MJ^{-1} (Table 4.4). In a previous study, Vicente et al. (2015) reported PM_{10} EFs ranging from 26.6 ± 3.14 (wood pellets) to 169 ± 23.6 mg MJ^{-1} (agricultural fuels). The EFs reported for the combustion of wood pellets in this latter study were 1.2-4.4 fold lower than those of the current work. The PM_{10} emissions obtained in the present study were, however, in the higher range of those reported by Venturini et al. (2018) for medium quality wood pellets (78-120 mg MJ^{-1}). The researchers tested three pellets with different quality levels in a top feed pellet stove and reported total suspended particles (TSP) EFs ranging from 46 (highest pellet quality) to 179 (lowest pellet quality) mg MJ^{-1}. Fournel et al. (2015b), based on sampling from the undiluted flue gas in the chimney, reported a PM EF of 202 mg MJ^{-1} for the combustion of wood pellets in a multi-fuel boiler. Lower PM_{10} EFs were documented by Chandrasekaran et al. (2013) from the combustion of five different grass pellets and wood pellets at different loads in a pellet boiler. The authors reported higher PM_{10} EFs for grass pellets (21.3 ± 6.4 to 49.8 ± 3.1 mg MJ^{-1}) compared to wood pellets (12.3 ± 4.2 to 13.4 ± 2.7 mg MJ^{-1}) at both low and high loads. A remarkable decrease in fine particle emissions (92%) was reported by Lamberg et al. (2017) for the combustion of pellets in a hybrid stove, capable of using both pellets and wood logs as fuel. PM_1 EFs ranged from 7.3 to 31 mg MJ^{-1}, depending on the version of the pellet batch burner tested. Schmidt et al. (2018) documented a two-fold reduction in TSP emissions through the fuel washing. The wood washing before pelleting allows the removal of some elements from the fuel (e.g. potassium, sodium, calcium, sulphur and chloride), which are key components for particle formation during biomass combustion (Deng et al., 2013; Gudka et al., 2016; Schmidt et al., 2018). Important factors affecting PM emissions are related to the combustion technology, and its operation, as well as the physicochemical characteristics of the fuel burned. The influence of the fuel properties on particle emissions during the combustion of pellets has been highlighted in several studies (Fournel et al., 2015b; Lamberg et al., 2013; Schmidt et al., 2018; Venturini et al., 2018; Vicente et al., 2015). Features such as the fuel ash content have been found to correlate with the particle emissions (Chandrasekaran et al., 2013; Khalil et al., 2013; Sippula et al., 2007).

Table 4.4.Comparison between PM, OC and EC EFs (mg MJ^{-1}) data from literature about residential biomass combustion and results of the present study.

Combustion appliance	Fuel	PM fraction	OC mg MJ^{-1}	EC	PM	Reference
Pellet stove	Acacia pellets	PM_{10}	22.9 ± 9.28	6.82 ± 2.47	118 ± 14.4	This study
Pellet boiler	Commercial wood pellets	PM_1	0.9	0.1	19.7	Lamberg et al. (2011)
Modern masonry heater	Birch wood logs		3.6	24	50.7	
Conventional masonry heater			11	24	81.4	
Conventional masonry heater			19	49	67	
Conventional masonry heater			3.5	28	51.6	
Sauna stove			160	130	257	
Pellet stove	Commercial	PM_1	3.8	0.9	58	Sippula et al. (2007)
	birch steam		2.5	0.64	69	
	alder bark		17	12	473	
	alder steam		5.2	0.75	129	
	pine steam		4.1	0.52	47	
	willow bark		42	7.1	604	
	willow steam		4.5	1.3	126	
Hybrid stove	Commercial wood pellets	PM_1	22 - 35	41 - 50	92 - 98	Lamberg et al. (2017)
	Birch wood logs		1.2 - 2.5	3.3-20	7.3 - 31	
Woodstove	Birch	PM_{tot}	2.89 - 10.8	14.8 - 38.6	23.3 - 63.6	Nyström et al. (2017)
	Aspen		1.56 - 8.22	20.6 - 41.3	31.5 - 72.8	
	Spruce		2.78 - 14.7	30.5 - 39.5	49.3 - 64.4	
	Pine		2.72 - 23.2	25.5 - 104	35.3 - 177	

Furthermore, the fuel content in alkali metals is responsible for the inorganic fraction of the PM emissions (Lamberg et al., 2013; Sippula et al., 2017; Tissari et al., 2008). Other relevant species is chlorine, which can increase the volatilisation of alkali metals causing their enrichment in the fly ash (Gudka et al., 2016). Silicon, on the other hand, can decrease the release of alkali metals to the gas phase through the formation of alkali metal silicates (Lamberg et al., 2013). Verma et al. (2011) reported lower particle emissions from the combustion of reed canary grass pellets than from wood pellets in a pellet boiler. The researchers observed that the silicon content was 2.6 times higher for the first biofuel, promoting the formation of high density silicates and subsequent deposition as bottom ash, instead of fly ash particles.

4.3.2.1. Water soluble ions

Particulate water soluble components have been reported to cause adverse effects, such as oxidative stress, which can result in cell damage (Zou et al., 2016). Thus, the characterisation of the inorganic water soluble component of PM emissions is of extreme importance regarding the potential health effects. In the present study, most of the sampled particles consisted of inorganic ionic species. Water soluble ions accounted for 62.6 ± 19.2 %wt. of the PM_{10} mass (Fig. 4.3). The inorganic mass fraction in PM_{10} was found to be inversely correlated with the OC mass fraction ($r^2 = 0.80$).

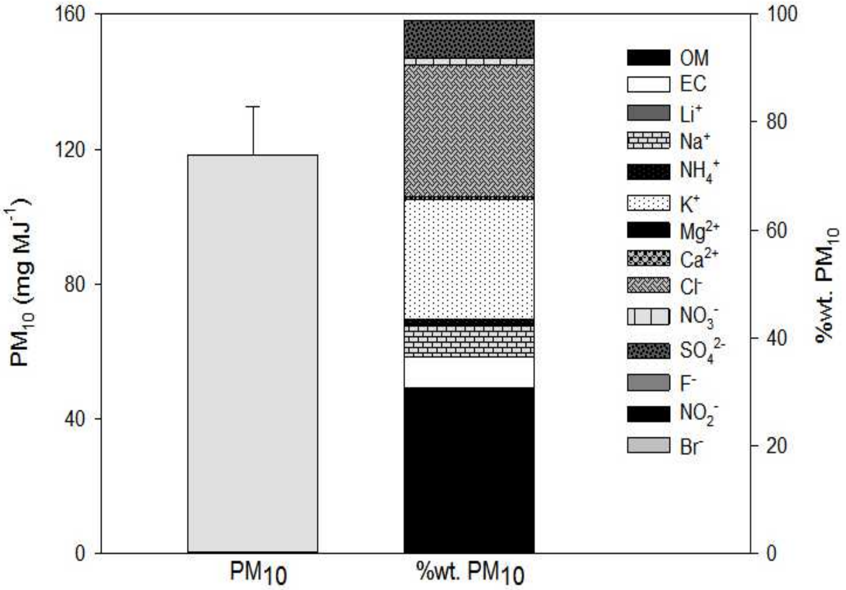

Figure 4.3. PM_{10} emission factor and PM_{10} chemical composition, from the combustion of acacia pellets in the stove.

The most prominent cations were potassium (22.4 ± 6.15 %wt.) and sodium (6.06 ± 3.72 %wt.) and the major anions found in the PM samples were chloride (24.5 ± 6.28 %wt.) and sulphate (6.93 ± 2.74 %wt.). A strong correlation between potassium and chloride ($r^2 = 0.94$) was observed leading to the supposition that ions are in the form of potassium chloride (KCl). Good correlations were also found between sodium and chloride ($r^2 = 0.83$), sodium and sulphate ($r^2 = 0.78$) and potassium and sulphate ($r^2 = 0.75$). These results are in agreement with the findings reported by Sippula et al. (2007), who investigated particle emissions from the combustion of stem and bark materials of five different wood species and a commercial pellet product in a pellet stove reporting that particles were mainly composed of potassium sulphates and chlorides. Although detected, lithium, calcium, magnesium, ammonium, fluoride, nitrite, nitrate and bromide did not account for significant percentages of the total ions mass in the PM_{10} of the present study. Phosphate was not detected in the samples.

Chandrasekaran et al. (2013) reported potassium (33.6-34.1 %wt.) and sulphate (17-24.7 %wt.) as dominant water soluble ions in PM emitted from combustion of wood pellets and potassium (19.4-32.8 %wt.), chloride (7.34-15.3 %wt.) and sulphate (2.31-24.5 %wt.) in PM emitted from combustion experiments with grass pellets in a pellet boiler under full and partial load. The importance of fuel characteristics (four types of wood species) and combustion conditions (nominal and high burn rates) on particle emission characteristics in a residential wood stove was investigated by Nyström et al. (2017). Regarding the PM inorganic fraction, the fuel content had the greatest effect rather than the combustion conditions. Lower water soluble ionic content (1.4-5.3 %wt. of PM mass) was found in particles emitted from wood log combustion in batch operated stoves (Calvo et al., 2015). Gonçalves et al. (2010) studied the combustion of common Portuguese woods, including *Acacia longifolia*, in a chimney type logwoodstove, and reported much higher ionic content (mainly chloride, sodium and potassium) in the PM samples from acacia combustion compared to the other wood types. *Acacia longifolia* is invasive in many coastal sand dunes (Marchante et al., 2004). Under saline conditions, plants need to overcome salt stress. Each plant has its adaptive mechanisms, which determine the plant tolerance to salinity. Under salt stress, it is common to plants to accumulate high intracellular concentrations of ions, mainly sodium and chloride, which affect the cell uptake and homeostasis of many indispensable cations, especially potassium and calcium (Morais et al., 2012, and references therein). Although several studies have documented particulate water soluble inorganic ions from pellet combustion (Chandrasekaran et al., 2013; Lamberg et al., 2011; Tissari et al., 2008), the characterisation of specific biofuels is important due to significant differences between biomass feedstocks.

4.3.2.2. Carbonaceous content

The total carbon represented 24.9 ± 9.23 %wt. of the PM_{10} mass emitted during the combustion experiments of acacia pellets in the stove. The carbonaceous content was dominated by OC (22.9 ± 9.28 mg MJ^{-1}), which was found to correlate negatively with the temperature in the combustion chamber ($r^2 = 0.76$) and with the water soluble potassium in PM_{10} samples ($r^2 = 0.82$). The EC mass fractions in particles were substantially lower (6.82 ± 2.47 mg MJ^{-1}) and increased with decreasing temperatures in the combustion chamber ($r^2 = 0.85$). In a previous study (Vicente et al., 2015), OC EFs ranging from 7.40 ± 1.86 (wood pellets) to 48.7 ± 30.9 (agricultural fuels) mg MJ^{-1} were recorded, whereas the EC contribution to the PM_{10} mass ranged from 3 to 47 %wt., corresponding to EC EFs ranging from 1.77 ± 0.44 (wood pellets) to 54.5 ± 23.5 (agricultural fuels) mg MJ^{-1}.

OC and EC emissions from biomass combustion in residential equipment vary broadly in the literature (Table 4.4). The OC contributions to the particulate mass range from 20 to 75 %wt., 12.5 to 67.9 %wt. and 0.0 to 32.7 %wt. for combustion in fireplaces, woodstoves and pellet stoves/boilers, respectively. The EC contribution to the PM emissions ranges from 1.1 to 17 %wt., 0.82 to 41.7 %wt. and 0.0 to 51.2 %wt. (Vicente and Alves, 2018). In the present study, carbonaceous PM emissions were noticeably lower compared to those from batch fired combustion appliances and are in the range of those reported for automatically controlled residential combustion equipment.

The average OC/EC ratio obtained for the combustion of acacia pellets (3.33 ± 0.374) is similar to the average ratio for combustion of European wood species in a tiled stove (Schmidl et al., 2008), and is much lower than the OC/EC ratio for the combustion of Southern and mid-European woods in a fireplace (Calvo et al., 2015), for prescribed burnings of a shrub-dominated forest (Alves et al., 2010) and for charcoal combustion in a barbecue grill (Vicente et al., 2018).

For mass balance calculations (Fig. 4.3), the analysed OC was converted into organic matter (OM), considering an OM/OC ratio of 1.6 in the present study (Vicente et al., 2015). OM comprised a PM mass fraction lower than 30%wt.

4.3.2.3. Organic speciation

The increased focus on potential adverse health effects associated with biomass burning emissions motivates a detailed characterisation of particulate matter. Some research work addressing particle-bound organic compounds from pellet combustion has been performed over the years. However, studies have mainly been devoted to the characterisation of PAHs, due to their recognised carcinogenic potential, common biomass burning tracers (e.g. levoglucosan) and some phenolic compounds (Alves et al., 2017; Orasche et al., 2012; Ozgen et al., 2014; Vicente et al., 2016). The novelty of this study stands in the detailed chemical characterization of particulate matter emissions, which is required to associate specific toxicological effects with exposure to combustion related PM.

The chromatographically resolved organic compounds in smoke particles comprised *n*-alkanes, *n*-alkenes, polycyclic aromatic hydrocarbons (PAH), saccharides, sterols, *n*-alkanols, phenolic compounds, acids and other oxygenated constituents (Table 4.5).

Table 4.5. Oxygenated compounds detected in particles emitted in flue gases during combustion of acacia pellets in the stove.

	PM_{10} mass fractions ($\mu g\ g^{-1}$)	Chemical formula
Saccharides		
Levoglucosan	284	$C_6H_{10}O_5$
Mannosan	24.2	$C_6H_{10}O_5$
Galactosan	10.4	$C_6H_{10}O_5$
Arabitol	4.27	$C_5H_{12}O_5$
Maltose	7.78	$C_{12}H_{22}O_{11}$
Other saccharides	118	
Total saccharides	*449*	
Phenolic compounds		
Benzyl alcohol	0.136	C_7H_8O
4-Hydroxybenzyl alcohol	0.093	$C_7H_8O_2$
Sinapic acid	0.152	$C_{11}H_{12}O_5$
Sinapyl alcohol	1.95	$C_{11}H_{14}O_4$
Coniferyl alcohol	3.62	$C_{10}H_{12}O_3$
Vanillin	1.48	$C_8H_8O_3$
Vannillic acid	8.81	$C_8H_8O_4$
Syringic acid	9.34	$C_9H_{10}O_5$
Syringic acid methyl ester	1.60	$C_{10}H_{12}O_2$
Syringaldehyde	29.1	$C_9H_{10}O_4$
Acetosyringone	3.75	$C_{10}H_{12}O_4$
Sinapaldehyde	14.0	$C_{11}H_{12}O_4$
Coniferyl aldehyde	4.24	$C_{10}H_{10}O_3$
Cinnamic acid	0.150	$C_9H_8O_2$
Hydrocinnamic (coumaric) acid	4.20	$C_9H_8O_3$
3-Methoxy-4-hydroxycinnamic (ferulic) acid	0.49	$C_{10}H_{10}O_4$
Hydrocinnamic acid, methylester	5.40	$C_{10}H_{12}O_2$
4-hydroxybenzaldehyde	12.3	$C_7H_6O_2$
3-Hydroxybenzoic acid	1.77	$C_7H_6O_3$
4-Hydroxybenzoic acid	2.07	$C_7H_6O_3$
3,4,5-Trihydroxybenzoic (gallic) acid	0.16	$C_7H_6O_5$
Acetophenone	1.91	C_8H_8O
4-*tert*-Butylphenol	1.99	$C_{10}H_{14}O$
4-Phenylphenol	0.151	$C_{12}H_{10}O$
2,4-Di-*tert*-butylphenol	11.7	$C_{14}H_{22}O$

4-Octylphenol	0.071	$C_{14}H_{22}O$
1,2,4,5-Benzenetetrol	0.822	$C_6H_6O_4$
Catechol	0.773	$C_6H_6O_2$
Resorcinol	3.55	$C_6H_6O_2$
1-Methyl-3,5-dihydroxybenzene (orcinol)	1.10	$C_7H_8O_2$
4-Hydroxyphenylethanol (tyrosol)	0.552	$C_8H_{10}O_2$
2-Isopropyl-5-methylphenol (thymol)	0.389	$C_{10}H_{14}O$
Tocopherol	0.030	$C_{29}H_{50}O_2$
Total phenolic compounds	*128*	
Resin acids		
Abietic acid	bdl	$C_{20}H_{30}O_2$
Dehydroabietic acid	4.92	$C_{20}H_{28}O_2$
Isopimaric acid	0.398	$C_{20}H_{30}O_2$
Total resin acids	*5.32*	
***n*-Alkenoic and alkanoic acids**		
9-Hexadecenoic (palmitoleic) acid	0.908	$C_{16}H_{30}O_2$
9-12-Octadecadienoic (linoleic) acid	1.70	$C_{18}H_{32}O_2$
9-Octadecenoic (oleic) acid	1.24	$C_{18}H_{34}O_2$
Octanoic (caprylic) acid	0.007	$C_8H_{16}O_2$
Nonanoic (pelargonic) acid	bdl	$C_9H_{18}O_2$
Decanoic (capric) acid	bdl	$C_{10}H_{20}O_2$
Undecanoic acid	bdl	$C_{11}H_{22}O_2$
Dodecanoic (lauric) acid	bdl	$C_{12}H_{24}O_2$
Tetradecanoic (myristic) acid	0.812	$C_{14}H_{28}O_2$
Pentadecanoic acid	0.166	$C_{15}H_{30}O_2$
Hexadecanoic (palmitic) acid	2.77	$C_{16}H_{32}O_2$
Heptadecanoic acid	0.096	$C_{17}H_{34}O_2$
Octadecanoic (stearic) acid	0.055	$C_{18}H_{36}O_2$
Nonadecanoic acid	0.009	$C_{19}H_{38}O_2$
Eicosanoic acid	0.323	$C_{20}H_{40}O_2$
Docosanoic acid	1.78	$C_{22}H_{44}O_2$
Tetracosanoic acid	1.90	$C_{24}H_{48}O_2$
Hexacosanoic acid	0.723	$C_{26}H_{52}O_2$
Octacosanoic acid	0.542	$C_{28}H_{56}O_2$
Total n-alkenoic and alkanoic acids	*12.5*	
Other acids		
Pyruvic acid	0.081	$C_3H_4O_3$
3-Hydroxypropanoic (hydracrylic) acid	0.854	$C_3H_6O_3$
3-Hydroxybutyric acid	0.063	$C_4H_8O_3$
Butanedioic (malic) acid	0.791	$C_4H_6O_5$
2-Furoic acid	0.184	$C_5H_4O_3$
1,5-Pentanedioic (glutaric) acid	1.04	$C_5H_8O_4$
Henanedioic (adipic) acid	bdl	$C_6H_{10}O_4$
Octanedioic (suberic) acid	bdl	$C_8H_{14}O_4$
Nonanedioic (azelaic) acid	0.649	$C_4H_8O_3$
Decanedioic (sebacic) acid	0.035	$C_{10}H_{18}O_4$
Hexadecanedioic (thapsic) acid	bdl	$C_{16}H_{30}O_4$
Phthalic acid	15.1	$C_8H_6O_4$
Pinonic acid	bdl	$C_9H_{14}O_4$
Pinic acid	7.21	$C_9H_{14}O_4$

Total other acids	*26.9*	
***n*-Alkanols**		
1-Decanol	0.003	$C_{10}H_{22}O$
1-Dodecanol	0.483	$C_{12}H_{26}O$
1-Tetradecanol	2.00	$C_{14}H_{30}O$
1-Pentadecanol	0.503	$C_{15}H_{32}O$
1-Hexadecanol	0.317	$C_{16}H_{34}O$
1-Eicosanol	0.069	$C_{20}H_{42}O$
1-Docosanol	0.217	$C_{22}H_{46}O$
1-Tricosanol	0.047	$C_{23}H_{48}O$
1-Tetracosanol	2.44	$C_{24}H_{50}O$
1-Pentacosanol	0.069	$C_{25}H_{52}O$
1-Hexacosanol	4.68	$C_{26}H_{54}O$
1-Heptacosanol	0.087	$C_{27}H_{56}O$
1-Octacosanol	2.51	$C_{28}H_{58}O$
1-Tricontanol	0.043	$C_{30}H_{62}O$
Total n-alcohols	*13.5*	
Sterols		
Cholesterol	0.222	$C_{27}H_{46}O$
5-Cholestan-3-ol (dehydrocholesterol)	0.005	$C_{27}H_{46}O$
Stigmasterol	0.416	$C_{28}H_{48}O$
β-Sitosterol	1.54	$C_{29}H_{50}O$
Total sterols	*2.18*	
Phthalates		
Dimethyl phthalate	0.188	$C_{10}H_{10}O_4$
di-Butyl phthalate (DBP)	2.74	$C_{16}H_{22}O_4$
di-Isobutyl phthalate (DiBP)	0.232	$C_{16}H_{22}O_4$
Diethylhexyl phthalate (DEHP)	27.2	$C_{22}H_{38}O_4$
Bis(2-ethylhexyl) phthalate	20.1	$C_{24}H_{38}O_4$
Total phthalates	*50.5*	
Other hidroxyl compounds		
Meso-Erythritol	0.003	$C_4H_{10}O_4$
1,2,3-Hexanetriol	0.020	$C_6H_{14}O_3$
2-Methylcyclohexanol	0.035	$C_7H_{14}O$
Quebrachitol	0.005	$C_7H_{14}O_6$
Citronellol	0.005	$C_{10}H_{20}O$
2,3-Pinanediol	0.011	$C_{10}H_{20}O_2$
1-Monopalmitin	1.36	$C_{19}H_{38}O_4$
Monostearin	2.25	$C_{21}H_{42}O_4$
Lupeol	3.25	$C_{30}H_{50}O$
Total other hydroxyl compounds	*6.94*	

bdl- below detection limit

Among the short-chain *n*-alkanes, only undecane was detected. A carbon preference index (CPI) of 1.65 revealed a slight predominance of odd over even *n*-alkanes. The homologous series (C_{20}-C_{32}) maximised for pentacosane and heptacosane. Globally, this organic class represented a

PM_{10} mass fraction of 520 µg g^{-1}. The only alkene worth mentioning was eicosene (3.25 µg g^{-1} PM_{10}).

The dominant PAH in PM_{10} from the combustion of acacia pellets was retene (Table 4.6). Vicente et al. (2016) pointed out this alkylated phenanthrene as a major PAH in emissions from manually and automatically controlled domestic combustion appliances. Overwhelming proportions of retene were also observed in the organic extracts of particles from the combustion of charcoal (Vicente et al., 2018) and wildfires (Vicente et al., 2012). Alves et al. (2017) performed *in vitro* assays with particles from forest and crop fires in the Amazon region. These particles, not only induced inflammation, oxidative stress and genetic damage in human lung cells, but also drove over 30% of the cultured cells to death after 72 h of exposure. The main culprit seems to be retene.

Table 4.6. PAH mass fractions in the particulate matter emitted in flue gases during combustion of acacia pellets in the stove.

Compound	ng g^{-1} PM_{10}
Phenanthrene	60.6
Anthracene	44.6
Carbazole	520
Fluoranthene	1455
Pyrene	2309
p-Terphenyl	34.2
Retene	8773
Benzo[a]anthracene	4807
Chrysene	6673
Benzo[b]fluoranthene	97.2
Benzo[e]pyrene	1466
Benzo[a]pyrene	2514
Indeno[1,2,3-cd]pyrene	1853
Benzo[g,h,i]perylene	1887

Anhydrosugars were one of the most important groups of organic compounds in smoke particles from acacia pellet combustion. While levoglucosan derives from the D-glucose units of the biopolymer (either cellulose or hemicelluloses) that composes the raw material of the pellets, its stereoisomers, mannosan and galactosan, originate from the mannose and galactose units of hemicelluloses. Levoglucosan mass fractions in particles emitted in the flue gases from a fireplace (49.8-149 mg g^{-1}) and traditional woodstove (22.4-232 mg g^{-1}) (Vicente and Alves, 2018) were one order of magnitude higher than those of the present study. However, it should be borne in mind that levoglucosan production is highly dependent on the combustion conditions with lower temperatures leading to higher emission rates (Vicente and Alves, 2018). It has been observed that very efficient combustion systems that reach high temperatures do not emit detectable amounts of levoglucosan, regardless of biofuel (Schmidl et al., 2011). The levoglucosan-to-mannosan ratio (11.7) observed in this study is in the range of values documented for hardwood combustion (Vicente and Alves, 2018, and references therein).

Many other saccharidic constituents, including monosaccharides, disaccharides and polyols, were present in PM_{10}. However, due to similar fragmentation patterns and isomerism among many compounds, their individual quantification was not possible. Medeiros and Simoneit (2008) detected many sugar compounds in particulate matter samples from controlled burnings of green vegetation from temperate climate forests. The presence of many saccharidic compounds was also documented for aerosols from wildfires (e.g. Alves et al., 2011; Vicente et al., 2011). Graham et al. (2002) argued that many of these sugars can be primary combustion products from the breakdown of polysaccharides. They may also be formed directly by volatilisation of plant matter or as products of the hydrolysis of the corresponding anhydrosugars under the acidic atmospheric conditions created by the biomass combustion plume. The detection of appreciable amounts of mannitol in the present study leads to question its use as a tracer for the quantification of airborne fungal spores (Bauer et al., 2008). Burshtein et al. (2011) had already suggested that mannitol might not be a specific biomarker for fungi, since it was weakly correlated with ergosterol, another fungal tracer.

The homologous series of *n*-alkanols from C_{10} to C_{33}, with a clear predominance of even carbon number compounds, was observed. The most abundant member was hexacosanol, which is naturally present in the epicuticular wax and plant cuticle of many plant species (Baker, 1982). Acids comprised resin, *n*-alkanoic (C_{14}-C_{28}), unsaturated ($C_{16:1}$, $C_{18:1}$ and $C_{18:2}$), alkanedioic (C_4-C_{10}), among other compounds, which, for the most part, were previously detected in particulate matter emissions from both the residential combustion of firewood (Gonçalves et al., 2012) and charcoal in barbecue grills (Vicente et al., 2018). Although described as ozonolysis products of α-pinene (Ma et al., 2007), the occurrence of pinic and pinonic acids in flue gas particles suggests that they are produced by additional mechanisms, including formation during the combustion process and/or immediate oxidation of gaseous precursors in the smoke plume, as postulated in previous works involving aerosols from residential biomass combustion processes (Vicente et al., 2018) or impacted by smoke plumes (Cheng et al., 2011). Similarly, although phthalic acid has been pointed out as a photochemical oxidation product of aromatic hydrocarbons, such as naphthalene (Kleindienst et al., 2012), concentrations several times higher during biomass burning episodes compared to non-smoky periods were reported for a rural site of Northeast China, stressing the complexity of aerosol sources

(Cao et al., 2017). Fu et al. (2012) described similar temporal patterns of phthalic acid to those of biomass burning tracers in the Mt. Tai (North China Plain) aerosols. Phthalic was one of the most abundant acids in the present study.

It is well established that, upon burning, conifer samples (gymnosperms) give rise to 2-methoxyphenols only, whereas angiosperm samples (e.g. acacia) lead to both 2-methoxyphenols and 2,6-dimethoxyphenols (Kjällstrand et al., 2000). The higher proportion of 2,6-dimethoxyphenols, such as syringic acid and syringaldehyde, observed in the present study, reflect the long-known lignin structure of angiosperm plants based on sinapyl alcohol monomers. The significant PM_{10} mass fraction of coumaric acid also deserves attention. This acid is important to the secondary metabolism of plants as it is a precursor of polyphenols, and other phenolic acids (e.g. caffeic and ferulic). It can be detected in plants in the free form, or conjugated to other molecules, such as amines, organic acids, alcohols, mono- or oligosaccharides, and lignin (Ferreira et al., 2018). Several alkyl phenols were also present in the organic extracts. The most expressive was 2,4-di-*tert*-butylphenol. This is one of the allelochemical natural compounds present in many plants (Chuah et al., 2016). Some constituents that have been described as pyrolysis products of coumaryl alcohol (Chuah et al., 2016), one of the primary lignin monomers, were detected in particles generated during combustion of acacia pellets. These include hydroxybenzoic acids and 4-hydroxybenzaldehyde. Other phenolic compounds comprised substituted benzenes, such as catechol, resorcinol, orcinol, tyrosol and thymol, most of which previously detected in particle emissions from both fireplace and woodstove combustion (Fine et al., 2004, 2002).

Among plant sterols, β-sitosterol was the most abundant. In residential wood combustion experiments, this phytosterol was found at very discrepant levels during the combustion of different wood types, suggesting that it can potentially be used to distinguish between emissions from the combustion of diverse wood species (Fine et al., 2002). Lupeol, previously identified as a major pentacyclic triterpene in particles emitted by wildfires (Vicente et al., 2012), as well as in the pyrolysates of biochar from combustion of various types of wooden briquettes in a manually loaded boiler (Růžičková et al., 2016), was a significant compound in emissions from acacia pellets. The detection of monostearin and monopalmitin raises the question of their suitability as tracers of cooking emissions (Abdullahi et al., 2013, and references therein). Several phthalates were also present in the PM_{10} samples. These components have been largely used as plasticisers in consumer products and building materials. They are easily released into the environment. Thus, phthalates have become ubiquitous environmental contaminants (Li et al., 2018). Since these compounds are not expected to be emitted during the combustion of woody biomass, it is assumed that biofuel contact with plastics has contributed to the contamination of the material. However, this supposition is merely speculative and further studies are needed to clarify the formation processes of phthalates in aerosols emitted during biomass combustion.

4.4. Conclusions

At present, there is an increasing search for alternative biomass feedstocks for pellet production. Despite the bioenergy opportunity that these new raw materials could provide, the emissions arising from their combustion may be significantly higher causing adverse effects on human health and the environment. The aim of the present study was to evaluate particle and gaseous emissions from the combustion of a pelletised invasive biomass species (*Acacia longifolia*). A detailed database of gaseous and particulate constituents emitted from the combustion of a new pelletised biofuel was obtained. The importance of particle properties other than mass concentration is widely recognised in the assessment of health and climate effects. Pellets of this species have an energy value comparable to that of other biomasses commonly used and commercialised. However, the ecosystem where the acacia trees have grown, which is characterised as a coastal salty habitat, appears to have a major influence on the emissions from the combustion of home-made pellets. In this study, relatively high emissions of CO were accompanied by emissions of other products of incomplete combustion, such as TOC. High emissions of NO_x, an important precursor for secondary aerosol formation in the atmosphere, were also recorded. The PM_{10} mass in the combustion flue gas was composed mainly of water soluble ions (63 %wt.). This overwhelming proportion of ionic species was dominated by potassium, chloride, sulphate and sodium. The analysed carbonaceous constituents constituted 25 %wt. of the PM_{10} mass. The wide variability of biomass properties can significantly influence the efficiency and environmental impacts associated with its use, constituting an issue of great research interest. Given that this study gives a detailed insight of the gaseous and particulate emissions from a fuel manufactured from an abundant biomass, it can support the subsequent development of a regulatory framework for the control of biomass burning emissions, as well as the adoption of measures to improve the quality of biofuels and to optimise the combustion process.

Pretreatment of fuel prior to pelleting can contribute to reducing the emission of gases and particulates. Natural leaching by rainfall can constitute a low-cost alternative to reduce key elements in the raw material, which are involved in the formation of pollutants. Fuel blends or the use of additives upon pelleting, although being a costlier alternative, can be used in order to change the release of volatile components from the fuel and reduce emissions. The pellet quality is directly related to their physical, mechanical and chemical properties. For that reason, further research is essential to optimise the raw material characteristics, allowing the manufacture of a suitable product for domestic use. The pellet production process at small-scale units and its influence on the physical characteristics of the product is also a topic to be investigated. Furthermore, since the air supply is one of the main features affecting the combustion process, the optimization of air supply could cut down the emissions and deserves further investigation.

Among the wide range of organic compounds detected, levoglucosan, retene and some phenolic compounds deserve attention. However, the detection of components such as phthalates, terpenic acids, monoglycerides and some polyols, whose origin has been attributed to other primary emission sources or to secondary oxidation processes, makes it impossible to use these constituents as tracers and indicates that the composition of aerosols, especially those from biomass burning, is very complex and that the formation mechanisms are far from being fully known, requiring additional studies.

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References

Abdullahi, K.L., Delgado-Saborit, J.M., Harrison, R.M., 2013. Emissions and indoor concentrations of particulate matter and its specific chemical components from cooking: A review. Atmos. Environ. 71, 260–294. doi:10.1016/J.ATMOSENV.2013.01.061

Almeida, D., Pereira, C., 2014. Monitoring Fluidization Quality and Combustion Efficiency of Invasive species pellets, in: 15th Brazilian Congress of Thermal Sciences and Engineering. Belém, PA, Brazil.

Alves, C.A., Gonçalves, C., Pio, C.A., Mirante, F., Caseiro, A., Tarelho, L., Freitas, M.C., Viegas, D.X., 2010. Smoke emissions from biomass burning in a Mediterranean shrubland. Atmos. Environ. 44, 3024–3033. doi:10.1016/j.atmosenv.2010.05.010

Alves, C.A., Vicente, E.D., Rocha, S., Vicente, A.M., 2017. Organic tracers in aerosols from the residential combustion of pellets and agro-fuels. Air Qual. Atmos. Health 10, 37–45. doi:10.1007/s11869-016-0406-3

Alves, N.D.O., Vessoni, A.T., Quinet, A., Fortunato, R.S., Kajitani, G.S., Peixoto, M.S., De Souza Hacon, S., Artaxo, P., Saldiva, P., Menck, C.F.M., De Medeiros, S.R.B., 2017. Biomass burning in the Amazon region causes DNA damage and cell death in human lung cells. Sci. Rep. 7, 1–13. doi:10.1038/s41598-017-11024-3

Alves, Vicente, A., Monteiro, C., Gonçalves, C., Evtyugina, M., Pio, C., 2011. Emission of trace gases and organic components in smoke particles from a wildfire in a mixed-evergreen forest in Portugal. Sci. Total Environ. 409, 1466–1475. doi:10.1016/J.SCITOTENV.2010.12.025

Arranz, J.I., Miranda, M.T., Montero, I., Sepúlveda, F.J., Rojas, C. V., 2015. Characterization and combustion behaviour of commercial and experimental wood pellets in South West Europe. Fuel 142, 199–207. doi:10.1016/j.fuel.2014.10.059

Baker, E.A., 1982. Chemistry and Morphology of Plant Epicuticular Waxes, in: Cutler, D.F., Alvin, K.L., Price, C.E. (Eds.), The Plant Cuticle. Academic Press, London, pp. 139–166.

Bauer, H., Schueller, E., Weinke, G., Berger, A., Hitzenberger, R., Marr, I.L., Puxbaum, H., 2008. Significant contributions of fungal spores to the organic carbon and to the aerosol mass balance of the urban atmospheric aerosol. Atmos. Environ. 42, 5542–5549. doi:10.1016/J.ATMOSENV.2008.03.019

Bernhardt, D., Gebauer, K., Pohl, M., Beckmann, M., 2012. Investigation of the combustion behavior of pulp pellets in a domestic pellet boiler, in: International Conference on Thermal Treatment Technologies and Hazardous Waste Combustors. New Orleans, USA, pp. 223–234.

Burshtein, N., Lang-Yona, N., Rudich, Y., 2011. Ergosterol, arabitol and mannitol as tracers for biogenic aerosols in the eastern Mediterranean. Atmos. Chem. Phys. 11, 829–839. doi:10.5194/acp-11-829-2011

Calvo, A.I., Martins, V., Nunes, T., Duarte, M., Hillamo, R., Teinila, K., Pont, V., Castro, A., Fraile, R., Tarelho, L., Alves, C., 2015. Residential wood combustion in two domestic devices: Relationship of different parameters throughout the combustion cycle. Atmos. Environ. 116, 72–82. doi:10.1016/j.atmosenv.2015.06.012

Cao, F., Zhang, S.-C., Kawamura, K., Liu, X., Yang, C., Xu, Z., Fan, M., Zhang, W., Bao, M., Chang, Y., Song, W., Liu, S., Lee, X., Li, J., Zhang, G., Zhang, Y.-L., 2017. Chemical characteristics of dicarboxylic acids and related organic compounds in $PM_{2.5}$ during biomass-burning and non-biomass-burning seasons at a rural site of Northeast China. Environ. Pollut. 231, 654–662. doi:10.1016/J.ENVPOL.2017.08.045

Carneiro, M., Moreira, R., Gominho, J., Fabião, A., 2014. Could control of invasive acacias be a source of biomass for energy under mediterranean conditions? Chem. Eng. Trans. 37, 187–192. doi:10.3303/CET1437032

Carvalho, L., Wopienka, E., Pointner, C., Lundgren, J., Verma, V.K., Haslinger, W., Schmidl, C., 2013. Performance of a pellet boiler fired with agricultural fuels. Appl. Energy 104, 286–296. doi:10.1016/j.apenergy.2012.10.058

Chandrasekaran, S.R., Hopke, P.K., Hurlbut, A., Newtown, M., 2013. Characterization of emissions from grass pellet combustion. Energ. Fuel. 27, 5298–5306. doi:10.1021/ef4010169

Cheng, Y., Brook, J.R., Li, S.-M., Leithead, A., 2011. Seasonal variation in the biogenic secondary organic aerosol tracer cis-pinonic acid: Enhancement due to emissions from regional and local biomass burning. Atmos. Environ. 45, 7105–7112. doi:10.1016/J.ATMOSENV.2011.09.036

Chrystelle, V., Ryckmans, Y., 2012. Industrial Wood Pellets Report. Enplus.

Chuah, T.S., Norhafizah, M.Z., Naimah, A.H., Ismail, B.S., 2016. phytotoxic activity of the allelochemical, 2,4-di-tert-butylphenol on two selected weed species (aktiviti fitotoksik alelokimia, 2,4-di-tert-butilfenol terhadap dua spesies rumpai terpilih). Sains Malaysiana 45, 963–967. doi:10.17576/jsm-2018-4702-07

Dale, V.H., Kline, K.L., Parish, E.S., Cowie, A.L., Emory, R., Malmsheimer, R.W., Slade, R., Smith, C.T.T., Wigley, T.B. BEN, Bentsen, N.S., Berndes, G., Bernier, P., Brandão, M., Chum, H.L., Diaz-Chavez, R., Egnell, G., Gustavsson, L., Schweinle, J., Stupak, I., Trianosky, P., Walter, A., Whittaker, C., Brown, M., Chescheir, G., Dimitriou, I., Donnison, C., Goss Eng, A., Hoyt, K.P., Jenkins, J.C., Johnson, K., Levesque, C.A., Lockhart, V., Negri, M.C., Nettles, J.E., Wellisch, M., 2017. Status and prospects for renewable energy using wood pellets from the southeastern United States. GCB Bioenergy 9, 1296–1305. doi:10.1111/gcbb.12445

De Almeida, J.D., Freitas, H., 2001. The exotic and invasive flora of Portugal. Bot. Complut. 317–327.

Deng, L., Zhang, T., Che, D., 2013. Effect of water washing on fuel properties, pyrolysis and combustion characteristics, and ash fusibility of biomass. Fuel Process. Technol. 106, 712–720. doi:10.1016/j.fuproc.2012.10.006

Fachinger, F., Drewnick, F., Gieré, R., Borrmann, S., 2017. How the user can influence particulate emissions from residential wood and pellet stoves: Emission factors for different fuels and burning conditions. Atmos. Environ. 158, 216–226. doi:10.1016/j.atmosenv.2017.03.027

FAO, 2017. Global forest products: Facts and Figures 2016. Forestry Department, Food and Agriculture Organization of the United Nations. Rome, Italy.

Ferreira, P.S., Victorelli, F.D., Fonseca-Santos, B., Chorilli, M., 2018. A Review of analytical methods for p-coumaric acid in plant-based products, beverages, and biological matrices. Crit. Rev. Anal. Chem. 1–11. doi:10.1080/10408347.2018.1459173

Ferreira, T., Paiva, J.M., Pinho, C., 2013. Performance assessment of Acacia dealbata as a fuel for a domestic pellets boiler. 8th Conf. Sustain. Dev. Energy, Water Environ. Syst. 1–10.

Fine, P.M., Cass, G.R., Simoneit, B.R.T., 2004. Chemical characterization of fine particle emissions from the fireplace combustion of wood types grown in the Midwestern and Western United States. Environ. Eng. Sci. 21, 387–409. doi:10.1089/109287504323067021

Fine, P.M., Cass, G.R., Simoneit, B.R.T., 2002. Chemical characterization of fine particle emissions from the fireplace combustion of woods grown in the Southern United States. Environ. Sci. Technol. 36, 1142–1451. doi:10.1021/ES0108988

Fournel, S., Palacios, J., Godbout, S., Heitz, M., 2015a. Effect of additives and fuel blending on emissions and ash-related problems from small-scale combustion of reed canary grass. Agriculture 5, 561–576. doi:10.3390/agriculture5030561

Fournel, S., Palacios, J.H., Morissette, R., Villeneuve, J., Godbout, S., Heitz, M., Savoie, P., 2015b. Influence of biomass properties on technical and environmental performance of a multi-fuel boiler during on-farm combustion of energy crops. Appl. Energy 141, 247–259. doi:10.1016/j.apenergy.2014.12.022

Fu, P.Q., Kawamura, K., Chen, J., Li, J., Sun, Y.L., Liu, Y., Tachibana, E., Aggarwal, S.G., Okuzawa, K., Tanimoto, H., Kanaya, Y., Wang, Z.F., 2012. Diurnal variations of organic molecular tracers and stable carbon isotopic composition in atmospheric aerosols over Mt. Tai in the North China Plain: An influence of biomass burning. Atmos. Chem. Phys. 12, 8359–8375. doi:10.5194/acp-12-8359-2012

Garcia-Maraver, A., Zamorano, M., Fernandes, U., Rabaçal, M., Costa, M., 2014. Relationship between fuel quality and gaseous and particulate matter emissions in a domestic pellet-fired boiler. Fuel 119, 141–152. doi:10.1016/j.fuel.2013.11.037

Goetzl, A., 2015. Developments in the Global Trade of Wood Pellets. Washington DC, USA.

Gonçalves, C., Alves, C., Evtyugina, M., Mirante, F., Pio, C., Caseiro, A., Schmidl, C., Bauer, H., Carvalho, F., 2010. Characterisation of PM_{10} emissions from woodstove combustion of common woods grown in Portugal. Atmos. Environ. 44, 4474–4480. doi:10.1016/j.atmosenv.2010.07.026

Gonçalves, C., Alves, C., Pio, C., 2012. Inventory of fine particulate organic compound emissions from residential wood combustion in Portugal. Atmos. Environ. 50, 297–306. doi:10.1016/j.atmosenv.2011.12.013

Graham, B., Mayol-Bracero, O.L., Guyon, P., Roberts, G.C., Decesari, S., Facchini, M.C., Artaxo, P., Maenhaut, W., Köll, P., Andreae, M.O., 2002. Water-soluble organic compounds in biomass burning aerosols over Amazonia 1. Characterization by NMR and GC-MS. J. Geophys. Res. Atmos. 107. doi:10.1029/2001JD000336

Gudka, B., Jones, J.M., Lea-Langton, A.R., Williams, A., Saddawi, A., 2016. A review of the mitigation of deposition and emission problems during biomass combustion through washing pre-treatment. J. Energy Inst. 89, 159–171. doi:10.1016/j.joei.2015.02.007

ICNF, 2013. IFN6 – Áreas dos usos do solo e das espécies florestais de Portugal continental em 1995, 2005 e 2010. 6º Inventário Florestal Nacional p.34.

Khalil, R.A., Bach, Q.V., Skreiberg, O., Tran, K.Q., 2013. Performance of a residential pellet combustor operating on raw and torrefied spruce and spruce-derived residues. Energ. Fuel. 27, 4760–4769. doi:10.1021/ef400595f

Kistler, M., Schmidl, C., Padouvas, E., Giebl, H., Lohninger, J., Ellinger, R., Bauer, H., Puxbaum, H., 2012. Odor, gaseous and PM_{10} emissions from small scale combustion of wood types indigenous to Central Europe. Atmos. Environ. 51, 86–93. doi:10.1016/j.atmosenv.2012.01.044

Kjällstrand, J., Ramnäs, O., Petersson, G., 2000. Methoxyphenols from burning of Scandinavian forest plant materials. Chemosphere 41, 735–41.

Kleindienst, T.E., Jaoui, M., Lewandowski, M., Offenberg, J.H., Docherty, K.S., 2012. The formation of SOA and chemical tracer compounds from the photooxidation of naphthalene and its methyl analogs in the presence and absence of nitrogen oxides. Atmos. Chem. Phys. 12, 8711–8726. doi:10.5194/acp-12-8711-2012

Lamberg, H., Nuutinen, K., Tissari, J., Ruusunen, J., Yli-Pirilä, P., Sippula, O., Tapanainen, M., Jalava, P., Makkonen, U., Teinilä, K., Saarnio, K., Hillamo, R., Hirvonen, M.R., Jokiniemi, J., 2011. Physicochemical characterization of fine particles from small-scale wood combustion. Atmos. Environ. 45, 7635–7643. doi:10.1016/j.atmosenv.2011.02.072

Lamberg, H., Sippula, O., Tissari, J., Virén, A., Kaivosoja, T., Aarinen, A., Salminen, V., Jokiniemi, J., 2017. Operation and emissions of a hybrid stove fueled by pellets and log wood. Energ. Fuel. 31, 1961–1968. doi:10.1021/acs.energyfuels.6b02717

Lamberg, H., Tissari, J., Jokiniemi, J., Sippula, O., 2013. Fine particle and gaseous emissions from a small-scale boiler fueled by pellets of various raw materials. Energ. Fuel. 27, 7044–7053. doi:10.1021/ef401267t

Li, Y., Wang, J., Ren, B., Wang, H., Qiao, L., Zhu, J., Li, L., 2018. The characteristics of atmospheric phthalates in Shanghai: A haze case study and human exposure assessment. Atmos. Environ. 178, 80–86. doi:10.1016/J.ATMOSENV.2018.01.042

Ma, Y., Willcox, T.R., Russell, A.T., Marston, G., 2007. Pinic and pinonic acid formation in the reaction of ozone with alpha-pinene. Chem. Commun. (Camb). 1328–30. doi:10.1039/b617130c

Marchante, E., Kjøller, A., Struwe, S., Freitas, H., 2008. Short- and long-term impacts of Acacia longifolia invasion on the belowground processes of a Mediterranean coastal dune ecosystem. Appl. Soil Ecol. 40, 210–217. doi:10.1016/j.apsoil.2008.04.004

Marchante, H., Marchante, E., Buscardo, E., Maia, J., Freitas, H., 2004. Recovery potential of dune ecosystems invaded by an exotic acacia species. Weed Technol. 18, 1427–1433. doi:10.1614/0890-037X(2004)018{[}1427:RPODEI]2.0.CO;2

Medeiros, P.M., Simoneit, B.R.T., 2008. Source profiles of organic compounds emitted upon combustion of green vegetation from temperate climate forests. Environ. Sci. Technol. 42, 8310–8316.

Miranda, T., Montero, I., Sepúlveda, F.J., Arranz, J.I., Rojas, C.V., Nogales, S., 2015. A review of pellets from different sources. Materials (Basel). 8, 1413–1427. doi:10.3390/ma8041413

Morais, M.C., Panuccio, M.R., Muscolo, A., Freitas, H., 2012. Salt tolerance traits increase the invasive success of Acacia longifolia in Portuguese coastal dunes. Plant Physiol. Biochem. 55, 60–65. doi:10.1016/j.plaphy.2012.03.013

Nunes, J., Freitas, H., 2016. An indicator to assess the pellet production per forest area. A case-study from Portugal. For. Policy Econ. 70, 99–105. doi:10.1016/j.forpol.2016.05.022

Nyström, R., Lindgren, R., Avagyan, R., Westerholm, R., Lundstedt, S., Boman, C., 2017. Influence of wood species and burning conditions on particle emission characteristics in a residential wood stove. Energ. Fuel. 31, 5514–5524. doi:10.1021/acs.energyfuels.6b02751

Orasche, J., Seidel, T., Hartmann, H., Schnelle-Kreis, J., Chow, J.C., Ruppert, H., Zimmermann, R., 2012. Comparison of emissions from wood combustion. Part 1: Emission factors and characteristics from different small-scale residential heating appliances considering particulate matter and polycyclic aromatic hydrocarbon (PAH) related toxicological potential of particle-bound organic species. Energ. Fuel. 26, 6695–6704. doi:10.1021/ef301295k

Ozgen, S., Caserini, S., Galante, S., Giugliano, M., Angelino, E., Marongiu, A., Hugony, F., Migliavacca, G., Morreale, C., 2014. Emission factors from small scale appliances burning wood and pellets. Atmos. Environ. 94, 144–153. doi:10.1016/j.atmosenv.2014.05.032

Parish, E.S., Herzberger, A.J., Phifer, C.C., Dale, V.H., 2018. Transatlantic wood pellet trade demonstrates telecoupled benefits. Ecol. Soc. 23. doi:10.5751/ES-09878-230128

Patzek, T.W., Pimentel, D., 2005. Thermodynamics of energy production from biomass. CRC. Crit. Rev. Plant Sci. 24, 327–364. doi:10.1080/07352680500316029

Perez-Jimenez, J.A., 2015. Gaseous Emissions from the Combustion of Biomass Pellets, in: Garcia-Maraver, A., Perez-Jimenez, J.A. (Eds.), Biomass Pelletization - Standards and Production. WIT Press, Boston, pp. 87–99. doi:10.2495/978-1-84566-062-8/006

Pizzi, A., Foppa Pedretti, E., Duca, D., Rossini, G., Mengarelli, C., Ilari, A., Mancini, M., Toscano, G., 2018. Emissions of heating appliances fuelled with agropellet produced from vine pruning residues and environmental aspects. Renew. Energy 121, 513–520. doi:10.1016/j.renene.2018.01.064

Růžičková, J., Kucbel, M., Raclavský, K., Raclavská, H., 2016. Chemical composition of biochar from combustion in local heating. Inz. Miner. Polish Miner. Eng. Soc. 17, 23–27.

Schmidl, C., Luisser, M., Padouvas, E., Lasselsberger, L., Rzaca, M., Ramirez-Santa Cruz, C., Handler, M., Peng, G., Bauer, H., Puxbaum, H., 2011. Particulate and gaseous emissions from manually and automatically fired small scale combustion systems. Atmos. Environ. 45, 7443–7454. doi:10.1016/j.atmosenv.2011.05.006

Schmidl, C., Marra, I.L., Caseiroa, A., Kotianová, P., Berner, A., Bauer, H., Kasper-Giebl, A., Puxbaum, H., 2008. Chemical characterisation of fine particle emissions from wood stove combustion of common woods growing in mid-European Alpine regions. Atmos. Environ. 42, 126–141. doi:10.1016/j.atmosenv.2007.09.028

Schmidt, G., Trouvé, G., Leyssens, G., Schönnenbeck, C., Genevray, P., Cazier, F., Dewaele, D., Vandenbilcke, C., Faivre, E., Denance, Y., Le Dreff-Lorimier, C., 2018. Wood washing: Influence on gaseous and particulate emissions during wood combustion in a domestic pellet stove. Fuel Process. Technol. 174, 104–117. doi:10.1016/j.fuproc.2018.02.020

Setiawan, Y., Surachman, A., 2015. Reject waste pellets of paper mills as fuel and their Contribution to Greenhouse Gas (GHG). Int. J. Technol. 6, 847–855. doi:10.14716/ijtech.v6i5.1790

Shen, G., Tao, S., Wei, S., Zhang, Y., Wang, R., Wang, B., Li, W., Shen, H., Huang, Y., Chen, Y., Chen, H., Yang, Y., Wang, W., Wei, W., Wang, X., Liu, W., Wang, X., Simonich, S.L.M., 2012. Reductions in emissions of carbonaceous particulate matter and polycyclic aromatic hydrocarbons from combustion of biomass pellets in comparison with raw fuel burning. Environ. Sci. Technol. 46, 6409–6416. doi:10.1021/es300369d

Sippula, O., Hytönen, K., Tissari, J., Raunemaa, T., Jokiniemi, J., 2007. Effect of wood fuel on the emissions from a top feed pellet stove. Energ. Fuel. 21, 1151–1160. doi:10.1021/ef060286e

Sippula, O., Lamberg, H., Leskinen, J., Tissari, J., Jokiniemi, J., 2017. Emissions and ash behavior in a 500 kW pellet boiler operated with various blends of woody biomass and peat. Fuel 202, 144–153. doi:10.1016/j.fuel.2017.04.009

Telmo, C., Lousada, J., 2011. Heating values of wood pellets from different species. Biomass and Bioenergy 35, 2634–2639. doi:10.1016/j.biombioe.2011.02.043

Tissari, J., Sippula, O., Kouki, J., Vuorio, K., Jokiniemi, J., 2008. Fine particle and gas emissions from the combustion of agricultural fuels fired in a 20 kW burner. Energ. Fuel. 22, 2033–2042. doi:10.1021/ef700766y

Venturini, E., Vassura, I., Agostini, F., Pizzi, A., Toscano, G., Passarini, F., 2018. Effect of fuel quality classes on the emissions of a residential wood pellet stove. Fuel 211, 269–277. doi:10.1016/j.fuel.2017.09.017

Verma, V.K., Bram, S., Delattin, F., Laha, P., Vandendael, I., Hubin, A., De Ruyck, J., 2012. Agro-pellets for domestic heating boilers: Standard laboratory and real life performance. Appl. Energy 90, 17–23. doi:10.1016/j.apenergy.2010.12.079

Verma, V.K., Bram, S., Gauthier, G., De Ruyck, J., 2011. Performance of a domestic pellet boiler as a function of operational loads: Part 2. Biomass Bioenergy 35, 272–279. doi:10.1016/j.biombioe.2010.08.043

Vicente, A., Alves, C., Monteiro, C., Nunes, T., Mirante, F., Cerqueira, M., Calvo, A., Pio, C., 2012. Organic speciation of aerosols from wildfires in central Portugal during summer 2009. Atmos. Environ. 57, 186–196. doi:10.1016/J.ATMOSENV.2012.04.030

Vicente, A., Alves, C., Monteiro, C., Nunes, T., Mirante, F., Evtyugina, M., Cerqueira, M., Pio, C., 2011. Measurement of trace gases and organic compounds in the smoke plume from a wildfire in Penedono (central Portugal). Atmos. Environ. 45, 5172–5182. doi:10.1016/j.atmosenv.2011.06.021

Vicente, E.D., Duarte, M.A., Calvo, A.I., Nunes, T.F., Tarelho, L.A.C., Custódio, D., Colombi, C., Gianelle, V., Sanchez de la Campa, A., Alves, C.A., 2015. Influence of operating conditions on chemical composition of particulate matter emissions from residential combustion. Atmos. Res. 166, 92–100. doi:10.1016/j.atmosres.2015.06.016

Vicente, E.D., Alves, C.A., 2018. An overview of particulate emissions from residential biomass combustion. Atmos. Res. 199, 159–185. doi:10.1016/j.atmosres.2017.08.027

Vicente, E.D., Duarte, M.A., Tarelho, L.A.C., Nunes, T.F., Amato, F., Querol, X., Colombi, C., Gianelle, V., Alves, C.A., 2015. Particulate and gaseous emissions from the combustion of different biofuels in a pellet stove. Atmos. Environ. 120, 15–27. doi:10.1016/j.atmosenv.2015.08.067

Vicente, E.D., Vicente, A., Evtyugina, M., Carvalho, R., Tarelho, L.A.C., Oduber, F.I., Alves, C., 2018. Particulate and gaseous emissions from charcoal combustion in barbecue grills. Fuel Process. Technol. 176, 296–306. doi:10.1016/j.fuproc.2018.03.004

Vicente, E.D., Vicente, A.M., Musa Bandowe, B.A., Alves, C.A., 2016. Particulate phase emission of parent polycyclic aromatic hydrocarbons (PAHs) and their derivatives (alkyl-PAHs, oxygenated-PAHs, azaarenes and nitrated PAHs) from manually and automatically fired combustion appliances. Air Qual. Atmos. Health 9, 653–668. doi:10.1007/s11869-015-0364-1

Wang, L., Skjevrak, G., Hustad, J.E., Gronli, M.G., 2011. Effects of sewage sludge and marble sludge addition on slag characteristics during wood waste pellets combustion. Energ. Fuel. 25, 5775–5785. doi:10.1021/ef2007722

Wilson, J.R.U., Gairifo, C., Gibson, M.R., Arianoutsou, M., Bakar, B.B., Baret, S., Celesti-Grapow, L., Ditomaso, J.M., Dufour-Dror, J.M., Kueffer, C., Kull, C.A., Hoffmann, J.H., Impson, F.A.C., Loope, L.L., Marchante, E., Marchante, H., Moore, J.L., Murphy, D.J., Tassin, J., Witt, A., Zenni, R.D., Richardson, D.M., 2011. Risk assessment, eradication, and biological control: Global efforts to limit Australian acacia invasions. Divers. Distrib. 17, 1030–1046. doi:10.1111/j.1472-4642.2011.00815.x

Win, K.M., Persson, T., 2014. Emissions from residential wood pellet boilers and stove characterized into start-up, steady operation, and stop emissions. Energ. Fuel. 28, 2496–2505. doi:10.1021/ef4016894

Wöhler, M., Jaeger, D., Reichert, G., Schmidl, C., Pelz, S.K., 2017. Influence of pellet length on performance of pellet room heaters under real life operation conditions. Renew. Energy 105, 66–75. doi:10.1016/j.renene.2016.12.047

Zakeri, B., Rinne, S., Syri, S., Zakeri, B., Rinne, S., Syri, S., 2015. Wind integration into energy systems with a high share of nuclear power-What are the compromises? Energies 8, 2493–2527. doi:10.3390/en8042493

Zou, Y., Jin, C., Su, Y., Li, J., Zhu, B., 2016. Water soluble and insoluble components of urban $PM_{2.5}$ and their cytotoxic effects on epithelial cells (A549) *in vitro*. Environ. Pollut. 212, 627–635. doi:10.1016/j.envpol.2016.03.022

CHAPTER 5

Chapter 5. *In vitro* toxicity of PM_{10} emissions from residential pellets combustion

Chapter section to be submitted as original article:

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Abstract

Particulate matter emissions (PM_{10}) from the combustion, in a residential stove, of two commercial brands of certified (ENplus A1) pellets, a non-certified brand and laboratory made pellets of acacia were tested for their ability to induce ecotoxic, cytotoxic, and mutagenic responses in unicellular organisms and a human cell line. Ecotoxicity was evaluated through the *Vibrio fischeri* bioluminescence inhibition assay. Moreover, cytotoxicity was assessed at two time points (24- and 48-h) through two complementary techniques in order to evaluate the cellular metabolic activity and membrane integrity of human lung epithelial cells A549. The Ames test using two *Salmonella typhimurium* strains (TA100 and TA98) was employed to assess the mutagenic potential of the samples. Results obtained with the bioluminescent bacteria indicated that only particles from the combustion of acacia pellets were toxic. All samples induced impairment on the A549 cells metabolic activity, while no significant release of lactate dehydrogenase was recorded. PM_{10} emissions from acacia pellets were the most cytotoxic, while samples from both certified pellets evoked significant cytotoxicity at lower doses. Cytotoxicity time-dependency was only observed for PM_{10} from the combustion of acacia pellets and one of the brands of certified pellets. Mutagenic activity was not detected in either *S. typhimurium* strains. This study emphasises the role of the raw material for pellet manufacturing on the toxicological profile of PM emissions. Alternative raw materials should be deeply investigated before their use in pelletisation and combustion in residential appliances.

Keywords: Ecotoxicity, Cytotoxicity, Mutagenicity, Fuel quality, Pellet combustion, PM_{10} emissions.

5.1. Introduction

Residential biomass combustion is regarded as a major source of airborne particulate matter (PM) all over the world (Vicente and Alves, 2018). The adverse impacts on health of biomass combustion smoke has been demonstrated and reviewed by several researchers (Naeher et al., 2007; Sigsgaard et al., 2015; Zelikoff et al., 2002).

In developed countries, the prevalence of batch fired traditional small combustion appliances is a major concern given their high PM emissions (Olsen et al., 2020; Vicente and Alves, 2018). Research focusing on the *in vivo* (Barregard et al., 2008, 2006; Danielsen et al., 2010; Unosson et al., 2013) and *in vitro* (Danielsen et al., 2009; Dilger et al., 2016; Kocbach et al., 2008) toxicity of particulate matter from manually operated devices has been carried out over the past years. *In vivo* studies, exposing experimentally healthy human subjects to wood combustion emissions, have reported mild inflammatory responses both in the respiratory tract and the systemic circulation, and a tendency towards increased blood coagulation (Barregard et al., 2008, 2006). Considering the mounting evidence pointing to the importance of combustion conditions and fuel quality on PM emissions and their physicochemical properties, studies have been designed to investigate the role of these features on the toxicological profiles (Erlandsson et al., 2020; Jalava et al., 2010; Kasurinen et al., 2017; Vu et al., 2012). Nevertheless, automatically fired appliances, fueled automatically with compressed biomass, have gained notoriety over the last years (Bioenergy Europe, 2018). Despite the better environmental performance of these systems compared to the conventional ones, the emissions arising from pellet combustion can still be noticeable depending on the fuel and appliance design and operation (Boman et al., 2011; Polonini et al., 2019; Venturini et al., 2018, 2015; Verma et al., 2013; Win and Persson, 2014; Wöhler et al., 2017). With the introduction of automatically fed small-scale combustion devices, the investigation has focused on these new heating systems, mainly aiming at comparing the toxicity of their emissions with those recorded for the batch fired appliances. Previously, *in vivo* and *in vitro* studies have demonstrated that pellet combustion generates biologically active PM. Employing the intratracheal aspiration technique to deliver particulate samples from biomass combustion into the lower airways of mice; Uski et al. (2012) reported that PM samples from modern technologies had higher potency to induce inflammation compared to those from old technology appliances. Additionally, the researchers found a positive correlation between inflammatory markers and ash related constituents of particles. Happo et al. (2013) found similar results regarding the inflammatory potential of particles from pellet combustion in comparison with those generated from wood. Additionally, the researchers observed the highest cytotoxic and genotoxic activities for PM emissions from modern technology appliances when assessing pulmonary tissue damage after exposure of mice for 24 h. *In vitro* studies, using cultures of different eukaryotic cells (human and animal) from different origins (e.g. epithelia, macrophage) revealed that particles from pellet combustion induce cytotoxicity, inflammation and genotoxicity (Corsini et al., 2013, 2017; Jalava et al., 2012; Kasurinen et al., 2016, 2017, 2018; Marabini et al., 2017; Tapanainen et al., 2011). Tapanainen et al. (2011) compared the cytotoxicity of PM_1 emitted from a pellet boiler and a conventional masonry heater. The researchers reported that both types of samples increased cell death in a dose-dependent manner and had similar potency in inducing acute cell death. On the contrary, Kasurinen et al. (2017) found emissions from log wood (birch, beech and spruce) combustion in a modern masonry heater considerably more toxic in all endpoints (cytotoxicity, genotoxicity, inflammation and oxidative stress) than the emissions from a pellet boiler fired with softwood pellets. Similar conclusions were drawn by Corsini et al. (2017). The researchers reported that pellet stoves generate less active ultrafine particles compared to the ones generate from woodstoves. The mutagenic activity of the PM-bound PAHs from the residential combustion of pellets and wood has been assessed by Canha et al. (2016) using the Ames test with different strains of *Salmonella typhimurium* (TA98 and TA100). The researchers found stronger mutagenic effects for the manually wood-fired appliance than for the automatically fired pellet stove.

The physicochemical characteristics of pelletised biofuels may significantly influence the combustion efficiency, emissions and toxicological properties, constituting an issue of great research interest. Despite the importance of the subject, few studies have been devoted to explore the effect of the pellet fuel on the toxicological profiles (Corsini et al., 2017, 2013; Kasurinen et al., 2016; Marabini et al., 2017). The study of Kasurinen et al. (2016) revealed that the raw material used for the pellet manufacturing influence the cytotoxicity, genotoxicity and potential to induce inflammation of the particulate emissions. The researchers concluded that alternative pellet materials may cause not only higher emissions but also increase the particle toxicity. Despite the innovative results, each fuel under evaluation was burned in a different combustion appliance, meaning that besides the fuel, the effect of the combustion technology also must be considered. The remaining studies were conducted using two pellet types (fir and beech pellets) and a pellet stove representing fuels and technologies typical of the Italian market (Corsini et al., 2017, 2013; Marabini et al., 2017).

In our previous study, it was observed that the pellet quality, based on certification criteria, may not ensure high combustion performance and low emissions. The combustion of two brands of ENplus certified pellets, with identical quality class (A1), and one brand of non-certified pellets showed that even certified material does not always meet emission requirements (Vicente et al., 2020). Additionally, the characterisation of emissions from the combustion of a pelletised invasive species growing in Portuguese coastal areas revealed that the raw material can have a great influence on the composition of the generated PM (Vicente et al., 2019). This study aims to be a step forward for a better characterisation of the toxicological potential of particles emitted in the combustion of different biofuels: i) similar quality fuels (ENplus A1 labelled), ii) commercial pellets without certification label, and iii) “homemade” pellets from alternative raw material (*Acacia longifolia*, an invasive species in Portugal). To achieve this goal, a battery of *in vitro* bioassays was used, including cost and time effective bacterial assays and tests with mammalian cells (human lung epithelium).

5.2. Material and methods

5.2.1. PM sampling and analysis

The combustion experimental setup and sample collection procedures were described in detail in previous studies (Vicente et al., 2019, 2020). PM_{10} samples were obtained from tests conducted on a commercial top-fed pellet stove fueled by two brands of ENplus A1 certified pellets (P and R), non-certified commercial pellets and laboratory manufactured acacia pellets.

Particulate matter (PM_{10}) samples were collected, after the full dilution of the flue gas (hood), in a dilution tunnel under isokinetic conditions onto 47 mm quartz filters (Pallflex®) using a low volume sampler (TCR TECORA). Filters were kept at -20 °C immediately after sampling and until PM_{10} extraction for chemical and toxicological analysis. Blank filter control substrates were treated similarly as the samples.

The content of organic (OC) and elemental carbon (EC) in the samples was determined by a thermal optical transmission technique. The analysis of the water soluble ions in the particulate samples was carried out by ion chromatography (DIONEX Thermo Scientific, ICS-5000 + DC). The detailed organic speciation was carried out by gas chromatography-mass spectrometry (Thermo Scientific, Trace Ultra, quadrupole DSQ II and Shimadzu, QP5050A). Details of these procedures were previously provided by Vicente et al. (2019, 2020).

5.2.2. Sample preparation for toxicological assays

The detailed procedure of PM_{10} extraction for the ecotoxicological analyses was described in detail elsewhere (Kováts et al., 2012). Briefly, one filter spot (14 mm) from each sample was grounded in an agate mortar and a suspension was made by adding 2 ml of high-purity water.

For the cytotoxicity and mutagenicity evaluation, portions of replicates samples obtained for each fuel were pooled to form PM_{10} composite samples representing each pellet type under analysis.

The composite samples were firstly extracted by refluxing dichloromethane for 24 h and subsequently extracted in methanol by sonication in a water bath at room temperature. After extraction, the samples were concentrated (0.5 ml) initially using a Turbo Vap® II evaporation system (Biotage, Charlotte, NC, USA) and then evaporated to dryness under nitrogen gas. Additionally, the mutagenic potential of the polycyclic aromatic hydrocarbon (PAH) fraction of the organic extracts was also evaluated. To obtain the PAH fraction, after the extraction with dichloromethane and methanol described above, the extracts were separated into different organic fractions using a glass chromatographic column packed with activated silica gel, which were eluted by solvents of increasing polarity under nitrogen flow. The PAH extracts were concentrated using the Turbo Vap® II, and completely dried under a gentle stream of nitrogen. PM_{10} samples and extracts were stored at -20 °C for subsequent toxicological analyses. In order to evaluate the contribution of the matrix, blank filters were extracted under the same conditions. No changes in any of the parameters measured compared to control were observed for blank filters. For the mutagenic and cytotoxic assays, the samples were resuspended in dimethyl sulfoxide (DMSO, Sigma Aldrich).

5.2.3. *Vibrio fischeri* inhibition assay

The bioluminescence inhibition assay was carried out in accordance with the ISO 21338:2010 (water quality - kinetic determination of the inhibitory effects of sediment, other solids and coloured samples on the light emission of *Vibrio fischeri*/kinetic luminescent bacteria test) using the LUMIStox test kit (Hach Lange) that includes the lyophilised bacteria, reconstitution solution and NaCl solution. The lyophilised bacteria were rehydrated with the reactivation solution and stabilised for 30 min at 12 °C. The assay was performed in 96-well white polypropylene microplates. Double determinations of eleven dilutions made in NaCl (2%) were carried out for each sample. The luminescence was recorded during the first 30 s after the dispensing of the bacteria in each well and then, after 30 min-incubation at 12 °C, the light output was recorded again. The luminescence was measured with a luminometer (Luminoskan Ascent, Thermo Scientific), which has a shaking feature that ensures effective mixing of the sample and bacteria during the measurements. The interfering losses of luminescence, due to light absorption by coloured samples, is compensated by using as reference the luminescence intensity of the peak value observed immediately after addition of bacteria into sample. EC_{50} values, PM_{10} concentration that induces a reduction of 50% in the bioluminescence of the *V. fischeri*, were determined using the Ascent Software provided by Aboatox Co. Toxicity units ($TU = 100/EC_{50}$) were calculated to evaluate the toxicity levels of the samples: $TU_{50} < 1$ non-toxic, $1 < TU_{50} < 10$ toxic, $10 < TU_{50} < 100$ very toxic and $TU_{50} > 100$ extremely toxic (Romano et al., 2020).

5.2.4. Cell culture and cytotoxicity assessment

The human alveolar epithelial cells A549 were routinely maintained at 37 °C in an atmosphere containing 5% CO_2. The cells were grown in Kaighn's Modification of Ham's F-12 Medium (F-12K), supplemented with 10% (v/v) of FBS (Fetal Bovine Serum, Gibco), 1% of penicillin-streptomycin (Gibco) and 1% Fungizone (Gibco). Cell confluence and morphology were observed under an inverted microscope (Nikon® Eclipse TS100) and subcultured when culture reached approximately 90% confluence.

For the cytotoxicity assays, A549 cells were counted and seeded at a concentration of 4×10^3 cells/well in 96-well plates. After an adhesion period of 24-h, cells were treated with increasing concentrations of PM_{10} for 24- and 48-h. For each sample, series of five two-fold serial dilution, starting at 150 µg ml^{-1}, were prepared in 96 well plates. The PM_{10} cytotoxicity was evaluated measuring the extracellular lactate dehydrogenase (LDH) from cell membrane-damaged cells in cell-free culture supernatants (Cytotoxicity Detection Kit LDH, Roche Diagnostics, France) and by evaluating mitochondrial activity (Cell Counting Kit CCK-8, Sigma Aldrich). In brief, after the exposure time, the supernatant was collected for LDH assay and fresh medium was added to each well to perform the WST-8 test. Cells were treated with 10 µl of WST-8 solution, incubated for 2 h at 37 °C, and cell viability was quantified by measuring the absorbance at 450 nm in a microplate reader (Biotek® - Gen5™ software). The supernatants were transferred into new 96-well plates, the reaction solution was added and incubated for 30 min at room temperature and protected from light. After incubation, the absorbance was measured at 490 nm using a microplate reader (Biotek® - Gen5™ software). The culture medium without cells was used as background. Cells were also treated with Triton-X (2%, 10 minutes at culture conditions) to lyse cells and obtain the positive control. Exposure of the cells was made in triplicate in two independent experiments. All experiments included DMSO and blank quartz filter (matrix) controls. DMSO were kept below 1.2 % (v/v) in the culture medium.

5.2.5. Ames test

The mutagenic potential of PM_{10}-bound PAHs was assessed by employing the *Salmonella typhimurium* preincubation assay (Mortelmans and Zeiger, 2000; OECD, 1997) using the base-substitution strain TA100 and the frameshift strain TA98 (Trinova Biochem GmbH). The tests were carried out in the presence (+S9) and absence (-S9) of metabolic activation using S9 from a pool of livers from male rats (Sigma Aldrich).

Before the experiments, the tester strains were inoculated in nutrient broth (Sigma Aldrich) overnight (15-18 h) at 37 °C, in the dark, and gently shaken. An aliquot of each sample (50 µl) was added to 500 µl of sterile phosphate buffer (-S9) or to 500 µl of S9 mixture freshly prepared (+S9), plus 100 µl of bacterial culture and then incubated at 37 °C for 20 min. Subsequently, a volume of 2 ml of overlay agar was added, and the mixture poured onto the surface of a glucose minimal agar plate containing a trace amount of histidine. After hardening, the plates were incubated at 37 °C for 48 h and subsequently the revertant colonies formed in each plate were counted and the results expressed as number of revertant colonies per plate. Due to limited sample quantity, the combustion extracts were resuspended in DMSO and applied to the plates at their maximum dose in triplicate. All the solutions used for the assay were prepared according to Mortelmans and Zeiger (2000).

In addition to the test plates containing combustion extracts, a negative control consisting of distilled sterilised water, a solvent control with DMSO, and positive control plates containing known mutagens were also included to confirm the reversion properties of each strain under the assay conditions. For experiments with S9, 2-minoanthracene (Sigma Aldrich) was used as positive control for both strains whereas for experiments without S9, sodium azide (Acros Organics) and 2-nitrofluorene (Sigma Aldrich) were used as positive control for TA100 and TA98, respectively. The spontaneous reversion frequency was found to be within the range reported by Mortelmans and Zeiger (2000).

5.2.6. Statistical analysis

The data were analysed using the SPSS software (IBM SPSS statistics version 26). Before the analysis, Shapiro-Wilk test for normality and Levene's test for equality of variances, were used. The cellular viability results obtained with both tests (WST-8 and LDH) were tested with the non-parametric Kruskall-Wallis test followed by Dunn’s post hoc tests and Bonferroni adjustment to the p-value. Differences between time points (24- and 48-h) were tested by Mann-Whitney’s U-test. Regarding the results of the Ames test, comparisons between the number of revertents in the test plates and the negative control were made by one-way-ANOVA followed by Dunnett’s post hoc test considering the first level as control (negative control). Additionally, a count of revertant colonies on the test plates over 2 times those in the negative controls was taken as a measure of mutagenicity at the applied dose level. DMSO was used as the control after verifying the inexistence of significant differences between the number of revertent colonies of the DMSO and sterilised water plate controls. The correlation analyses between the toxicological responses and chemical composition were made by Spearman's correlations. All the differences were regarded as statistically significant at $p < 0.05$.

5.3. Results

5.3.1. PM_{10} emission factors and particle chemical composition

The detailed characterisation of combustion conditions, emissions and comprehensive chemical composition of particulate emissions was provided in previous studies (Vicente et al., 2020, 2019) and will be only briefly summarised here.

PM_{10} emission factors varied greatly depending on the pellet type burned (Table 5.1). Acacia pellets generated PM_{10} emissions, on average, 3 to 4 times higher than commercial pellets. Acacia pellets also generated the highest OC emission factors (12 – 41 times), while the highest EC emissions were recorded for non-certified pellets (Table 5.1).

Table 5.1. PM_{10} and carbonaceous species emission factors from the combustion of the distinct types of pellets. Modified from Vicente et al. (2020, 2019).

	PM_{10} mg MJ^{-1}	OC mg MJ^{-1}	EC mg MJ^{-1}
Acacia pellets	118 ± 14.4	22.9 ± 9.28	6.82 ± 2.47
Non-certified pellets	39.8 ± 8.79	1.84 ± 0.676	12.1 ± 1.46
Certified pellets R	40.7 ± 3.70	1.98 ± 1.27	2.32 ± 0.089
Certified pellets P	27.1 ± 7.91	0.555 ± 0.519	8.33 ± 5.66

EC: elemental carbon; OC: organic carbon. Emission factors for commercial pellets are presented as mean ± standard deviation of different operational conditions of the stove including operation under low, medium and nominal load. Emission factors of acacia pellets are mean ± standard deviation from the stove operation under medium load.

EC dominated the carbonaceous fraction of the PM_{10} emitted by commercial pellets while the total carbon was mainly constituted by OC in PM_{10} from the combustion of acacia pellets. The emissions from all pellets under analysis were dominated by water soluble ions. Substantial differences were observed for the contribution of water soluble ions to the PM_{10} mass (Table 5.2). The dominant water soluble species in particles resulting from the combustion of certified pellets was sulphate, while chloride was the most abundant in PM_{10} generated from the combustion of acacia and non-certified pellets. The second major contributing species to the PM_{10} mass was potassium regardless of the pellet type burned. The sodium content in particles from acacia pellets was, on average, 3 to 7 times higher than in samples from commercial pellets. In contrast, the sum of PM_{10}-bound PAHs was substantially lower in the emissions from acacia pellets (Table 5.2). Differences in the composition of PM_{10}-bound oxygenated compounds were also recorded.

Table 5.2. Chemical constituents in PM_{10} emitted during the combustion of different pellets. Modified from Vicente et al. (2020, 2019).

	Acacia pellets	Non-certified pellets	Certified pellets R	Certified pellets P
Water soluble ions (%wt. PM_{10})				
Sodium	6.06	1.82	1.50	0.884
Potassium	22.4	16.8	17.7	20.9
Chloride	24.5	16.9	9.09	9.71
Nitrate	1.14	1.42	4.70	0.335
Sulphate	6.93	10.0	23.2	22.6
Σ of other inorganic ions analysed[a]	1.52	1.22	1.31	1.12
PAHs (µg g^{-1} PM_{10})				
Fluorene	-	7.22	-	-
Phenanthrene	0.061	-	1.72	4.28
Anthracene	0.045	0.067	0.120	0.790
Retene	8.77	105	177	88.9
Fluoranthene	1.46	45.7	26.9	96.5
Pyrene	2.31	51.1	23.5	101
Chrysene	6.67	33.1	13.9	15.7
Benzo[a]anthracene	4.81	12.8	9.00	6.90
Benzo[b]fluoranthene	0.097	5.50	6.91	-
Benzo[k]fluoranthene	-	6.18	5.55	-
Benzo[e]pyrene	1.47	6.52	5.99	0.150
Benzo[a]pyrene	2.51	3.58	6.11	0.261
Perylene	-	-	0.157	0.906
Dibenzo[a,h]anthracene	-	-	0.625	-
Indeno[1,2,3-cd]pyrene	1.85	-	4.89	-
Benzo[g,h,i]perylene	1.89	0.369	5.77	-
Monosaccharide anhydrides (µg g^{-1} PM_{10})				
Levoglucosan	284	90.3	153	68.9
Mannosan	24.2	13.3	17.8	9.88
Galactosan	10.4	8.57	57.0	5.68
Phenolic compounds (µg g^{-1} PM_{10})				
Benzyl alcohol	0.136	37.3	30.9	305
Coniferyl alcohol	3.62	-	0.148	-
Vanillin	1.48	2.75	2.54	3.20

Vanillic acid	8.81	-	2.97	0.481
Syringic acid	9.34	0.051	0.204	-
Sinapyl alcohol	1.95	-	-	-
Cinnamic acid	0.150	1.50	10.4	1.16
Hydrocinnamic (coumaric) acid	4.20	-	8.15	-
3-Methoxy-4-hydroxycinnamic (ferulic) acid	0.490	-	0.155	-
4-Hydroxybenzaldehyde	12.3	26.4	3.98	23.6
4-Hydroxybenzoic acid	2.07	1.71	0.596	2.33
4-Phenylphenol	0.151	-	0.163	-
2,4-Di-tert-butylphenol	11.7	104	14.7	1.64
Resorcinol	3.55	0.141	0.729	0.343
4-Hydroxyphenylethanol (tyrosol)	0.552	28.3	-	132
2-Isopropyl-5-methylphenol (thymol)	0.389	-	1.63	-
Isoeugenol	1.77	1.06	-	1.19
2,6-Di-tert-butyl-1,4-benzoquinone	0.16	32.3	0.965	38.6
Resin acids (μg g^{-1} PM$_{10}$)				
Abietic acid	-	2.84	-	-
Dehydroabietic acid	4.92	7.08	54.1	-
Isopimaric acid	0.398	1.06	1.19	0.744
Sterols (μg g^{-1} PM$_{10}$)				
Cholesterol	0.222	13.0	-	15.8
β-Sitosterol	1.54	6.03	-	10.5
Stigmasterol	0.416	-	-	-
5-Cholestan-3-ol (dehydrocholesterol)	0.005	-	-	-

[a] Lithium, magnesium, calcium, fluoride, bromide and nitrite. – not detected or below detection limit.

5.3.2. *Vibrio fischeri* bioluminescence inhibition

The ecotoxicity of PM$_{10}$ samples was assessed using the aqueous extracts and expressed as percentage of the *V. fischeri* bioluminescence inhibition after 30 min of exposure. Toxicity increased in the following order: certified pellets P < certified pellets R < non-certified pellets < acacia pellets. PM$_{10}$ collected from the combustion of acacia pellets resulted in the highest toxicity with an EC$_{50}$ of 21 μg ml^{-1}. Although the EC$_{50}$ for the certified pellets P was 4.0 and 6.9 times higher than the one obtained for the certified pellets R and non-certified pellets, respectively, the TU$_{50}$ values indicate that none of these samples are toxic (Figure 5.1).

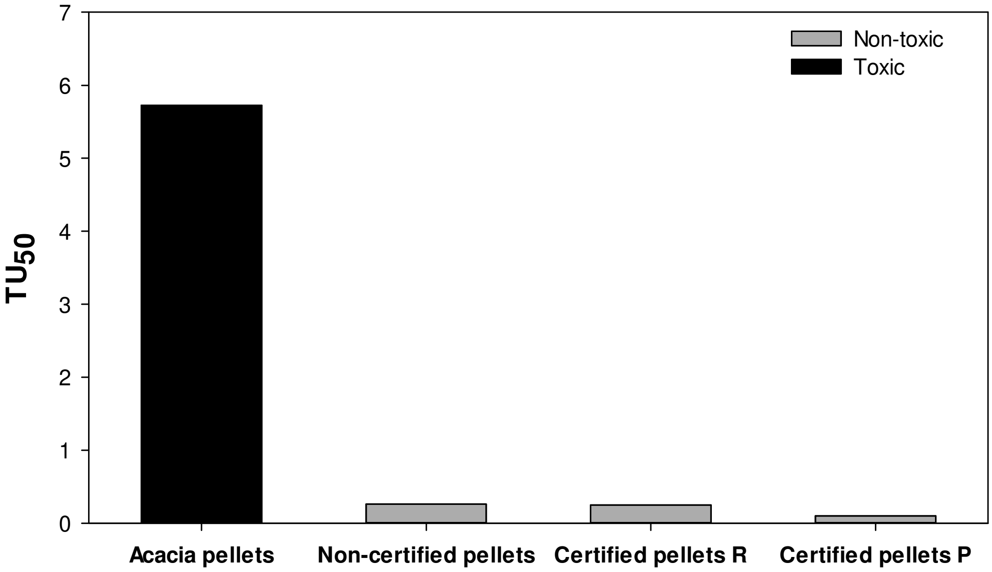


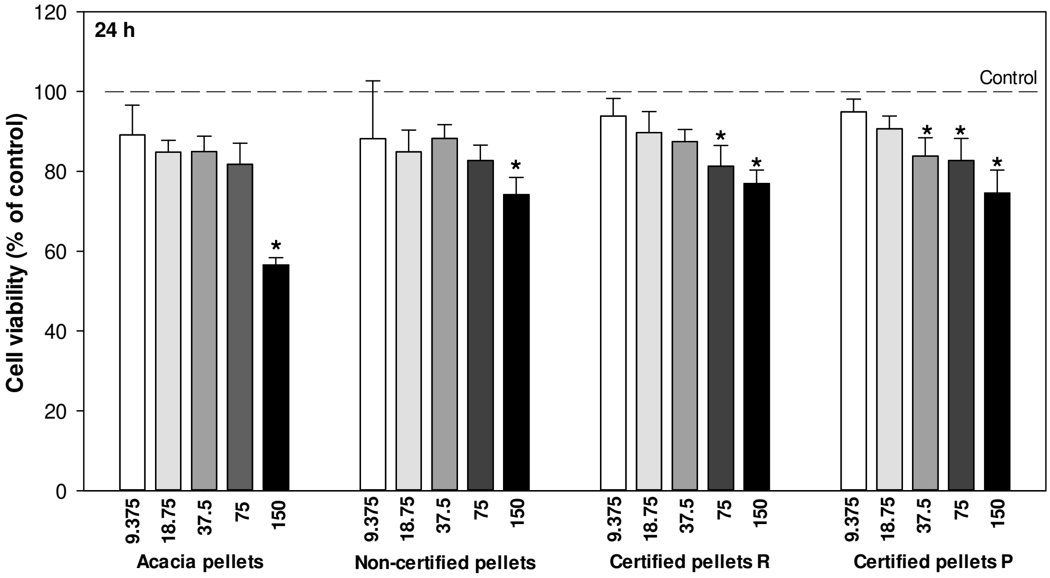
Figure 5.1. Toxicity of each sample, expressed in toxic units, based on the results of the *Vibrio fischeri* bioluminescence inhibition bioassay.

In a previous study, Turóczi et al. (2012) compared the ecotoxicity of particulate samples from wood combustion collected downwind an open fireplace, urban aerosol, diesel PM, resuspended road dust and particles from cigarette smoking. Fresh biomass smoke and cigarette smoke presented similar level of ecotoxicity being more potent than particles from modern diesel engines. In the present study, significant correlations between the organic component of the samples and the increase in toxicity were not detected.

5.3.3. Cellular metabolic activity

All the organic extracts of the PM_{10} samples collected during the combustion of different pellets caused a significant decline in cell viability/mitochondrial function when assessed with the WST-8 test. After 24-h of exposure, the most severe increase in cytotoxicity was recorded for the PM_{10} organic extracts from acacia pellets (Figure 5.2). The decrease of the cellular metabolic activity caused by the particles from the combustion of these pellets was dose-dependent with significance from control at the highest dose (150 μg ml^{-1}), which caused a decline in mitochondrial function over 40%. A dose-dependent decrease in the viability of A549 cells was also recorded after exposure to combustion particles from certified pellets. Under the 150-μg ml^{-1} dosage, particles from certified pellets R and P decreased metabolic activity down to 77.0 ± 3.36% and 74.1 ± 3.33%, respectively. Despite the lower decrease in relation to the one produced by combustion-derived particles from acacia pellets, samples from certified pellet produced statistically significant declines in cellular metabolic activity, when compared to the corresponding control, starting at lower concentrations (37.5 µg $ml^{-1}$and 75 µg ml^{-1} for certified pellets P and R, respectively). The cell metabolic activity impairment evoked by particles from the combustion of non-certified pellets was only statistically significant at the highest dose (150 µg ml^{-1}). The comparison between the different types of pellets tested revealed that, after an exposure period of 24-h, significant differences were only statistically significant at the highest dose (150 µg ml^{-1}). The statistical analysis indicated that PM_{10} from the combustion of acacia pellets was a significantly more potent inducer of cellular metabolic activity impairment than those from other pellets (certified R and P and non-certified) in terms of the percentage of viable cells. Similarly, Kasurinen et al. (2016) tested particulate emissions from the combustion of softwood pellets and three alternative pellets (poplar, miscanthus and wheat straw) for their ability to induce cytotoxic responses (MTT assay) in a murine macrophage cell line (RAW264.7). The researchers reported that PM_1 emissions from the softwood pellets caused dose-dependent decrease of the cellular metabolic activity and significant at all concentrations (15, 50, 150 and 300 µg ml^{-1}). Significant differences between the softwood and alternative pellets were only detected for poplar and straw at the highest dose. Marabini et al. (2017) also found differences in the cytotoxic responses in A549 cells, assessed by the MTT assay, from ultrafine particles emitted by the combustion of distinct pellets (hardwood and softwood) in a small scale pellet stove.

In the present study, the cellular metabolic activity was found to further decrease at the highest doses after 48-h of exposure. PM_{10} from the combustion of acacia pellets induced a significant reduction of the cellular metabolic activity starting at 37.5 µg ml^{-1}; however, dose-dependency was lacking, and the highest reduction (86%) was recorded at 75 µg ml^{-1}. For the remaining samples, the cellular metabolic activity was decreased in a dose-dependent manner for 48 h exposure. At the highest dosage (150 µg ml^{-1}), a significantly higher decrease in cellular metabolic activity was recorded after 48-h for certified pellets R and acacia pellets while no significant difference in cellular viability was recorded for non-certified pellets and certified pellets P after 24- and 48-h. After 48-h exposure, significant differences between acacia pellets and non-certified pellets started at 18.75 µg ml^{-1}. At the highest dose (150 µg ml^{-1}) significant differences were also detected between acacia pellets and certified pellets P, while certified pellets R showed no statistically significant differences with any of the other biofuels.



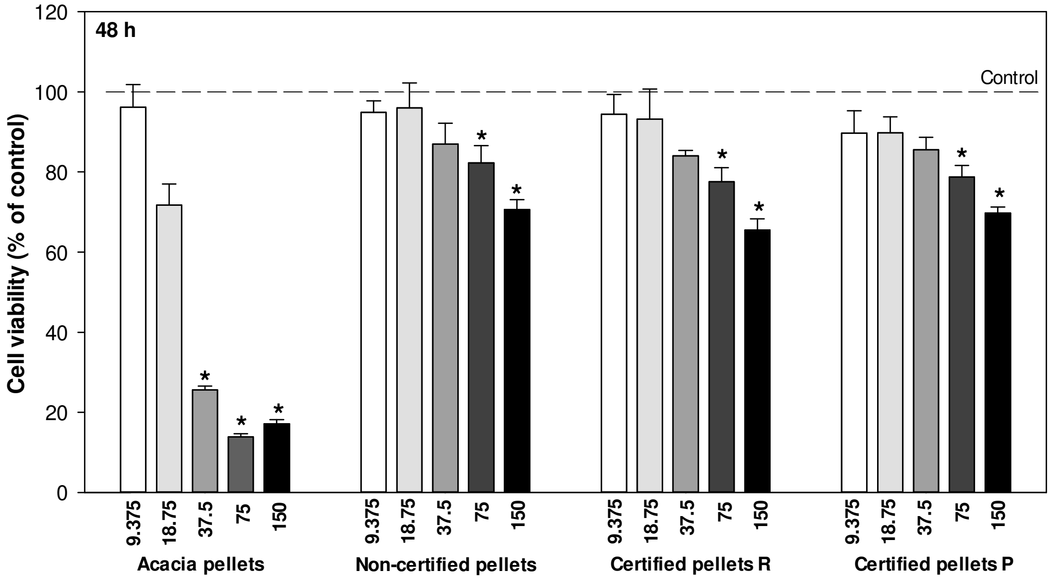


Figure 5.2. Cell viability of A549 cells assessed with WST-8 assay after a 24- and 48-h exposure of the cells to increasing concentrations of PM_{10} (9.375, 18.75, 37.5, 75 and 150 µg ml^{-1}) from the combustion of different pellets. Bars represent the experimental mean ± standard deviation. Asterisks indicate statistical significance relative to the control (Kruskal-Wallis, n = 6, $p < 0.05$).

No significant correlations were found between the impairment of cellular metabolic activity and PM_{10} chemical composition after 24-h exposure. After an exposure period of 48-h, significant correlation ($p < 0.05$) was found between the increase in cytotoxicity and the total ionic content in PM_{10} samples, as well as with PM_{10} mass fractions of vanillic acid. No correlations ($p > 0.05$) were observed between the increase in cytotoxicity and the particulate phase PAHs. Several other previous studies have failed to detect correlations between the decline in cellular metabolic activity and the PM-bound PAHs from biomass combustion (Arif et al., 2017; Jalava et al., 2012; Kasurinen et al., 2017). Kasurinen et al. (2018) also found distinct results for this relationship, depending on the cell line being tested. In addition to PAHs, various studies have pointed significant correlations between the impairment of mitochondrial function and several PM-bound elements such as Pb, Zn, Cu, Sr and Ca (Arif et al., 2017; Kasurinen et al., 2017, 2016; Uski et al., 2015). Uski et al. (2015) investigated the role of Zn in the toxicity of PM emissions from the combustion of pellets. The researchers found that the lowest dose tested caused extensive cell cycle arrest and massive cell death of the murine macrophage cell RAW 264.7.

5.3.4. Lactate dehydrogenase enzyme activity

The A549 cellular membrane integrity/cell viability was also evaluated by measuring the release of LDH in cell-free supernatants after 24- and 48-h of exposure to combustion-generated PM_{10} from the different pellet types (Figure 5.3). After both exposure periods, no significant elevation in LDH secretion was observed at any of the tested concentrations. These results are in accordance with previous studies that also pointed to the absence of any significant cellular damage as assessed with the LDH test and propidium iodide (PI) exclusion assay after exposure of different cell lines (A549, THP-1 and co-cultures) to PM emissions from pellet combustion (Corsini et al., 2017, 2013; Kasurinen et al., 2018, 2017). Corsini et al. (2013) treated epithelial and monocytic cells with increasing concentrations of $PM_{2.5}$ obtained from biomass combustion (0–100 $\mu g\ ml^{-1}$) for different times (3-48 h) and assessed cell viability by LDH leakage from damaged cells reporting no statistical significant release of LDH following exposure of the two cell types for any period. Similar results were found by Kasurinen et al. (2018) employing the PI exclusion assay on three cell culture setups (two monocultures of either human macrophage-like cells or human alveolar epithelial cells, and a co-culture of these two cell lines). The researchers reported that PM_1 emissions from the combustion of spruce pellets in a fully automated pellet boiler did not induce a significant decrease of membrane integrity in A549 cells, THP-1 cells and the co-cultured cells.

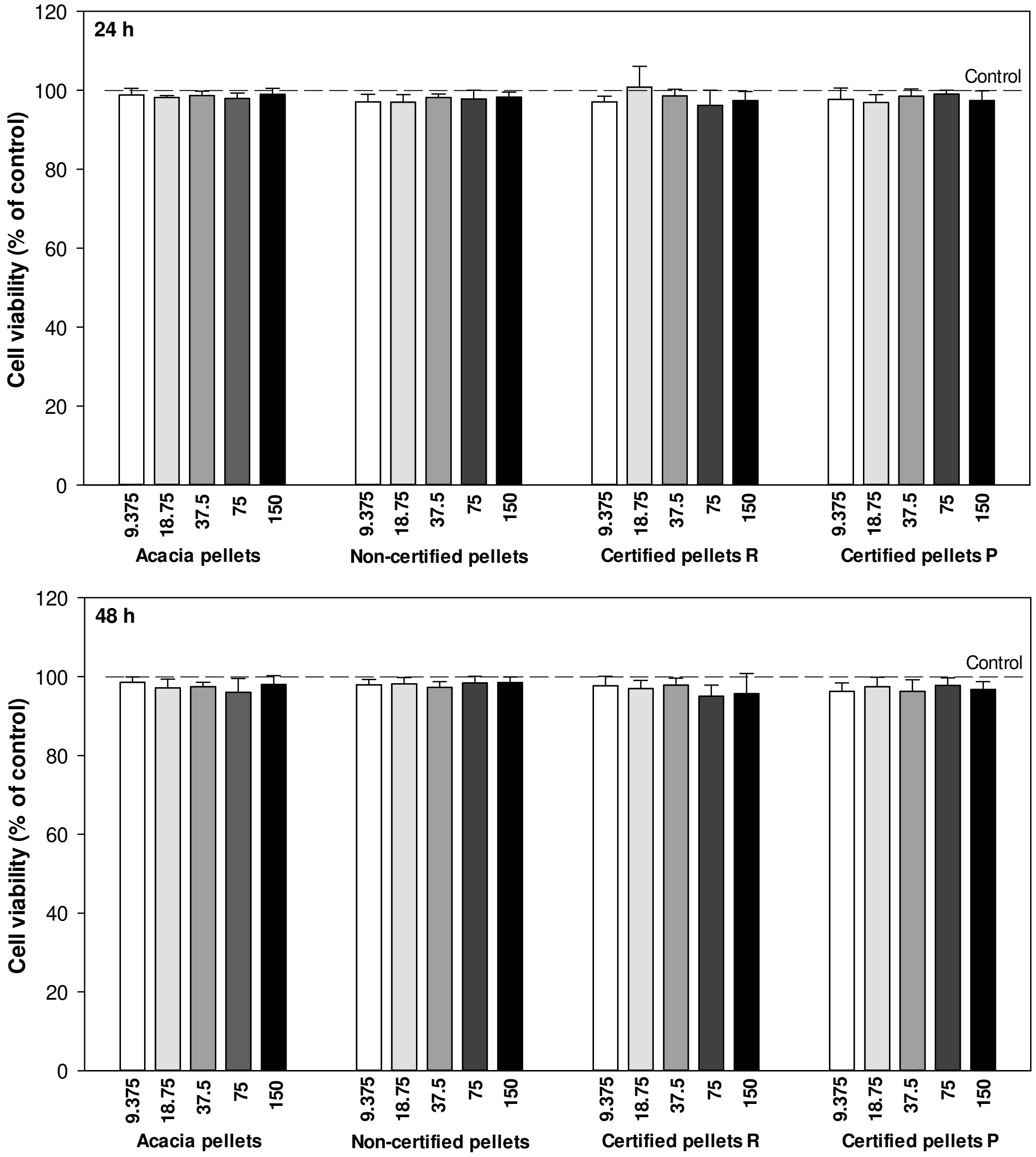


Figure 5.3. Cell viability of A549 cells assessed with LDH assay after a 24- and 48-h exposure of the cells to increasing concentrations of PM_{10} (9.375, 18.75, 37.5, 75 and 150 $\mu g\ ml^{-1}$) from the combustion of different pellets. Bars represent the experimental mean ± standard deviation. Asterisks indicate statistical significance relative to the control (Kruskal-Wallis, $n = 6$, $p < 0.05$).

5.3.5. Mutagenicity

Results of the *Salmonella* mutagenicity assay are displayed in Table 5.3. No mutagenic activity was detected after exposure to PAH extracts of PM_{10} from the combustion of the four types of pellets in any of the *Salmonella* strains tested, either with or without metabolic activation. In a similar study, Vu et al. (2012) tested PAH extracts of particles ($PM_{2.5}$) collected during the combustion of seven wood species and briquettes. While most of the samples were direct-acting mutagenic with positive response by TA98 or TA100, the $PM_{2.5}$-bound PAH extracts from the combustion of pine and acacia wood logs in traditional appliances exhibited no mutagenic activity in the tester strains. Canha et al. (2016) evaluated the mutagenicity of the PAH fraction of particulate emissions from a pellet stove fuelled with four types of pellets and three agro-fuels. Only one of the fuels (almond shell) presented a weak direct-acting mutagenic effect through a shift mutation mechanism.

In several investigations, the mutagenicity of the extractable organic matter from particles collected during the combustion of wood (Oanh et al., 2002; Mutlu et al., 2016) and pellets (Champion et al., 2020) has been established. In order to evaluate if other organic compounds might be behind a mutagenic response, the total organic extracts were also tested for their mutagenicity in the present study (Table 5.3). No mutagenic effect (direct and indirect) was found for any of the biofuels towards both strains (TA98 and TA100).

Table 5.3. Mutagenicity of PAH extracts of particles collected during the combustion of different pellets to S. typhimurium TA98 and TA100 in the absence (-S9) and presence (+S9) of metabolic activation.

		TA98		TA98 + S9		TA100		TA100 +S9	
Fuel	ng PAHs[a] per plate	Rev/plate	MR	Rev/plate	MR	Rev/plate	MR	Rev/plate	MR
Acacia pellets	15	26 ± 10	1.3	29 ± 3	1.1	138 ± 6	0.88	136 ± 18	0.88
Non-certified pellets	20	14 ± 2	0.74	23 ± 4	0.83	179 ± 28	1.1	154 ± 28	0.99
Certified pellets R	26	15 ± 3	0.79	23 ± 2	0.85	167 ± 75	1.1	149 ± 18	0.96
Certified pellets P	37	16 ± 3	0.82	32 ± 3	1.2	179 ± 24	1.1	151 ± 12	0.97
PC		134 ± 10*	**6.8**	237 ± 38*	**8.8**	3086 ± 784*	**20**	489 ± 72*	**3.2**
DMSO		20 ± 6		27 ± 5		157 ± 27		155 ± 14	
	µg PM_{10} per plate								
Acacia pellets	50	24 ± 4	1.2	37 ± 6	1.0	133 ± 11	1.0	153 ± 23	0.82
Non-certified pellets	10	25 ± 3	1.2	44 ± 9	1.2	160 ± 22	1.2	179 ± 21	0.96
Certified pellets R	25	20 ± 3	1.1	35 ± 6	0.96	150 ± 13	1.1	168 ± 19	0.90
Certified pellets P	18	18 ± 3	0.85	42 ± 10	1.2	151 ± 7	1.1	177 ± 17	0.94
PC		122 ± 14*	**6.0**	153 ± 60*	**4.3**	2090 ± 275*	**16**	686 ± 129*	**3.7**
DMSO		21 ± 2		36 ± 10		133 ± 21		187 ± 5	

Values are means ± standard deviation of 3 plates. PC = positive control; MR = mutagenicity ratio. Statistical analysis was performed by one-way ANOVA with Dunnett's multiple comparison test. Asterisks indicate statistical significance compared to negative control ($p<0.05$). Mutagenicity ratios above 2 are marked in bold. [a] PAHs -16 EPA priority PAHs plus benzo[e]pyrene, perylene, p-terphenyl and retene.

5.4. Conclusions

The present study indicated that the selection of the pellet fuel for residential combustion can have a significant effect on the toxicological properties of the emitted PM_{10}. The toxicity results from the *V. fischeri* bioluminescent inhibition assay indicated non-toxic responses for commercial pellets, while the combustion of acacia pellets generated toxic particles. Particles collected from the combustion of acacia pellets were more potent inducers of cellular metabolic activity impairment in human lung epithelial cells than those emitted from commercial pelletised fuels. At 24-h exposure, differences between acacia pellets and the three commercial pellets were only detected for the highest dose. The effect of exposure time on cytotoxicity was only observed for acacia pellets and certified pellets R. Combined results from WST-8 and LDH assays suggest that PM_{10} from pellets may trigger cell apoptosis pathways (programmed cell death), as cell membrane permeability was preserved. The decrease in cellular metabolic activity seemed to be associated with PM-bound organic components (vanillic acid) and with water soluble ions. However, further research is needed to establish the causative chemical components in particles emitted from residential pellet combustion. The organic extracts, in general, and the PM_{10}-bound PAHs, in particular, showed no direct or indirect mutagenic responses towards TA98 and TA100 tester strains.

In conclusion, although emissions from automatically fired pellet appliances are generally low, the woody raw material selected for pelletisation can dramatically increase emissions, affecting not only the chemical properties of the released particles, but also their toxicological potency.

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References

Arif, A.T., Maschowski, C., Garra, P., Garcia-Kaufer, M., Petithory, T., Trouve, G., Dieterlen, A., Mersch-Sundermann, V., Khanaqa, P., Nazarenko, I., Gminski, R., Gier, R., 2017. Cytotoxic and genotoxic responses of human lung cells to combustion smoke particles of Miscanthus straw, softwood and beech wood chips. Atmos. Environ. 163, 138–154. https://doi.org/10.1016/j.atmosenv.2017.05.019

Barregard, L., Sällsten, G., Andersson, L., Almstrand, A.C., Gustafson, P., Andersson, M., Olin, A.C., 2008. Experimental exposure to wood smoke: Effects on airway inflammation and oxidative stress. Occup. Environ. Med. 65, 319–324. https://doi.org/10.1136/oem.2006.032458

Barregard, L., Sällsten, G., Gustafson, P., Andersson, L., Johansson, L., Basu, S., Stigendal, L., 2006. Experimental exposure to wood-smoke particles in healthy humans: Effects on markers of inflammation, coagulation, and lipid peroxidation. Inhal. Toxicol. 18, 845–853. https://doi.org/10.1080/08958370600685798

Bioenergy Europe, 2018. Bioenergy Europe Statistical Report 2018 - Pellet Report. Brussels.

Boman, C., Pettersson, E., Westerholm, R., Boström, D., Nordin, A., 2011. Stove performance and emission characteristics in residential wood log and pellet combustion, part 1: Pellet stoves. Energ. Fuel 25, 307–314. https://doi.org/10.1021/ef100774x

Canha, N., Lopes, I., Vicente, E.D., Vicente, A.M., Bandowe, B.A.M., Almeida, S.M., Alves, C.A., 2016. Mutagenicity assessment of aerosols in emissions from domestic combustion processes. Environ. Sci. Pollut. Res. 23. https://doi.org/10.1007/s11356-016-6292-2

Champion, W.M., Warren, S.H., Kooter, I.M., Preston, W., Krantz, Q.T., DeMarini, D.M., Jetter, J.J., 2020. Mutagenicity- and pollutant-emission factors of pellet-fueled gasifier cookstoves: Comparison with other combustion sources. Sci. Total Environ. 739, 139488. https://doi.org/10.1016/j.scitotenv.2020.139488

Corsini, E., Budello, S., Marabini, L., Galbiati, V., Piazzalunga, A., Barbieri, P., Cozzutto, S., Marinovich, M., Pitea, D., Galli, C.L., 2013. Comparison of wood smoke $PM_{2.5}$ obtained from the combustion of FIR and beech pellets on inflammation and DNA damage in A549 and THP-1 human cell lines. Arch. Toxicol. 87, 2187–2199. https://doi.org/10.1007/s00204-013-1071-z

Corsini, E., Ozgen, S., Papale, A., Galbiati, V., Lonati, G., Fermo, P., Corbella, L., Valli, G., Bernardoni, V., Dell'Acqua, M., Becagli, S., Caruso, D., Vecchi, R., Galli, C.L., Marinovich, M., 2017. Insights on wood combustion generated proinflammatory ultrafine particles (UFP). Toxicol. Lett. 266, 74–84. https://doi.org/10.1016/j.toxlet.2016.12.005

Danielsen, P.H., Loft, S., Jacobsen, N.R., Jensen, K.A., Autrup, H., Ravanat, J.L., Wallin, H., Møller, P., 2010. Oxidative stress, inflammation, and DNA damage in rats after intratracheal instillation or oral exposure to ambient air and wood smoke particulate matter. Toxicol. Sci. 118, 574–585. https://doi.org/10.1093/toxsci/kfq290

Danielsen, P.H., Loft, S., Kocbach, A., Schwarze, P.E., Møller, P., 2009. Oxidative damage to DNA and repair induced by Norwegian wood smoke particles in human A549 and THP-1 cell lines. Mutat. Res. - Genet. Toxicol. Environ. Mutagen. 674, 116–122. https://doi.org/10.1016/j.mrgentox.2008.10.014

Dilger, M., Orasche, J., Zimmermann, · Ralf, Paur, H.-R., Silvia Diabaté, ·, Weiss, · Carsten, 2016. Toxicity of wood smoke particles in human A549 lung epithelial cells: The role of PAHs, soot and zinc. Arch. Toxicol. 90, 3029–3044. https://doi.org/10.1007/s00204-016-1659-1

Erlandsson, L., Lindgren, R., Nääv, Å., Krais, A.M., Strandberg, B., Lundh, T., Boman, C., Isaxon, C., Hansson, S.R., Malmqvist, E., 2020. Exposure to wood smoke particles leads to inflammation, disrupted proliferation and damage to cellular structures in a human first trimester trophoblast cell line. Environ. Pollut. 264, 114790. https://doi.org/10.1016/j.envpol.2020.114790

Happo, M.S., Uski, O., Jalava, P.I., Kelz, J., Brunner, T., Hakulinen, P., Mäki-Paakkanen, J., Kosma, V.M., Jokiniemi, J., Obernberger, I., Hirvonen, M.R., 2013. Pulmonary inflammation and tissue damage in the mouse lung after exposure to PM samples from biomass heating appliances of old and modern technologies. Sci. Total Environ. 443, 256–266. https://doi.org/10.1016/j.scitotenv.2012.11.004

Jalava, Pasi I, Happo, M.S., Kelz, J., Brunner, T., Hakulinen, P., Mäki-Paakkanen, J., Hukkanen, A., Jokiniemi, J., Obernberger, I., Hirvonen, M.-R., 2012. *In vitro* toxicological characterization of particulate emissions from residential biomass heating systems based on old and new technologies. Atmos. Environ. 50, 24–35. https://doi.org/10.1016/j.atmosenv.2012.01.009

Jalava, P.I., Salonen, R.O., Nuutinen, K., Pennanen, A.S., Happo, M.S., Tissari, J., Frey, A., Hillamo, R., Jokiniemi, J., Hirvonen, M.R., 2010. Effect of combustion condition on cytotoxic and inflammatory activity of residential wood combustion particles. Atmos. Environ. 44, 1691–1698. https://doi.org/10.1016/j.atmosenv.2009.12.034

Kasurinen, S., Happo, M.S., Rönkkö, T.J., Orasche, J., Jokiniemi, J., Kortelainen, M., Tissari, J., Zimmermann, R., Hirvonen, M.R., Jalava, P.I., 2018. Differences between co-cultures and monocultures in testing the toxicity of particulate matter derived from log wood and pellet combustion. PLoS One 13, 1–20. https://doi.org/10.1371/journal.pone.0192453

Kasurinen, S., Jalava, P.I., Happo, M.S., Sippula, O., Uski, O., Zimmermann, R., Jokiniemi, J., Koponen, H., Hirvonen, M., 2017. particulate emissions from the combustion of birch, beech, and spruce logs cause different cytotoxic responses in A549 cells. Environ. Toxicol. 32, 1487–1499. https://doi.org/10.1002/tox

Kasurinen, S., Jalava, P.I., Uski, O., Happo, M.S., Mäki-paakkanen, J., Jokiniemi, J., Obernberger, I., Hirvonen, M., 2016. Toxicological characterization of particulate emissions from straw, miscanthus, and poplar pellet combustion in residential boilers. Aerosol Sci. Technol. 50, 41–51. https://doi.org/10.1080/02786826.2015.1121198

Kim Oanh, N.T., Nghiem, L.H., Phyu, Y.L., 2002. Emission of polycyclic aromatic hydrocarbons, toxicity, and mutagenicity from domestic cooking using sawdust briquettes, wood, and kerosene. Environ. Sci. Technol. 36, 833–839. https://doi.org/10.1021/es011060n

Kocbach, A., Namork, E., Schwarze, P.E., 2008. Pro-inflammatory potential of wood smoke and traffic-derived particles in a monocytic cell line. Toxicology 247, 123–132. https://doi.org/10.1016/j.tox.2008.02.014

Kováts, N., Ács, A., Kovács, A., Ferincz, Á., Turóczi, B., Gelencsér, A., 2012. Direct contact test for estimating the ecotoxicity of aerosol samples. Environ. Toxicol. Pharmacol. 33, 284–287. https://doi.org/10.1016/j.etap.2011.12.021

Marabini, L., Ozgen, S., Turacchi, S., Aminti, S., Arnaboldi, F., Lonati, G., Fermo, P., Corbella, L., Valli, G., Bernardoni, V., Dell'Acqua, M., Vecchi, R., Becagli, S., Caruso, D., Corrado, L.G., Marinovich, M., 2017. Ultrafine particles (UFPs) from domestic wood stoves: genotoxicity in human lung carcinoma A549 cells. Mutat. Res. - Genet. Toxicol. Environ. Mutagen. 820, 39–46. https://doi.org/10.1016/j.mrgentox.2017.06.001

Mortelmans, K., Zeiger, E., 2000. The Ames Salmonella / microsome mutagenicity assay. Mutat. Res. - Fundam. Mol. Mech. Mutagen. 455, 29–60.

Mutlu, E., Warren, S.H., Ebersviller, S.M., Kooter, I.M., Schmid, J.E., Dye, J.A., Linak, W.P., Ian Gilmour, M., Jetter, J.J., Higuchi, M., Demarini, D.M., 2016. Mutagenicity and pollutant emission factors of solid-fuel cookstoves: Comparison with other combustion sources. Environ. Health Perspect. 124, 974–982. https://doi.org/10.1289/ehp.1509852

Naeher, L.P., Brauer, M., Lipsett, M., Zelikoff, J.T., Simpson, C.D., Koenig, J.Q., Smith, K.R., 2007. Woodsmoke health effects: A review. Inhal. Toxicol. 19, 67–106. https://doi.org/10.1080/08958370600985875

OECD, 1997. Test Guideline 471. Bacteria reverse mutation. In: OCED Guidelines for the Testing of Chemicals. Organisation for Economic Co-operation and Development, Paris, France.

Olsen, Y., Nøjgaard, J.K., Olesen, H.R., Brandt, J., Sigsgaard, T., Pryor, S.C., Ancelet, T., Viana, M. del M., Querol, X., Hertel, O., 2020. Emissions and source allocation of carbonaceous air pollutants from wood stoves in developed countries: A review. Atmos. Pollut. Res. https://doi.org/10.1016/j.apr.2019.10.007

Polonini, L.F., Petrocelli, D., Parmigiani, S.P., Lezzi, A.M., 2019. Influence on CO and PM emissions of an innovative burner pot for pellet stoves: An experimental study. Energies 12, 1–13. https://doi.org/10.3390/en12040590

Romano, S., Perrone, M.R., Becagli, S., Pietrogrande, M.C., Russo, M., Caricato, R., Lionetto, M.G., 2020. Ecotoxicity, genotoxicity, and oxidative potential tests of atmospheric PM_{10} particles. Atmos. Environ. 221, 117085. https://doi.org/10.1016/j.atmosenv.2019.117085

Sigsgaard, T., Forsberg, B., Annesi-Maesano, I., Blomberg, A., Bølling, A., Boman, C., Bønløkke, J., Brauer, M., Bruce, N., Héroux, M.E., Hirvonen, M.R., Kelly, F., Künzli, N., Lundbäck, B., Moshammer, H., Noonan, C., Pagels, J., Sallsten, G., Sculier, J.P., Brunekreef, B., 2015. Health impacts of anthropogenic biomass burning in the developed world. Eur. Respir. J. 46, 1577–1588. https://doi.org/10.1183/13993003.01865-2014

Tapanainen, M., Jalava, P.I., Mäki-paakkanen, J., Hakulinen, P., Happo, M.S., Lamberg, H., Ruusunen, J., Tissari, J., Nuutinen, K., Yli-pirilä, P., Hillamo, R., Salonen, R.O., Jokiniemi, J., Hirvonen, M., 2011. *In vitro* immunotoxic and genotoxic activities of particles emitted from two different small-scale wood combustion appliances. Atmos. Environ. 45, 7546–7554. https://doi.org/10.1016/j.atmosenv.2011.03.065

Turóczi, B., Hoffer, A., Tóth, Á., Kováts, N., Ács, A., Ferincz, Kovács, A., Gelencsér, A., 2012. Comparative assessment of ecotoxicity of urban aerosol. Atmos. Chem. Phys. 12, 7365–7370. https://doi.org/10.5194/acp-12-7365-2012

Unosson, J., Blomberg, A., Sandström, T., Muala, A., Boman, C., Nyström, R., Westerholm, R., Mills, N.L., Newby, D.E., Langrish, J.P., Bosson, J.A., 2013. Exposure to wood smoke increases arterial stiffness and decreases heart rate variability in humans. Part. Fibre Toxicol. 10, 1–8. https://doi.org/10.1186/1743-8977-10-20

Uski, O., Jalava, P.I., Happo, M.S., Torvela, T., Leskinen, J., Mäki-Paakkanen, J., Tissari, J., Sippula, O., Lamberg, H., Jokiniemi, J., Hirvonen, M.R., 2015. Effect of fuel zinc content on toxicological responses of particulate matter from pellet combustion *in vitro*. Sci. Total Environ. 511, 331–340. https://doi.org/10.1016/j.scitotenv.2014.12.061

Uski, O.J., Happo, M.S., Jalava, P.I., Brunner, T., Kelz, J., Obernberger, I., Jokiniemi, J., Hirvonen, M.R., 2012. Acute systemic and lung inflammation in C57Bl/6J mice after intratracheal aspiration of particulate matter from small-scale biomass combustion appliances based on old and modern technologies. Inhal. Toxicol. 24, 952–965. https://doi.org/10.3109/08958378.2012.742172

Venturini, E., Vassura, I., Agostini, F., Pizzi, A., Toscano, G., Passarini, F., 2018. Effect of fuel quality classes on the emissions of a residential wood pellet stove. Fuel 211, 269–277. https://doi.org/10.1016/j.fuel.2017.09.017

Venturini, E., Vassura, I., Zanetti, C., Pizzi, A., Toscano, G., Passarini, F., 2015. Evaluation of non-steady state condition contribution to the total emissions of residential wood pellet stove. Energy 88, 650–657. https://doi.org/10.1016/j.energy.2015.05.105

Verma, V.K., Bram, S., Delattin, F., De Ruyck, J., 2013. Real life performance of domestic pellet boiler technologies as a function of operational loads: A case study of Belgium. Appl. Energy 101, 357–362. https://doi.org/10.1016/j.apenergy.2012.02.017

Vicente, E.D., Alves, C.A., 2018. An overview of particulate emissions from residential biomass combustion. Atmos. Res. 199, 159–185. https://doi.org/10.1016/j.atmosres.2017.08.027

Vicente, E.D., Vicente, A.M., Evtyugina, M., Carvalho, R., Tarelho, L.A.C., Paniagua, S., Nunes, T., Otero, M., Calvo, L.F., Alves, C., 2019. Emissions from residential pellet combustion of an invasive acacia species. Renew. Energy 140, 319–329. https://doi.org/10.1016/j.renene.2019.03.057

Vicente, E.D., Vicente, A.M., Evtyugina, M., Tarelho, L.A.C., Almeida, S.M., Alves, C., 2020. Emissions from residential combustion of certified and uncertified pellets. Renew. Energy 161, 1059–1071. https://doi.org/10.1016/j.renene.2020.07.118

Vu, B., Alves, C.A., Gonçalves, C., Pio, C., Gonçalves, F., Pereira, R., 2012. Mutagenicity assessment of aerosols in emissions from wood combustion in Portugal. Environ. Pollut. 166, 172–181. https://doi.org/10.1016/j.envpol.2012.03.005

Win, K.M., Persson, T., 2014. Emissions from residential wood pellet boilers and stove characterized into start-up, steady operation, and stop emissions. Energ. Fuel. 28, 2496–2505. https://doi.org/10.1021/ef4016894

Wöhler, M., Jaeger, D., Reichert, G., Schmidl, C., Pelz, S.K., 2017. Influence of pellet length on performance of pellet room heaters under real life operation conditions. Renew. Energy 105, 66–75. https://doi.org/10.1016/j.renene.2016.12.047

Zelikoff, J.T., Chen, L.C., Cohen, M.D., Schlesinger, R.B., 2002. The toxicology of inhaled woodsmoke. J. Toxicol. Environ. Heal. Part B 269–282. https://doi.org/10.1080/1093740029007006

CHAPTER 6

Chapter 6. Impact of wood combustion on indoor air quality

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Abstract

The incomplete wood combustion in appliances operated in batch mode is a recognised source of both in- and outdoor airborne pollutants, especially particulate matter (PM). Data on pollutant levels and PM characteristics in households with wood burning devices in developed countries are scarce with most studies describing stove change out programmes or other intervention measures. The aim of the present study was to simultaneously evaluate indoor and outdoor concentrations of CO, CO_2 and PM_{10} during the operation of wood burning appliances (open fireplace and woodstove) in unoccupied rural households. PM_{10} samples were analysed for water soluble inorganic ions, major and trace elements, organic carbon (OC), elemental carbon (EC), and detailed organic speciation. The CO 8-hour average concentrations did not exceed the protection limit despite the sharp increases observed in relation to background levels. During the open fireplace operation, PM_{10} levels rose up 12 times compared to background concentrations, while the airtight stove resulted in a 2-fold increase. The inhalation cancer risk of particulate bound PAHs in the room equipped with wood stove was estimated to be negligible while the long-term exposure to PAH levels measured in the fireplace room may contribute to the development of cancer. The excess lifetime cancer risk resulting from the particle-bound Cr (VI) exposure during the fireplace and woodstove operation was higher than 1.0×10^{-6} and 1.0×10^{-5}, respectively. Levoglucosan was one of the most abundant individual species both indoors and outdoors. This study underlines air pollution hazards and risks arising from the operation of traditional wood burning appliances.

Keywords: Mediterranean region, Indoor air quality, OC/EC, Organic markers, PM_{10}, Residential biomass combustion

6.1. Introduction

The World Health Organisation (WHO) ranked air pollution as the biggest environmental health risk. In 2012, about three million deaths were estimated to be a direct consequence of outdoor air pollution (WHO, 2016). However, people spend most of their time indoors (Brasche and Bischof, 2005; Klepeis et al., 2001; Leech et al., 1996; Schweizer et al., 2007) and, for this reason, the majority of the inhalation exposure occurs in built environments where the indoor concentrations of many pollutants are higher than their outdoor levels (Morawska et al., 2013; Oeder et al., 2012; Pegas et al., 2012; Weisel et al., 2008). Thus, indoor air pollution may pose a greater health threat than outdoor pollution (Oeder et al., 2012; Taneja et al., 2008). As people in industrialised countries spend more than half of the daytime at home (Brasche and Bischof, 2005; Buonanno et al., 2011; Leech et al., 1996; Schweizer et al., 2007), a rather extensive amount of work has been performed to characterise residential settings (e.g. Bloom et al., 2015; Custódio et al., 2014; Delgado-Saborit et al., 2011; Derbez et al., 2014; Kaunelien et al., 2016; Molloy et al., 2012; Tang and Wang, 2018). These and other studies provided remarkable data on residential air quality. Besides gaseous and particulate matter (PM) concentrations, several studies encompassed a more detailed characterisation of the PM samples (e.g. Custódio et al., 2014; Delgado-Saborit et al., 2011; Long et al., 2000; Massey et al., 2013; Rohra et al., 2018; Slezakova et al., 2014; Varshney et al., 2016). Exposure to indoor generated particles is responsible for up to 30% of the total burden of disease from PM exposure, indicating that this pollutant is one of the biggest health hazards in indoor environments (Morawska et al., 2013). PM is a complex mixture of different inorganic and organic substances that is determined by contributions from diverse indoor sources, infiltration from outdoors and reactions occurring indoors (Morawska et al., 2013, 2017; Morawska and Salthammer, 2003). Thus, the daily exposure to PM in residential settings strongly depends on residential activities and source events (Morawska et al., 2013). Specific household activities, such as cigarette smoking, cleaning, cooking, combustion/thermal related activities, among others, have also been assessed in several studies (Abdullahi et al., 2013; Géhin et al., 2008; Glytsos et al., 2010; Isaxon et al., 2015; McCormack et al., 2008; Salthammer et al., 2014). Indoor particle generation is often short in duration, but can highly increase particulate mass and number above background values for an extended period (e.g. He et al., 2004; Long et al., 2000; Wallace, 2006).

Residential biomass burning has been pointed out as an important source of ambient PM (Vicente and Alves, 2018 and references therein). Nevertheless, the contribution of this emission source to indoor air pollution may be even higher. Several studies on household air pollution from cooking with biomass fuels reported PM concentrations largely exceeding the WHO indoor air quality guidelines in low-income settings (e.g. Bartington et al., 2017; Parajuli et al., 2016), where this source is a major health concern (WHO, 2014). An increasing body of literature has illustrated the role of household air pollution arising from biomass fuel combustion on several respiratory (Ezzati and Kammen, 2001; Kim et al., 2011 and references therein; Pokhrel et al., 2010; Raspanti et al., 2016; Regalado et al., 2006; Smith et al., 2011) and non-respiratory diseases, such as low birth weight and infant mortality, cardiovascular disease, cataract, nasopharyngeal and laryngeal cancer (Boy et al., 2002; Kim et al., 2011 and references therein; Wylie et al., 2014). Although indoor air pollution from household use of biofuels is a major public health concern, mostly in developing areas, in higher income countries biomass burning appliances have regained popularity (Sigsgaard et al., 2015). Over the past years, studies have been performed to assess PM levels in indoor air when operating wood burning appliances (e.g. Castro et al., 2018; De Gennaro et al., 2015; Guo et al., 2008; McNamara et al., 2013; Salthammer et al., 2014; Saraga et al., 2015; Semmens et al., 2015). Studies focused on the reduction of household air pollution through stove change out programmes in the United States (Noonan et al., 2012; Ward and Noonan, 2008; Ward et al., 2011) and Canada (Allen et al., 2009) have also been conducted. Recently, other household interventions to reduce indoor PM exposure from biomass combustion appliances have also been a topic of research (McNamara et al., 2017; Ward et al., 2017). Regarding PM characterisation, few studies have evaluated endotoxins in indoor samples during the use of biomass burning appliances in the United States (McNamara et al., 2013), Scotland and Ireland (Semple et al., 2012). Other studies focused on particulate PAH levels from residential biomass combustion (De Gennaro et al., 2015; Salthammer et al., 2014). Particulate organic and elemental carbon (OC and EC) were measured in Greek (Saraga et al., 2015), Spanish (Castro et al., 2018) and American households (Ward et al., 2011). Ward et al. (2011) also evaluated the levels of some chemical markers of wood smoke in 16 American households. Castro et al. (2018) and Saraga et al. (2015) included PM-bound trace and major elements in their analysis and, the latter, also water soluble ions. Despite the large body of knowledge provided by the mentioned studies, in most researches, only gaseous and particulate matter mass/number concentrations were measured. Moreover, studies on the chemical composition of particles have focused on a small number of compounds, lacking an exhaustive characterisation of PM samples. It should be noted that most studies were carried out in the USA, where the combustion appliances and fuels are quite different from the ones in use in Europe. Furthermore, much of the work mentioned above was conducted under real life conditions and based on conclusions drawn from questionnaires of activity patterns addressed to homeowners. This practice may result in incorrect estimations of the influence of combustion emissions on indoor air quality. Additionally, there is the possibility that the monitoring campaign may cause some disturbance and modification in the behaviour of the homeowner.

This study aims at estimating the effect of biomass burning on indoor pollutant concentrations. The assessment was carried out in unoccupied houses equipped with low efficiency wood burning appliances currently in use in several Southern European countries (Gonçalves et al., 2012; Pastorello et al., 2011). This approach allows to obtain results that, although corresponding to real life environmental and draught conditions, are not influenced by the owner's daily routines and hence more reliable for health risk assessment. The possible contribution of the outdoor environment to the indoor levels was also estimated. In addition to monitoring of concentrations of gaseous and particulate pollutants, this study aims to obtain an in-depth characterisation of particulate matter, including a screening of both organic and inorganic constituents. Thus, the prime goal in this study is to address the need for a detailed characterisation of a relevant indoor pollution source and, thus, to better understand the health risk posed by wood burning emissions. This research encompasses the evaluation of comfort parameters and ventilation rates, gaseous and particulate daily profiles, PM_{10} emission rates and a comprehensive PM_{10} chemical characterisation, which was the basis for a carcinogenic and noncarcinogenic risk assessment. Despite the specificities, the findings can be extended to other regions, particularly to other Mediterranean countries, where log burning in traditional woodstoves and fireplaces is a common practice in winter.

6.2. Materials and methods

6.2.1. Sampling sites and strategy

In Portugal, wood combustion is an important source of PM during winter (Amato et al., 2016). The impact of wood burning on air quality is mainly due to the use of low efficiency combustion appliances, which are widespread, especially in inland rural areas of the country (Gonçalves et al., 2012). Taking into account the wood burning patterns, as well as the lack of other major sources in the region (i.e. traffic and industry), the effects of using traditional batch-fired systems on indoor and outdoor air quality were assessed in a Portuguese rural area where, in colder months, biomass is used as the main heating source.

Table 6.1. Summary of the experimental conditions.

Housing Characteristics		
Type of house	Detached	Detached
Nº of windows	1	2
Type of windows	Double glazed casement windows	
Window frames	Aluminium frames	
Nº of doors	1 (hallway)	2 (outdoor/stairs)
Room volume (m^3)	37.7	67.1
Air exchange rate (α, h^{-1})	0.779 ± 0.123	0.718 ± 0.130
Combustion tests		
N	4	3
Combustion appliance	Open fireplace	Woodstove
Wood	Pine and eucalypt logs	
Decay rate (κ, h^{-1})	2.45 ± 1.24	0.933 ± 0.312
PM_{10} initial concentration ($\mu g\ m^{-3}$)	30.5 ± 9.88	13.7 ± 2.52
PM_{10} peak concentration ($\mu g\ m^{-3}$)	2328 ± 1853	76.7 ± 28.6
Emission rate PM_{10} ($mg\ min^{-1}$)	1.29 ± 1.25	0.049 ± 0.035

The monitoring campaign was performed in January 2017 at two uninhabited houses: one equipped with an open fireplace as heating system, and the other one equipped with a cast iron woodstove, both installed in the kitchen area. The main features of the two rooms are described in Table 6.1. Similarly to the approach described by Castro et al. (2018), during the monitoring campaign, only the wood burning devices were operated and no other domestic activities took place. The measurements were performed under minimum ventilation, i.e., all the doors and windows were closed, which are typical conditions during the cold weather months. The ventilation rates were determined by simultaneous CO_2 monitoring, indoors and outdoors, following the methodology described by Alves et al. (2013). A total of four combustion experiments were performed using the fireplace and three with the woodstove (Table 6.1). In each experiment, the fireplace was fed three times with pine and eucalypt logs. Due to the higher combustion rates, the woodstove was fed five times with the same biofuels. To start the combustion cycle, split pine wood logs, eucalypt logs and two pine cones were inserted into the combustion chamber and ignited. Both devices were operated for about 8-h and refuelled only when a hot bed of charcoal remained in the combustion chamber. The duration of the experiments and number of batches to refuel the combustion chambers tried to mimic common European burning practices (Gustafson et al., 2008; Wöhler et al., 2016). To reproduce the daily routines of rural residents, wood logs were added to the combustion chamber at common time intervals and the bed of charcoal and wood was periodically stirred. To assess whether the combustion appliances affected indoor air quality, background concentrations were monitored for four days in each room, without biomass burning, for periods of time similar to those recorded during sampling with combustion equipment in operation. Outdoors, the equipment was placed in a balcony of one of the houses. Since both houses are in front of each other, they share the same outdoor air.

6.2.2. IAQ monitoring

Temperature, relative humidity, CO_2, and CO were continuously monitored with indoor air quality probes inside (TSI, model 7545) and outside (Gray Wolf®, WolfSense IQ-610) the houses. Real time measurements of airborne PM (PM_1, $PM_{2.5}$, PM_4 and PM_{10}) mass concentrations were carried out by a laser photometric instrument (TSI, DustTrak DRX 8533) in the indoor and outdoor environments, simultaneously. All the continuous monitoring instruments were operated with 1-minute resolution. In addition, PM_{10} was measured gravimetrically with two high volume air MCV (model CAV-A/mb) instruments working with a constant flow of 30 m^3 h^{-1}. Concurrent indoor and outdoor samples were collected during the operation of combustion appliances. Indoors, the high-volume sampler and the real time monitoring instruments were placed in the middle of the room (a location not unduly influenced by the studied source) at about 1.2 m above the floor, to simulate the breathing height when one sits on the sofa (Morawska et al., 2013). PM_{10} samples were collected on pre-weighed 150 mm quartz fibre filters (Pallflex®) for gravimetric and chemical analyses. The gravimetric quantification was performed with a microbalance (Mettler Toledo, XPE105 DeltaRange®).

6.2.3. Analytical techniques

Two circular filter punches of 9 mm were used to analyse the carbonaceous content in the PM_{10} samples by a thermal optical transmission technique. The method consists on a multiple step temperature protocol, first in an inert atmosphere of nitrogen and then in an oxidising atmosphere (nitrogen and oxygen). The filter light transmittance measurement, through a laser beam and a photodetector, allows separating the EC formed by OC pyrolysis during the heating process from the one that was originally in the sample. The OC and EC determination is based on the quantification of the CO_2 released during the controlled heating by a non-dispersive infrared (NDIR) analyser. Calibration gas cylinders were used daily to construct the calibration curve. To assess carbon recovery, a standard solution of potassium hydrogen phthalate in double-deionised water was spiked in pre-baked quartz filters and analysed periodically.

The analysis of major and trace elements was performed by inductively coupled plasma atomic emission spectrometry (ICP-AES: THERMO, IRIS Advantage TJA Solutions) and trace elements were determined by mass spectrometry (ICP-MS: THERMO, X Series II). Two circular punches of 9 mm from the various replicate filter samples obtained for each condition (fireplace and woodstove indoors, outdoors and background) were combined and analysed together in order to obtain mean values. Each set of filter punches was subjected to acid digestion (1.25 mL HNO_3: 2.5 mL HF: 1.25 mL $HClO_4$). Three multi-elemental solutions Spec® 1 (rare earth elements, REE), Spec® 2 (alkalis, earth alkalis, and metals) and Spec® 4 (Nb) were used to construct external calibration curves. The methodology (Querol et al., 2001) enables to determine the content of around 50 major and trace elements with a relative error < 5% for most elements, and around 10% for Al and Na. The actual detection limits achieved are close to 0.005 μg m^{-3} for major elements and 0.05 ng m^{-3} for most trace elements. Repeated measurements were performed on acid blanks, quality control standard solutions and standard reference material (SRM 1633b, fly ash). Additionally, a multi standard composed of the same elements was introduced in each batch of samples to check the accuracy of measurements.

Water soluble ions were analysed by ion chromatography. Two circular filter punches of 9 mm were extracted with 6 mL of ultrapure Milli-Q water under ultrasonic agitation for 30 min (15 + 15 min). Extracts were filtered (PVDF syringe filter 0.2 μm pore size, Whatman™) and injected in an ion chromatograph (DIONEX, ICS-5000 + DC, USA). The chromatograph comprises a dual-system ion chromatograph conductance detector (ICS-5000), an AS-DV 40 auto sampler and an eluent regenerator system (Dual RFIC-EG, Dionex, USA). Anions were analysed with a DIONEX Ionpac AS11-HC-4 μm analytical column (2 × 250 mm) with guard column and the eluent used was potassium hydroxide (30 mM). The analysis of cations was performed with a DIONEX Ionpac CS16 analytical column (3 × 250 mm) with guard column and methanesulfonic acid as eluent (30 mM). Stock solutions of 1000 μg ml^{-1} were made from high-purity grade solutions from Sigma-Aldrich and kept refrigerated until use. Fresh analytical standard mixtures were prepared by dilution of each individual stock solution. Eight concentration levels of analytical standards were prepared for the external calibration analytical curves. Each standard solution was injected three times in the ion chromatograph in each batch of samples.

Two circular filter punches of 47 mm from each sample were extracted separately with dichloromethane (125 mL) for 24 h and then two times with methanol in an ultrasonic bath (25 mL for 10 min, each extraction). After each extraction, the extracts were filtered. The total organic extracts (TOEs) were then concentrated to a volume lower than 1 mL using a Turbo Vap® II concentrator (Biotage) and dried under a gentle nitrogen stream. Each TOE was then transferred onto silica gel columns (activated at 150 °C during 3 h) and fractionated using solvents of different polarity: (i) n-hexane (aliphatics), (ii) toluene-n-hexane (polycyclic aromatic hydrocarbons), (iii) ethyl acetate-n-hexane (n-alkanols, sterols and other hydroxyl compounds) and (iv) formic acid in methanol (4%, v/v) (acids and sugars). After each elution, the different organic fractions were vacuum concentrated using the Turbo Vap® II system, transferred to 1.5 mL vials, and dried by nitrogen blow down. The aliphatic and polycyclic aromatic hydrocarbons were analysed with a GC-MS from Shimadzu, model QP5050A, with automatic injection and equipped with a TRB-5MS 30 m × 0.25 mm × 0.25 µm column. The oxygenated compounds were analysed with a GC-MS from Thermo Scientific (Trace Ultra, quadrupole DSQII), equipped with a TRB-5MS 60 m × 0.25 mm × 0.25 µm column. The carrier gas was helium. Before injection, the compounds with hydroxylic and carboxylic groups were converted into the corresponding trimethylsilyl derivatives. N,O-bis (trimethylsilyl) trifluoroacetamide (BSTFA): trimethylchlorosilane (TMCS) 99:1 (Supelco 33,149-U) was used as silylation reagent. The GC-MS multipoint calibration was performed with injection of hundreds of authentic standards (Sigma-Aldrich). Standards and samples were both co-injected with internal standards. A detailed description of the analytical methodology, including recovery efficiency tests for several compounds, can be found in Oliveira et al. (2007).

Except for background samples, each filter was individually extracted for analysis of water soluble ions by ion chromatography and for organic speciation by GC-MS. For background air, circular filter punches from the various replicate samples were combined and analysed together in order to obtain masses high enough to detect the target compounds. Furthermore, for the analysis of major and trace elements, replicate samples were also digested together, as described above. The results obtained from each analytical technique were blank-corrected. Blank filters were analysed in the same way as the samples.

6.3. Results

6.3.1. Comfort parameters and gaseous compounds

The mean indoor temperatures during the burning periods were lower in the room equipped with fireplace (14 ± 1.6 °C) than the one measured in the room equipped with woodstove (20 ± 0.94 °C). The mean temperature recorded in the first day of burning, in both spaces, was lower compared to the following days of measurements, which may be related to the fact that both houses were unoccupied. Mean relative humidity values of 52 ± 1.3% and 55 ± 4.4% were obtained, respectively, for the rooms equipped with fireplace and woodstove. The room temperature rose by 4 to 5 °C and by 4 to 8 °C within 2 h of firing up the fireplace and the woodstove, respectively. On the other hand, the relative humidity in the room dropped by 11 to 14% and by 6 to 10% during the operation of the fireplace and the woodstove, respectively. The American Society of Heating, Refrigerating, and Air-

Conditioning Engineers (ASHRAE, 2010) indicates that, for thermal comfort purposes (for 80% occupant acceptability) considering low metabolic rate (sedentary activities) and assuming low clothing (normal indoor clothing), the indoor temperatures should range from 20.0 to 24.2 °C for a relative humidity of 30% and from 19.7 to 23.3 °C when the relative humidity reaches 60%. The woodstove operation allowed temperatures in the room within the comfort zone while the open fireplace did not deliver enough heat to provide thermal comfort in the room. Under minimum ventilation conditions, the air exchange rate (renovations per hour) was 0.78 ± 0.12 and 0.72 ± 0.13 h^{-1} in the rooms equipped with the fireplace and the woodstove, respectively (Table 6.1).

Relatively low concentrations of carbon dioxide (CO_2) were measured in both rooms, averaging 563 ± 60.0 ppm (8-h) and 503 ± 13.1 ppm (8-h) during the operation of the woodstove and fireplace, respectively. In both cases, the maxima were below 1000 ppm. Furthermore, it should be noted that one person was always in the room during the sampling period, whose exhalation contributed to the measured CO_2 levels. Carbon monoxide (CO) was found indoors, reflecting the occurrence of incomplete combustion processes. Sudden increases in concentrations were observed for both residential combustion appliances. The highest values were measured when the fireplace was being used (3.20 ± 0.946 ppm, 8-h average). Outdoors, CO levels were below the corresponding indoor concentration and highly variable, ranging from 0.247 to 1.72 ppm (8-h average).

Fig. 6.1 depicts the CO_2 and CO profiles indoors during the operation of the fireplace (Fig. 6.1A) and the woodstove (Fig. 6.1B). The main pollutant generating phases were the lighting and refuelling of the combustion chambers of both devices. Additionally, higher CO and CO_2 levels were also recorded during the charcoal combustion at low temperatures at the end of the combustion process. After ignition, the rise in CO concentrations in the room generally occurred after about 1 (fireplace) to 2 (woodstove) hours. Despite the similar profiles for the various days, the peak concentration values showed significant differences (Fig. A2.1).

6.3.2. Particulate matter

Fig. 6.1 depicts the time resolved indoor PM_{10} concentrations during the operation of the fireplace (Fig. 6.1A) and the woodstove (Fig. 6.1B). The ignition phase, whether for the fireplace or for the woodstove, produced a sudden increase in the PM concentrations. As observed for the gaseous pollutants, PM peak concentrations were associated with lighting and refuelling of the combustion appliance.

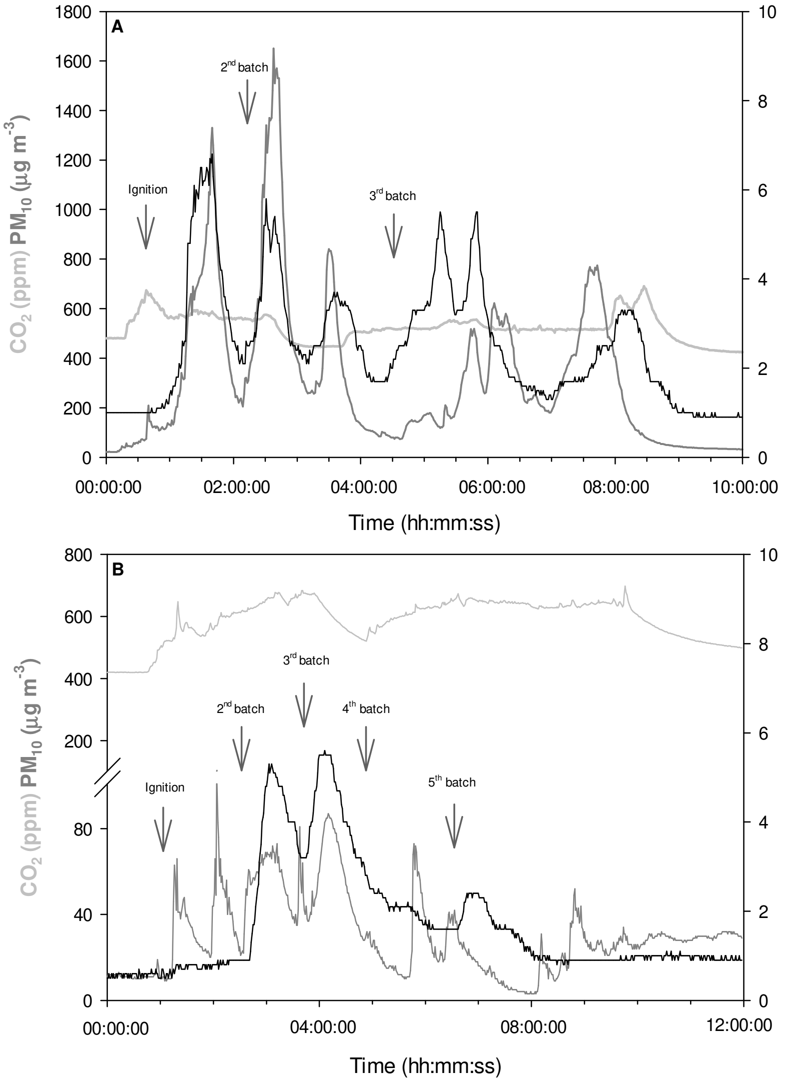


Figure 6.1. Indoor profiles of PM_{10} (µg m^{-3}) CO_2 and CO concentrations (ppm) measured during fireplace (A) and woodstove (B) operation.

The maximum outdoor PM_{10} concentrations were observed during the morning and early night hours (Fig. A2.2 and A2.3). In several days, very high night-time PM_{10} concentrations were recorded outdoors, which might be associated with limited dispersion due to inversion build-up. On the other hand, some days of rain during the sampling campaign contributed to particle scavenging and, consequently, to lower outdoor PM_{10} concentrations (Fig. A2.2 and A2.3).

The indoor to outdoor (I/O) particle concentration ratio is often used as a proxy of the infiltration from outdoors. Morawska et al. (2017) highlighted the importance of the contribution from outdoor air through infiltration/ventilation to PM levels in households. In the present study, the indoor to outdoor particle concentration ratio was found to be quite high during the operation of the fireplace. When this source was present (burning period), I/O ratios for PM_{10} ranged from 3.2 to 25 (average = 14 ± 9.0). Lower I/O PM_{10} ratios were obtained during the woodstove operation (1.37 ± 0.92).

A strong linear relationship between PM_{10} measurements obtained by photometric and gravimetric monitoring devices was observed ($r^2 = 0.98$). It is important to highlight that the DustTrak used to record PM_{10} over time is not the reference method and the comparisons with the air quality standards or other studies employing the gravimetric method should be viewed with caution. Although a strong correlation has been found between the measurements with the high-volume sampler and DustTrak, the latter over-reports PM_{10} mass measurements by a factor of ~1.76. This value agrees with previous studies comparing gravimetric or filter-based methods with DustTrak measurements. For indoor wood smoke, McNamara et al. (2011) reported a factor of 1.65 for $PM_{2.5}$ measurements with DustTraks, while Kingham et al. (2006) found that in a wood smoke ambient airshed, DustTraks over-recorded PM_{10} by a factor of 2.73.

From the gravimetric determination of PM_{10} (Fig. 6.2), the indoor concentrations (8-h average) ranged from 146 to 558 $\mu g\ m^{-3}$ in the room equipped with the fireplace (average = 319 ± 173 $\mu g\ m^{-3}$) and from 51.8 to 98.6 $\mu g\ m^{-3}$ in the woodstove equipped room (average = 78.5 ± 24.0 $\mu g\ m^{-3}$).

Several studies have employed mass balances to calculate the indoor particle generation rate of different sources (Guo et al., 2008; He et al., 2004; Nasir and Colbeck, 2013). Eq. (1), which is employed to calculate indoor particle concentrations, takes into consideration the indoor and outdoor particle concentrations (C_{in} and C_{out}, respectively), the penetration efficiency (P), the air exchange rate (α), the deposition rate (κ), the indoor particle generation rate (Q_s), the time (t) and the efficient volume (V), assuming homogenous concentration in the room.

$$\frac{DC_{in}}{Dt} = P\alpha C_{out} + \frac{Q_s}{V} - (\alpha + k)C_{in} \qquad (1)$$

To simplify the equation, several assumptions are made: use of average values instead of functions, assume that the penetration efficiency is close to unity for both fine and coarse particles, approximate the indoor particle concentration by outdoor particle concentration when no indoor source is in operation and the initial indoor particle concentration (C_{in0}) could be used to replace outdoor particle concentrations (Eq. 2) (Guo et al., 2008; He et al., 2004; Nasir and Colbeck, 2013).

$$\overline{Q_s} = V \times \left[\frac{C_{in} - C_{in0}}{\Delta t} + \overline{(\alpha + k)C_{in}} - \alpha C_{in0}\right] \qquad (2)$$

Thus, the average particle emission rate ($\bar{Q}_s$) is determined taking into consideration the peak (C_{in}) and initial indoor particle concentrations (C_{in0}), the average air exchange rate (α), the average removal rate (α + κ) and the time difference between the initial and peak particle concentration (Δt). The decay of indoor PM levels after an indoor source stopped, considering that the indoor concentration from source operation is significantly higher than outdoor concentration, can be described by the exponential Eq. 3 (Abt et al., 2000; He et al., 2005; Vette et al., 2001; Zhang et al., 2010).

$$C_t = e^{-(\alpha+k)t} C_0 \qquad (3)$$

The particle removal rate is the slope of the line obtained by plotting $\ln(C_{in}/C_{in0})$ versus time (Abt et al., 2000; He et al., 2005; Vette et al., 2001). The PM_{10} deposition rates, κ, varied from day to day, averaging 2.45 ± 1.24 h^{-1} and 0.933 ± 0.312 h^{-1} for fireplace and woodstove, respectively. The estimated PM_{10} emission rates (Table 6.1) from biomass burning in the open fireplace were much higher (1.29 ± 1.25 mg min^{-1}), compared with indoor particle generation rates from woodstove operation (0.049 ± 0.035 mg min^{-1}).

6.3.2.1. Major and trace elements

Elements accounted for 2.20 and 12.7 wt% of the PM_{10} mass during the fireplace and woodstove operation, respectively. The prevailing major elements in the PM_{10} samples collected during the operation of both combustion appliances were Ca and K. Outdoors, these components accounted for PM_{10} mass fractions ranging from 4.61 to 14.1 wt % and Na, Ca, Al and K were the most abundant elements (Table A2.1).

For the purpose of making a PM_{10} mass balance and taking into account that elements exist at the highest oxidation states, the concentration of each one was converted into the respective mass concentrations of the most common oxides. When accounting for the unmeasured oxygen, elements in their oxide form represented 3.13 (fireplace operation) to 18.2 (woodstove operation) wt% of PM_{10} mass indoors and 6.74 to 19.6 wt% of PM_{10} outdoors.

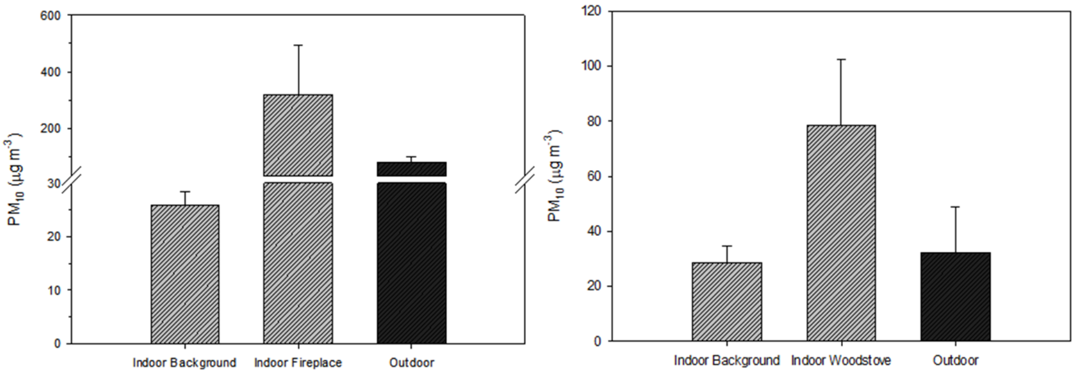


Figure 6.2. PM_{10} concentrations indoors (while using combustion appliances and room background air) and outdoors.

For each element, enrichment factors were calculated using the average composition of the upper continental crust (Fig. A2.4). The enrichment factor (EF) is defined according to Eq. (4), where E and R represent the concentrations of the element under analysis and the reference element, respectively:

$$EF = (E/R)_{air}/(E/R)_{cust} \qquad (4)$$

A reference element is that whose concentration is so abundant in the earth's crust that anthropogenic contributions do not change it substantially. In the present study, Al was used as reference element and the average element concentrations in the upper continental crust were taken from Wedepohl (1995).

Values of EF close to unity are indicative of major inputs from crustal sources while higher values express the contribution from non-crustal sources. It is assumed that EF higher than 5 suggests that non-crustal sources contribute to a significant fraction of the element (Gao et al., 2002).

Indoors, during the operation of combustion appliances, minimal enrichments (lower than 5) were obtained for elements such as Ga, Fe, Li, Ti, Nd and V, indicating that these metals were mostly derived from soil dust. Other elements like Ce, Co, K, Mg, As, Mn, Ca, Sn, Cr and Pb were enriched, suggesting an anthropogenic source ($5 \leq EF \leq 78$). Cu and Cd were highly enriched elements during fireplace ($101 \leq EF \leq 621$) and woodstove operation ($91 \leq EF \leq 488$). Additionally, high enrichments were recorded for Se (160) and Sb (737) when the fireplace was in use.

Outdoors, EFs > 5 were obtained for As, Cr, Cu, Pb, Sn and W during both sampling campaigns and higher enrichments (> 450) were found for Cd. During the second sampling campaign (woodstove), the outdoor samples were also enriched in K, Mg, Ca, V and Na ($9 \leq EF \leq 31$) (Fig. A2.4).

The inhalation exposure to major and trace elements was estimated according to the methodology provided in "supplemental guidance for inhalation risk assessment" (USEPA, 2009). The exposure concentration depends on the duration and human activity patterns, as follows:

$$EC = (CA \times ET \times EF \times ED)/AT \qquad (5)$$

where EC is the exposure concentration (ng m^{-3}), CA corresponds to the element concentration (ng m^{-3}), ET is the exposure time (8 h d^{-1}), EF is the exposure frequency (181 d y^{-1}), ED is the exposure duration(70y) and AT is the averaging time (70y × 365dy^{-1} × 24 h d^{-1}). The exposure time used in the calculations was based on the average time of the combustion experiments performed in the present study, which has also been reported as the average wood burning time in other European countries (Gustafson et al., 2008). The exposure frequency, 181 days per year, takes into account the highest usage frequencies (November to March) according to the results of a European survey on real life operation of biomass combustion appliances (Wöhler et al., 2016).

The excess cancer risk for a receptor exposed via the inhalation pathway was estimated following Eq. (6), where IUR is the inhalation unit risk (ng $m^{-3})^{-1}$.

$$Risk = IUR \times EC \qquad (6)$$

The IUR values were retrieved from the database provided by USEPA (2017) for six elements (As, Cr(VI), Pb, Co, Cd and Ni). Considering that in the present study total Cr was determined and that the tabulated IUR is for Cr(VI), which is based on a Cr(III):Cr(VI) proportion of 1/6, one seventh of the total concentration was used to estimate the risk. The health risks posed by the individual metals were calculated to assess the potential health risks associated with PM_{10} inhalation (Fig. 6.3). Risks < 1 in a million are below the level of concern, while risks above 1.0×10^{-4} are typically considered of concern. The results indicate that the lifetime cancer risk associated with particle bound metals exposure during the operation of wood burning appliances might be of concern for householders.

The noncarcinogenic risk of each individual metal was assessed by the noncancer hazard quotient (HQ) according to Eq. (7), where R_fC is the reference concentration (ng m^{-3}).

$$HQ = EC/R_fC \qquad (7)$$

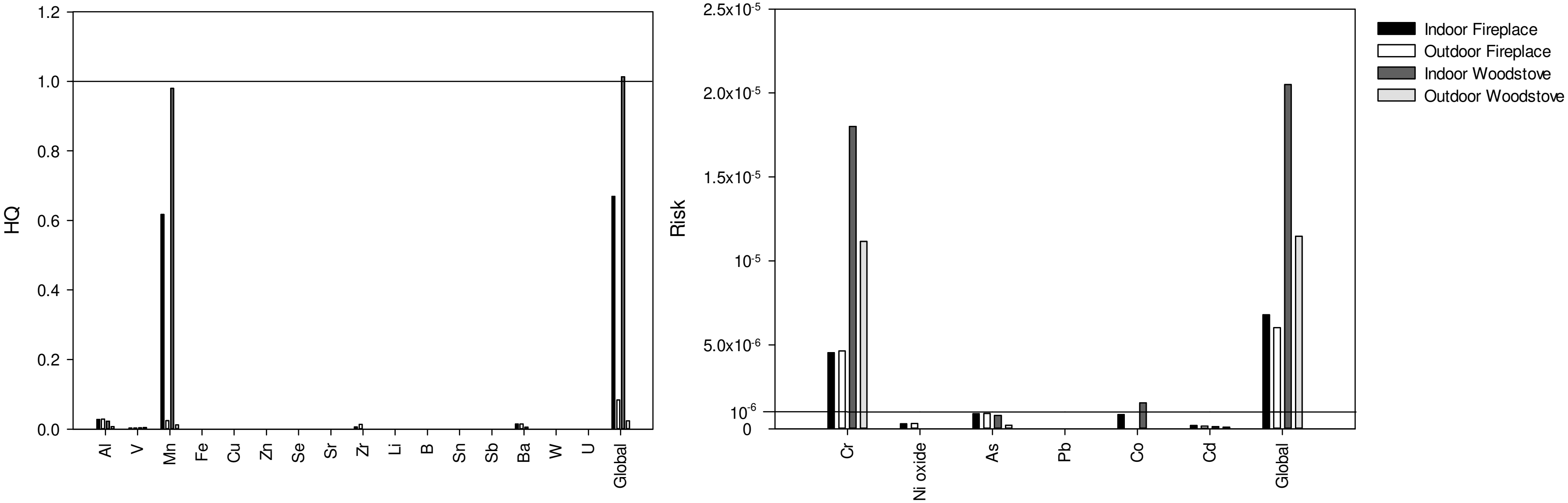


Figure 6.3. Mean risks from inhalation exposure to noncarcinogenic and carcinogenic PM_{10}-bound metals. IUR: arsenic (4.3×10^{-3} ($\mu g\ m^{-3})^{-1}$), lead (1.2×10^{-5} ($\mu g\ m^{-3})^{-1}$), chromium (VI) (8.4×10^{-2} ($\mu g\ m^{-3})^{-1}$), cobalt (9×10^{-3} ($\mu g\ m^{-3})^{-1}$), cadmium (1.8×10^{-3} ($\mu g\ m^{-3})^{-1}$).

Since for several elements only the reference doses for oral exposure (R_fD) are available (USEPA, 2017), the values were converted into the respective reference concentration (R_fC) following the methodology described by USEPA (2013). These reference values were taken from databases provided by the Integration Risk Information System (IRIS) (USEPA, 2019) and USEPA (USEPA, 2017). The noncarcinogenic risks associated with inhalation exposure to airborne PM_{10}-bound elements are presented in Fig. 6.3. The HQ assumes that below the R_fC level it is unlikely to experience adverse health effects. Values of HQ above 1 indicate greater levels of concern. In the present study, HQ for PM_{10}-bound metals ranged from null values for many elements to 0.98 for Mn during woodstove operation. The HQ sum of the sixteen PM_{10}-bound elements was higher indoors during the operation of the fireplace (0.669) and the woodstove (1.01) than the outdoor HQ values with major contributions to the total noncarcinogenic risk from Mn (92 and 97% during fireplace and woodstove operation, respectively) and Al (4.1 and 2.3% during fireplace and woodstove operation, respectively).

6.3.2.2. Water soluble inorganic ions

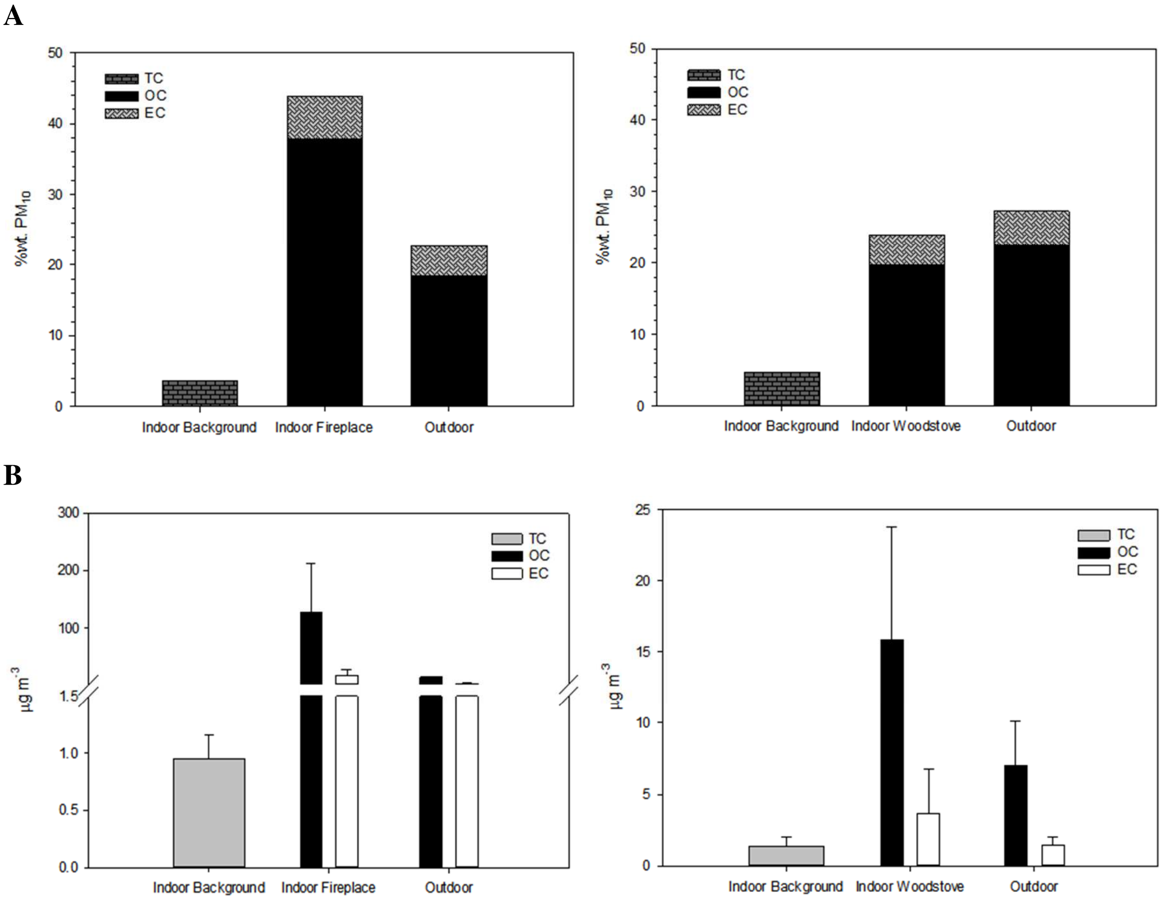
Water soluble ions accounted for 5.4 ± 2.0 wt% and 15 ± 7.7 wt% of the PM_{10} mass sampled during fireplace and woodstove operation, respectively. Outdoors, the PM_{10} mass fraction of inorganic ions was 3.2 and 1.8 times higher than the ones observed in the room with the fireplace and the woodstove, respectively. Among the measured ions, the most abundant in the outdoor environment during the first week of sampling (fireplace) were NO_3^- (6.1 %wt PM_{10}) and PO_4^{3-} (3.2 wt% PM_{10}), while in the second sampling campaign (woodstove) the major ion was PO_4^{3-} (8.8 wt% PM_{10}), followed by SO_4^{2-} (5.1 wt% PM_{10}).

Throughout the operation of both combustion appliances, the most noticeable cations in indoor particles were Ca^{2+} (1.3 and 0.88 wt% PM_{10}, for the fireplace and the woodstove, respectively) and Na^+ (1.5 and 0.69 wt% PM_{10}, during woodstove and fireplace operation, respectively). The major anions in the PM_{10} samples from fireplace operation were NO_3^- (0.83 wt% PM_{10}) and Cl^- (0.66 wt% PM_{10}), while when the woodstove was operating, particles contained mainly SO_4^{2-} (4.1 wt% PM_{10}) and PO_4^{3-} (3.2 wt% PM_{10}). Indoors, Ca^{2+} showed a good correlation with K^+ ($r^2 = 0.78$) and Mg^{2+} ($r^2 = 0.73$). The concentrations of K^+ and Na^+ also correlated well ($r^2 =0.74$).

The ionic balance is expressed by the ratio between the sum of the equivalents of cations and the sum of the equivalents of anions. On average, the ratio was greater than unity indoors (1.6 and 1.2 for fireplace and woodstove, respectively) and slightly below outdoors (0.8 to 0.9). Indoors, the alkaline character of aerosols indicates that carbonate is probably the missing anion that has not been measured. On the other hand, the acidic character of the outdoor aerosol might be attributed to the presence of H⁺, which has not been measured either.

6.3.2.3. Carbonaceous content

The carbonaceous (EC and OC) content of particles sampled during the woodstove operation (TC = 24.0 ± 7.37 wt% of PM_{10}) was almost half the one obtained during the combustion experiments with fireplace (43.9 ± 5.04 wt% of PM_{10}). OC constituted the major mass fraction, accounting for 37.9 ± 6.45 wt% and 19.7 ± 4.91 wt% of PM_{10} during the fireplace and woodstove operation, respectively (Fig. 6.4). The EC particulate mass fractions were substantially lower (5.97 ± 2.47 wt% of PM_{10} and 4.28 ± 2.59 wt% of PM_{10} for the fireplace and woodstove, respectively). Indoors, PM_{10} concentrations correlated well with the carbonaceous components (Fig. 6.4C).



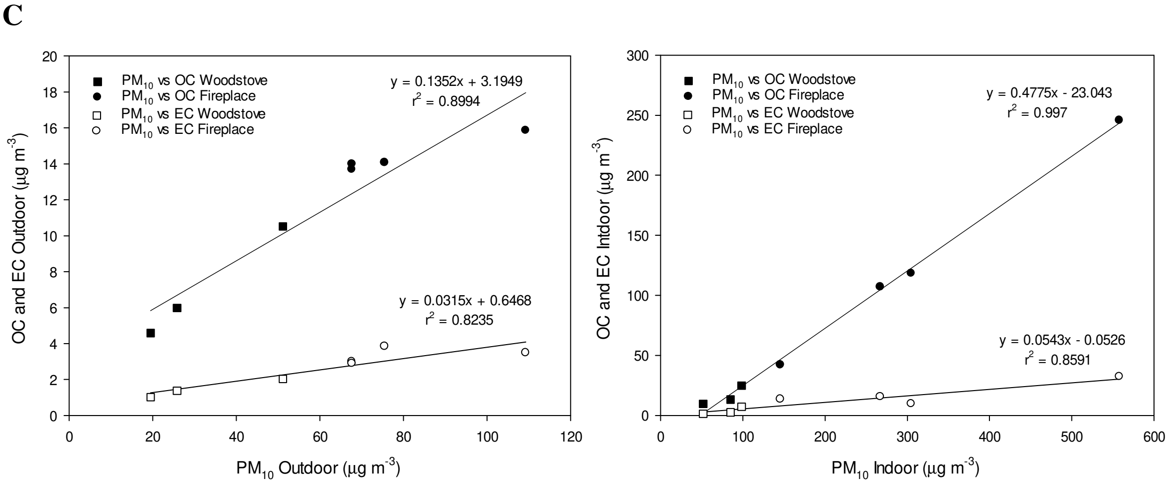


Figure 6.4. Carbonaceous mass fractions in PM$_{10}$ samples (%wt.) (A) and concentrations (µg m^{-3}) (B) indoors (while using combustion appliances and room background air) and outdoors. Correlations between concentrations (µg m^{-3}) of PM$_{10}$ and its carbonaceous fractions (C).

Furthermore, a strong correlation was also found between indoor OC and EC concentrations (r^2 = 0.86).

On average, OC accounted for 18.5 ± 2.80 and for 22.4 ± 1.59 wt% of the PM$_{10}$ mass outdoors during the sampling campaign with the fireplace and the woodstove, respectively. The EC mass fractions showed lower fluctuations, contributing on average from 4.2 to 4.8 wt% of the PM$_{10}$ mass. A good relationship between OC and EC concentrations in the outdoor air (r^2 = 0.91) was found, suggesting common sources for the carbonaceous particles. A strong correlation was also observed between outdoor OC and PM$_{10}$ concentrations (r^2 = 0.90) and between the outdoor PM$_{10}$ and EC concentrations (r^2 = 0.82) (Fig. 6.4C). The relationship between indoor and outdoor OC and EC concentrations showed weak correlations (r^2 = 0.40 and r^2 = 0.37, respectively), indicating little contribution of the outdoor air to the measured indoor levels.

The average indoor OC/EC ratio was 7.5 and 5.3 in the rooms equipped with the fireplace and the woodstove, respectively. Outdoors, the ratio ranged from 3.7 to 5.2. Since biomass burning generates many oxygenated organic compounds, to derive the organic matter content in PM$_{10}$, a total organic mass to organic carbon ratio (OM/OC) of 2.2 was adopted (Chow et al., 2015). As reviewed by Chow et al. (2015) the multiplier value remains a research subject and biomass burning values ranging from 1.5 to 2.6 have been suggested. As Fig. 6.6 shows, the sum of all components allowed determining from 64 to 97% of the PM$_{10}$ mass. The fraction of unidentified mass was considerably higher outdoors, during the first sampling campaign (fireplace), which might be attributed to aerosol growth under distinct relative humidity conditions (Zhang et al., 2017). In addition to the selection of the multiplier factor to derive the OM and particle-bound water on the filter deposits, other factors affecting the mass balance are related to sampling artefacts, the carbon analysis method and NH_4^+ and NO_3^- volatilisation (Chow et al., 2015). The unaccounted mass can also be partly assigned to the presence of unanalysed constituents (Fig. 6.5).

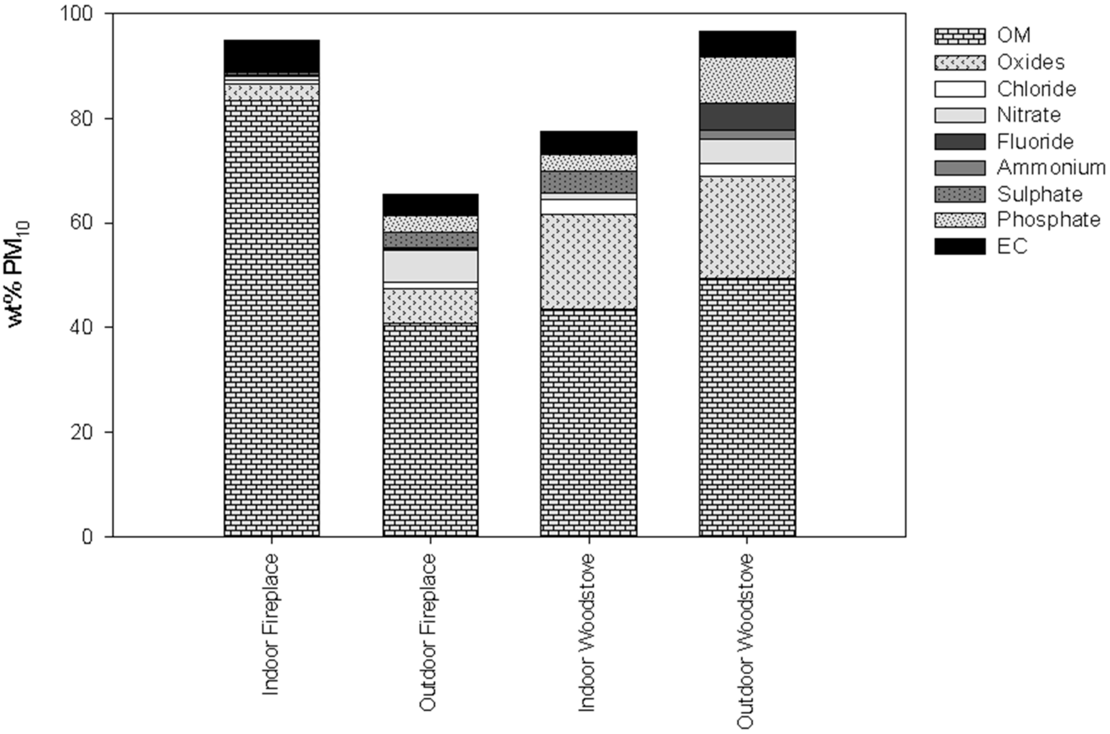


Figure 6.5. Chemical mass closure of PM_{10}.

6.3.2.4. Organic compounds

6.3.2.4.1. Homologous compound series

Alkanes were in the range from C_{10} to C_{35} (Table A2.2), accounting for OC mass fractions from 0.01 (fireplace operation) to 1.3 wt% (woodstove operation) indoors, while outdoors the contributions ranged from 0.01 to 1.2 wt% of OC mass. n-Alkanes were absent in background samples collected in the room where the woodstove was installed. No correlation was found between the sum of n-alkanes and PM_{10} both indoors and outdoors. n-Alkane concentrations in PM_{10} samples during woodstove operation were higher (over 15 times) than in those collected during fireplace operation.

A series of n-alkanoic acids from C_7 to C_{30} were detected in the organic extracts, representing, on average, 1.0 and 2.2 wt% of the OC mass during the operation of the fireplace and woodstove, respectively. Concentrations of n-alkanoic acids during fireplace operation were 3 times higher than the ones recorded during woodstove operation. Outdoors, n-carboxylic acids accounted for OC mass fractions ranging from 0.89 to 4.2 wt%. Concentrations of these homologous series showed a strong correlation with PM_{10} both indoors ($r^2 = 0.91$) and outdoors ($r^2 = 0.84$). Contributions of some unsaturated fatty acids to the PM samples were also recorded. The most abundant alkenoic acid was 9-octadecenoic acid (oleic), followed by 9-cis-hexadecenoic (linoleic), which was found at lower concentrations (Table A2.2). The concentrations of this organic class were highly correlated with PM_{10} levels, both indoors ($r^2 = 0.90$) and outdoors ($r^2 = 0.71$).

Dicarboxylic acids accounted for 2.1 and 4.6 wt% of the OC mass during the operation of the fireplace and woodstove, respectively. The most abundant compound was always ethanedioic acid (oxalic acid), followed by butanedioic acid (succinic acid) (Table A2.2). The main formation pathway of oxalic acid, an abundant and ubiquitous diacid, is via atmospheric oxidation of organic precursors (Kawamura and Bikkina, 2016). Taking into account that EC and primary OC are mostly emitted by combustion sources, EC has been used as a conservative tracer for primary combustion-generated OC (Polidori et al., 2007; Srivastava et al., 2018). In this study, oxalic acid exhibited a good correlation with EC indoors ($r^2 = 0.74$), while outdoors no correlation was found, indicating that secondary photochemical production in the ambient air is not negligible. On the other hand, succinic acid exhibited a good correlation with EC both indoors ($r^2 = 0.84$) and outdoors ($r^2 = 0.72$), suggesting that primary combustion sources are the predominant contributor to this alkanedioic acid.

A sequence of n-alkanols ($C_{10} – C_{30}$), representing, on average, 0.96 and 1.3 wt% of the OC mass, were detected in the organic extracts obtained from samples collected during fireplace and woodstove operation, respectively. The n-alkanol contribution to the OC mass outdoors ranged from 0.64 to 1.7 wt%. Behenyl alcohol comprised, on average, 57 and 34% of the total n-alkanol mass in the PM_{10} samples from the rooms equipped with fireplace and woodstove, respectively. The Σ_{17} of n-alkanols was correlated with PM_{10} concentrations indoors ($r^2 = 0.71$) and moderately correlated outdoors ($r^2 = 0.58$).

6.3.2.4.2. Polycyclic aromatic hydrocarbons (PAHs)

Twenty polycyclic compounds were quantified in the PM_{10} samples. Indoors, the quantified PAHs constituted OC mass fractions of 0.08 ± 0.03 wt% (fireplace) and 0.05 ± 0.03 wt% (woodstove). Outdoors, PAHs accounted for 0.08 to 0.25 wt% of the OC mass. The high-molecular-weight PAHs (four rings and larger) represented, on average, 80 wt% of the total PAH concentrations. The average concentration of total particulate bond PAHs (Table 6.2) collected during fireplace operation (92.0 ± 31.5 ng m^{-3}) largely exceeded the one obtained from the woodstove experiments (8.82 ± 6.50 ng m^{-3}). The PAHs with highest concentrations during woodstove operation were indeno[1,2,3-cd]pyrene, benzo[k]fluoranthene and benzo[b]fluoranthene. The use of fireplace resulted in high concentrations of retene, chrysene and benzo[a]anthracene in the room. On average, a 59-fold increase in PAH concentrations compared to the background measurements (ΣPAHs = 1.55 ng m^{-3}) was observed during fireplace operation, while the use of the woodstove contributed to a 3-fold enhancement compared to the baseline situation (ΣPAHs = 3.27 ng m^{-3}). On average, the outdoor PAH levels were 28.3 ± 5.4 and 6.02 ± 2.65 ng m^{-3} during the sampling campaign with the fireplace and the woodstove, respectively. The dominant compounds found outdoors were chrysene and retene. PAH concentrations correlated well with PM_{10} concentrations both indoors ($r^2 = 0.85$) and outdoors ($r^2 = 0.74$).

Benzo[a]pyrene (B[a]P), classified as one of the most potent carcinogenic PAHs (WHO, 2010), was present in all samples. Average B[a]P levels in samples collected during fireplace operation (6.09 ± 1.82 ng m^{-3}) were much higher than the ones recorded during woodstove operation (0.639 ± 0.386 ng m^{-3}). WHO has estimated a unit risk of 8.7×10^{-5} per ng m^{-3} B[a]P, based on epidemiological data on cohorts of coke-oven workers. The B[a]P dose producing an excess lifetime cancer risk of 1 in 10,000 was calculated to be 1.2 ng m^{-3} (WHO, 2010). The average indoor B[a]P level in the fireplace equipped home was 5 times higher than this value. The reference level of 0.12 ng m^{-3} estimated by WHO assuming an excess lifetime cancer risk of approximately 1 in 100,000 was exceeded by 5 times in the room equipped with the woodstove. The average outdoor B[a]P concentration (1.4 ng m^{-3}) was above the ambient air quality target value of 1 ng m^{-3} (annual average) set by EU legislation.

B[a]P is used as a marker compound for different environmental PAH source mixtures (USEPA, 1993; WHO, 2010). The carcinogenic risk due to exposure to PAHs is estimated and expressed per B[a]P equivalents (B[a]Peq). $B[a]P_{eq}$ are calculated multiplying the individual PAH concentration by its toxic equivalent factor (TEF). Different TEFs for PAHs in relation to the potency of B[a]P have been proposed. In the present study, the toxicity of the PAHs mixture was assessed through the modified version of Nisbet and LaGoy (1992) presented by Bari et al. (2010a). $B[a]P_{eq}$ values measured indoors during the wood burning experiments (8.6 and 1.2 ng m^{-3} for fireplace and woodstove operation, respectively) were higher than those outdoors (Table 6.2). Outdoors, the $B[a]P_{eq}$ concentrations were in the range from 0.46 to 5.7 ng m^{-3}.

Table 6.2. Concentrations of PAHs (ng m^{-3}), carcinogenic potency of total PAHs (BaP_{eq}, ng m^{-3}) and cancer risk.

PAHs (ng m^{-3})	**TEF**	**Indoor fireplace**	**Indoor background**	**Outdoor**	**Indoor woodstove**	**Indoor background**	**Outdoor**
Naphthalene	0.001	0.0151±0.0242	-	0.0392±0.0395	0.0261±0.0452	-	-
Acenaphthylene	0.001	0.0098±0.0095	-	0.0011±0.0014	-	0.0007	-
Acenaphthene	0.001	0.0029±0.0021	-	0.0012±0.0024	0.0001±0.0001	-	-
Fluorene	0.001	0.0001±0.0002	-	0.0023±0.0028	-	-	-
Phenanthrene	0.001	0.370±0.311	0.0103	0.0245±0.0139	0.0129±0.0051	0.0095	0.0008±0.0014
Anthracene	0.01	0.0674±0.0714	-	0.0027±0.0024	0.0037±0.0018	0.0007	0.0002±0.0003
Fluoranthene	0.001	1.81±1.27	0.0577	0.525±0.196	0.0676±0.0388	0.0621	0.0784±0.0651
Pyrene	0.001	2.12±1.52	0.0867	0.526±0.150	0.176±0.279	0.0533	0.0674±0.0831
Chrysene	0.01	7.86±2.44	0.197	3.99±1.56	0.586±0.279	0.310	0.675±0.316
Benzo[a]anthracene	0.1	7.07±2.41	0.0643	2.82±0.991	0.321±0.160	0.160	0.446±0.207
p-Terphenyl		0.0810±0.0519	-	0.0319±0.0094	0.0053±0.0028	0.0002	0.0036±0.0017
Retene		46.8±30.1	0.168	3.26±1.56	0.726±0.677	0.101	0.414±0.285
Perylene		0.724±0.270	0.0127	0.314±0.120	0.100±0.0491	0.0461	0.0646±0.0320
Benzo[b]fluoranthene	0.1	4.73±1.42	0.198	3.69±0.816	0.728±0.434	0.460	1.04±0.462
Benzo[k]fluoranthene	0.1	5.00±1.59	0.201	3.56±1.16	0.746±0.366	0.432	0.967±0.436
Benzo[e]pyrene		3.57±1.02	0.188	2.71±0.746	0.708±0.336	0.401	0.694±0.276
Benzo[a]pyrene	1	6.09±1.82	0.170	2.25±0.831	0.639±0.386	0.447	0.382±0.188
Benzo[g,h,i]perylene	0.01	2.06±1.04	0.0960	1.79±0.662	0.654±0.287	0.367	0.478±0.137
Dibenzo[a,h]anthracene	1	0.381±0.177	0.0043	0.379±0.175	0.0744±0.0070	0.0341	0.0768±0.0491
Indeno[1,2,3-cd]pyrene	0.1	3.21±1.54	0.0932	2.40±1.21	3.25±4.06	0.380	0.631±0.267
BaP_{eq} (ng m^{-3})		8.6 ± 2.6	0.23	3.9 ± 1.2	1.2 ± 0.85	0.63	0.78 ± 0.35
Cancer Risk		1.3×10^{-6}	3.6×10^{-8}	6.0×10^{-7}	1.9×10^{-7}	9.7×10^{-8}	1.2×10^{-7}

-Below detection limit or not detected. TEF: Toxic equivalent factor.

For both indoor and outdoor environments, B[a]P was the compound that contributed the most to the carcinogenic potential of the PAH mixture with values ranging from 48 ± 10% (outdoor, woodstove) to 71 ± 0.90% (indoor, fireplace). The second highest contributor to the carcinogenic potential found in the samples collected during the fireplace operation was benzo[a]anthracene (8.4 ± 1.8%), while in the corresponding outdoor samples the second major compound was dibenzo[a,h]anthracene (9.7 ± 4.4%). Indoors, during the heating period with the woodstove, indeno[1,2,3-cd]pyrene (21 ± 14%) had the second major share in the carcinogenic potential, while benzo[b]fluoranthene was once again the second major compound outdoors (14 ± 2.8%).

The inhalation exposure to PAHs was estimated by Eq. (5), where CA corresponds to the $B[a]P_{eq}$ concentration in air (ng m^{-3}). The excess cancer risk for a receptor exposed via the inhalation pathway was estimated by applying Eq. (6), where IUR indicates the calculated, theoretical upper limit possibility of contracting cancer when exposed to B[a]P at a concentration of 1 μg m^{-3}. IUR is calculated multiplying the cancer potency for B[a]P of 3.9 (mg kg^{-1} day^{-1}) by the reference human inhalation rate (20 m^3 day^{-1}) and dividing by the reference human body weight (70 kg). Table 6.2 displays the total carcinogenic risk calculated from the particle-phase PAH mixture. The typical USEPA target range for risk management is a 1/1,000,000 to a 1/10,000 increased lifetime risk (USEPA, 2005). The increment in the cancer risk due to exposure to indoor wood smoke during the open fireplace operation is slightly higher than the acceptable benchmark level (1×10^{-6}) recommended by USEPA.

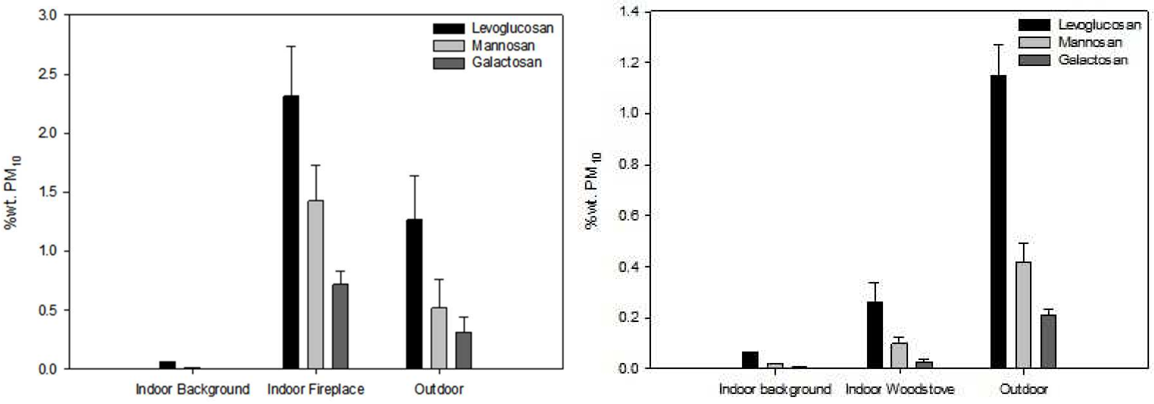
6.3.2.4.3. Saccharides and polyols

Anhydrosugars were the dominant group of organic compounds in samples collected both indoors (from 3.8 to 5.7 and from 0.31 to 0.49 wt% PM_{10} during fireplace and woodstove combustion, respectively) and outdoors (from 1.3 to 2.9 wt% PM_{10}) (Fig. 6.6A). During the fireplace operation, the anhydrosugars accounted for 10 to 13 wt% of the OC mass while lower mass fractions (1.2 to 3.1 wt%) were recorded during the woodstove operation. In this study, levoglucosan was found to be one of the most abundant species among the individually identified compounds with a concentration range of 2859 – 16,282 ng m^{-3} and 119 – 296 ng m^{-3} during the use of the fireplace and woodstove, respectively. The contribution of levoglucosan to the total monosaccharide anhydrides was between 50 and 74 wt%, whereas mannosan and galactosan accounted for 14 to 33% and 6.1 to 20 wt%, respectively. Levoglucosan mass fractions in particles collected in the room equipped with the fireplace (2.3 ± 0.42 wt% PM_{10}) were almost 9 times higher than the ones measured in the room during the traditional woodstove operation (0.26 ± 0.07 wt% PM_{10}). As predicted, indoor PM_{10} levels were strongly correlated with levoglucosan concentrations ($r^2 = 0.99$), since in these homes indoor

PM_{10} was primarily from wood combustion sources (Fig. 6.6B). Excluding a data point, a strong relationship between PM_{10} and levoglucosan (Fig. 6.6B) was also found outdoors ($r^2 = 0.98$), proving that biomass burning is a dominant active source during the winter in rural areas. The levoglucosan outdoor concentrations varied from 219 to 1227 ng m^{-3}, contributing to 1.0 – 1.8 wt% of the PM_{10} mass. A strong correlation between total PAHs and levoglucosan ($r^2 = 0.67$) concentrations was also observed, which increase ($r^2 = 0.89$) if the outlier is excluded, thus confirming their common emission source.

The levoglucosan to mannosan (L/M) ratio can be employed to distinguish biomass categories. In the present study, low L/M ratios in the range from 1.6 (indoor) to 5.3 (outdoor) were recorded (Fig. 6.6C). Other saccharides detected and identified in smoke samples encompassed disaccharides (sucrose) and polyols, such as inositol, ribitol, glucitol (also known as sorbitol) and erythritol (Table A2.3).

A



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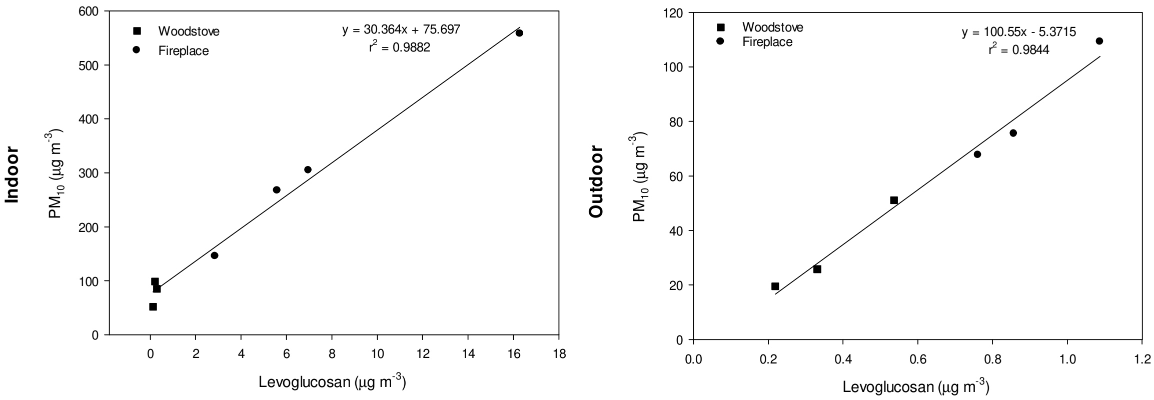

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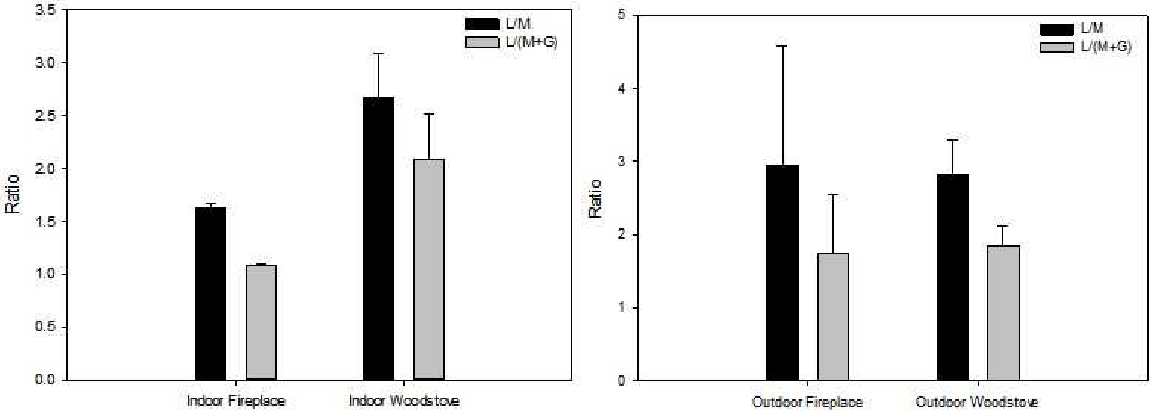

Figure 6.6. Anhydrosugar mass fractions in PM_{10} (%wt.) (A), correlation between levoglucosan and PM_{10} concentrations (µg m^{-3}) (B) and anhydrosugar ratios (C).

6.3.2.4.4. Other biomarkers

Lignin pyrolysis produces other biomass combustion specific organic compounds. The guaiacyl derivative 3-vanillyl propanol was the dominant compound in the PM_{10} samples collected during the fireplace operation but was absent from samples collected while using the woodstove. During the use of the fireplace, a wide variety of methoxyphenols were detected (coniferyl aldehyde, acetosyringone, sinapaldehyde and syringaldehyde), while the operation of the woodstove led to undetectable levels of these compounds in the particulate samples (Table A2.4). This may be linked to the higher combustion temperatures usually registered in woodstoves. The presence of guaiacol and syringol type methoxyphenols in the smoke that impacts the indoor environments indicates the combustion of a mixture of hard and soft firewood. Other lignin products, such as 3-hidroxybenzoic, vanillic and syringic acids, were detected in all aerosol samples, including background.

Pyrogallol was also detected in all samples. The highest concentration of this benzenetriol was recorded when the fireplace was under operation (Table A2.4). The occurrence of hydroquinone in samples impacted by emissions of this combustion appliance is also noteworthy. This benzenediol was not present in PM_{10} samples collected during the woodstove operation.

Bisphenol A was found at considerable concentrations in samples collected during the operation of the woodstove and was absent in the room where the fireplace was installed during both operation and non-operation periods (Table A2.4). No correlation was found between PM_{10} and bisphenol A concentrations both indoors and outdoors. Burning of plastics was found to be an important source of this compound in urban areas, although it has been detected in ambient aerosol samples from urban, rural, marine and the Polar Regions, indicating that it is a ubiquitous compound in the atmosphere (Fu and Kawamura, 2010). Terephthalic acid was also a major compound in PM_{10} samples collected while using the woodstove and was also found outdoors in lower concentrations (Table A2.4). Despite being a major pyrolysis product from poly (ethylene terephthalate) (PET), this compound is not source specific and can be emitted by other combustion processes (Simoneit et al., 2005). The other phthalic isomers, phthalic acid and isophthalic acid, were also detected in the PM_{10} samples (Table A2.4).

Among sterols and triterpenoids, β-sitosterol was the most abundant compound indoors, representing 87% and 52 wt% of the mass of this organic group in the PM_{10} samples during the operation of the fireplace and woodstove, respectively (Table A2.5). Despite being the most abundant compound, its contribution to the OC mass was small, averaging 0.13, 0.35 and 0.08 wt% OC in samples obtained outdoors and during the operation of the fireplace and the woodstove, respectively. Good correlations were found between β-sitosterol and PM_{10} concentrations, both indoors ($r^2 = 0.99$) and outdoors ($r^2 = 0.64$). Stigmasta-3,5-dien-7-one, a thermal alteration product of β-sitosterol (Oros and Simoneit, 2001a), was only detected in samples collected when using the fireplace. Lupeol, a pentacyclic triterpene referred to as a tracer of angiosperm smoke (Oros and Simoneit, 2001a), was found indoors for both combustion appliances, as well as outdoors.

Indoors, resin acids and derivatives represented 7.7 ± 1.5 (fireplace operation) and 1.8 ± 0.79 wt% of the OC mass (woodstove operation). Good correlations were observed between the sum of these compounds and OC concentrations in the indoor environments ($r^2 = 0.91$), while outdoors a stronger correlation with EC concentrations was found ($r^2 = 0.64$). The contribution of these organic compounds to the OC mass outdoors showed high variability, with contributions ranging from 2.9 to 11 wt% OC. The main compound in all particulate samples was dehydroabietic acid, an altered resin acid. Indoors, this oxidised derivative represented, on average, 68% and 69% of the mass of total resin acids in the PM_{10} samples during the operation of the fireplace and the woodstove, respectively. Outdoors, the contribution of this polar diterpenoid to the total mass of this class or organic compounds ranged from 67 to 85%. Abietic acid, an unaltered compound, was the second most abundant resin acid in PM_{10} samples impacted by combustion in the fireplace, representing 11% of the total mass of resin acids. During the operation of the woodstove, outdoors and in the background samples, this compound was found in very low concentrations or was not detected (Table A2.5).

6.4. Discussion

6.4.1. Physical parameters, gaseous compounds and PM levels

The results of this research clearly show that the operation of different batch fired combustion appliances leads to substantial differences in indoor pollutant concentrations. Previous studies have highlighted the distinct operating conditions of open fireplaces and woodstoves (e.g. Calvo et al., 2015, Calvo et al., 2014). Furthermore, the room volume where the measurements took place and the ventilation and removal rates also played a role in the concentration of pollutants (Eq. (1)). The removal mechanisms of indoor aerosols, such as deposition, are also affected by the building characteristics (surface area/volume and surface properties) and ventilation (Vu and Harrison, 2019). In this study, the ventilation rates were kept to a minimum and were similar in both rooms (Table 6.1). These values are close to the ones obtained by He et al. (2005) in households under minimum ventilation conditions (0.61 ± 0.45 h^{-1}) and by Long et al. (2001) during winter months in residential houses located in the suburban neighbourhoods of Boston (0.89 h^{-1}).

The 8-h average CO_2 concentrations were far below the protection limit of 1250 ppm (8-h average) set by the Portuguese Ordinance no. 353-A/2013. The average concentrations are similar to those observed by Castro et al. (2018) during the operation of an open brick fireplace similar to the one used in the present study (480 ± 110 ppm). As regards CO, although an increase of 11-fold (fireplace) and 3.5-fold (woodstove) over background levels was recorded, concentrations were below the 8-h guideline value and protection limit of 9 ppm set by WHO (2010) and the Portuguese Ordinance no. 353-A/(2013), respectively.

From the PM photometric measurements, PM_1/PM_{10} ratios always above 95% were obtained in the biomass burning periods. The predominance of submicron particles is in agreement with studies reporting on household combustion related particles (e.g. Castro et al., 2018; Salthammer et al., 2014). Despite the relatively low gaseous concentrations, PM_{10} levels in both rooms (8-h average, gravimetrically determined) were above the protection limit of 50 $\mu g\ m^{-3}$ (8-h average) set by the Portuguese Ordinance no. 353-A/2013. During the operation of the fireplace, PM_{10} levels increased dramatically and were, on average, 12 times higher than background concentrations and 4 times higher than the values registered outdoors. The average PM_{10} concentrations in the room with the airtight stove were much lower, but still over 2 times higher than the background and outdoor levels (Fig. 6.2). Although woodstoves are designed to seal off the combustion chamber from the room, the door is periodically open to refuel. Furthermore, leaks may cause a stove to emit smoke into the room. Castro et al. (2018) reported an average PM_{10} concentration of 58.5 ± 6.2 $\mu g\ PM_{10}\ m^{-3}$ during the operation of an open fireplace (4–5h) installed in the living room of a rural Spanish house. $PM_{2.5}$ concentrations reported by Salthammer et al. (2014) in seven German households equipped with closed (6 homes) and open (1 home) wood burning appliances were in the range from 6 $\mu g\ m^{-3}$ to 55 $\mu g\ m^{-3}$ (24-h average). The 24-h average $PM_{2.5}$ concentration before a stove intervention programme (21 households), in a rural mountain valley community (United States), was 45.0 ± 33.0 $\mu g\ m^{-3}$. The stove change out programme allowed an average PM reduction of 18.5 $\mu g\ m^{-3}$ (Noonan et al., 2012). In developing countries, indoor exposure to pollutants from burning biomass fuels is a major health concern, and concentrations are substantially higher in comparison with those reported in developed countries (Table A2.6). The large discrepancies may be related to the differences in household characteristics, type of fuel burned, combustion appliances and flues (e.g. Ezzati and Kammen, 2002; Fullerton et al., 2009).

The indoor PM_{10} generation rate from biomass burning in the open fireplace was, on average, > 25 times higher than those recorded for the woodstove (Table 6.1). The emission rates reported by Guo et al. (2008), who evaluated the impact of fireplace usage on the indoor air quality of Irish houses, were lower than the ones reported in the present study for the open fireplace (1.29 ± 1.25 mg min^{-1}) but higher than those obtained for the woodstove (0.049 ± 0.035 mg min^{-1}). The authors documented a PM_{10} emission rate of 0.69 ± 0.28 mg min^{-1} for household wood combustion, while emission rates ranging from 0.32 ± 0.12 to 1.39 ± 1.15 mg min^{-1} were found in houses where peat and coal were burned.

In the present study, although the same procedure was followed over the various days of experiments (ignition method, air settings in the woodstove operation, wood species burnt, fuel amount and sequence of loading), a high day-to-day variability in pollutant concentrations was recorded, which may reflect disparities in stove operation and weather conditions. Since the combustion appliances operate in natural draught conditions, the differences between chimney and outdoor air temperatures may increase or decrease the flue draft, reducing or enhancing indoor pollution.

6.4.2. Particle matter chemical composition

6.4.2.1. Major and trace elements

Elements accounted for a higher particulate mass fraction during the operation of the woodstove compared to the fireplace (Table A2.1). The effect of combustion conditions on the particulate matter chemical composition has been reported in several source characterisation studies

(Alves et al., 2011a; Calvo et al., 2015; Lamberg et al., 2011; Leskinen et al., 2014). The predominance of K and Ca in wood burning households is in agreement with previous studies (Molnár et al., 2005). Indoor particles were also enriched in Cu, Pb, Cr and Cd. Some of these elements might be released from the combustion appliance alloys when exposed to high combustion temperatures and corrosive species (Brady et al., 2017) or from household wood materials (e.g. furniture, building materials) that are treated with chromated‑copper-arsenate against insect, bacterial, and fungal activity (Rivas et al., 2015). Molnár et al. (2005) also pointed out Cu and Pb as possible markers of wood smoke indoors. Heavy metals are usually present at low concentrations in biomass fuels, however, after the combustion process they remain in the bottom ashes at relatively high concentrations (Nzihou and Stanmore, 2013). Stirring the fire and refuelling the combustion appliance may contribute to the enrichment of several metals by ash re-suspension and leakage into the room. Although K has been pointed out as a tracer for biomass combustion, only moderate enrichments were obtained for this compound ($3 \leq EF \leq 9$). Potassium emission is highly dependent on the combustion temperature of biomass, starting at around 700–900 °C and reaching the emission peak at 1300 °C (Van Lith et al., 2006 and references therein). The conventional biomass burning appliances of the present study operate at relatively low temperatures reaching maximum values in the combustion chamber of 580 (fireplace) and 750 °C (woodstove) (Calvo et al., 2014).

6.4.2.2. Water soluble ions

The alkali (Na^+ and K^+) and alkaline earth (Mg^{2+} and Ca^{2+}) cations correlated with each other, suggesting common indoor sources. Bottom ash resuspension from the combustion chamber during refuelling operations or due to the wood stirring might be responsible for the predominance of Ca^{2+} and K^+. Kajda-Szcześniak (2014) reported that ashes from fireplaces in dwelling houses were dominated by CaO, followed by MgO and K_2O. In addition to ash leakage into the room, these ionic species might arise from floor dust resuspension induced by the movement of the combustion appliance operator. Outdoors, PO_4^{3-} correlated well with K^+ ($r^2 = 0.70$) and NH_4^+ ($r^2 = 0.62$). Potassium-phosphate has been associated with agricultural fuels burning (Lamberg et al., 2013; Tissari et al., 2008), which is a common practise in rural areas during the wet season. Saraga et al. (2015) conducted indoor and outdoor PM measurements in a Greek apartment during the wood burning season, reporting SO_4^{2-} and NO_3^- as the most abundant, followed by Ca^{2+}, PO_4^{3-} and Na^+ for both in- and outdoor particles. In the present study, the I/O ratios for nitrate, sulphate and phosphate were below 1 during fireplace operation, while for the other ions the ratios were generally higher than unity. Indoors, the two secondary ions, NO_3^- and SO_4^{2-}, did not correlate, while the good relationship outdoors ($r^2 = 0.66$) suggests that their precursors were released from similar emission sources. Nitrate is a secondarily formed through the oxidation of NO_x emitted from combustion processes (Ho et al., 2003). In the household with woodstove, the I/O ratios for the other ions were generally higher than unity.

6.4.2.3. Carbonaceous content

The carbonaceous fraction contributed significantly to the PM_{10} mass (Fig. 6.4A). An increase in TC concentration of > 150 times compared to the background measurements was observed during fireplace operation. Despite the lower contribution, the woodstove operation still increased the TC levels 14 times compared to background. The measured carbonaceous mass fractions are similar to the ones observed by Castro et al. (2018) in the living room of a Spanish rural house equipped with an open fireplace (TC = 31 ± 3 wt% of PM_{10} mass). Ward et al. (2011) reported carbonaceous concentrations in $PM_{2.5}$ samples before and after a woodstove exchange programme in Idaho, United States. The authors registered a decrease in OC concentrations after the stove change out programme and an increase in EC concentrations. The EC concentrations documented by the researchers (0.3 and 0.7 $\mu g\ m^{-3}$, pre and post change out programme, respectively) are much lower than the ones obtained in the present study during both fireplace and woodstove operation (18 and 3.7 $\mu g\ m^{-3}$, respectively) (Fig. 6.4B). OC/EC ratios obtained in the present study are in the range of values reported for different types of biomass combustion by Vicente and Alves (2018) and are comparable to those obtained by Saraga et al. (2015) inside (5.9) and outside (6.7) an Athenian home during a period of extensive fireplace use for domestic heating. Although being used as source apportionment tool, the separation between sources based on this ratio is uncertain, due to overlapping with other sources (e.g. Alves et al., 2014).

6.4.2.4. Organic compounds

The chromatographically resolved organics were mainly composed of degradation products from biopolymers (e.g. levoglucosan from cellulose, methoxyphenols from lignin). The compound classes also included homologous series (n-alkanes, n-alkenes, n-alkanoic acids and n-alkanols), steroid and terpenoid biomarkers, and PAHs.

The diagnostic parameters, C_{max} (the carbon number of the compound with maximum concentration in the homologous series) and CPI (carbon preference index), for n-alkanes, n-alkanols and n-alkanoic acids (Table A2.2) are within the range reported for biomass burning emissions (Oros and Simoneit, 2001a, 2001b; Oros et al., 2006).

The incomplete combustion of biomass generates a wide range of PAHs. Among the identified PAHs, retene was one of the most abundant, both indoors (during fireplace operation) and outdoors. Although this compound has been pointed out as a tracer of softwood combustion, it was also detected in hardwood, crop residues and coal combustion samples (Shen et al., 2012), as well as in particles emitted in an urban road tunnel (Alves et al., 2016). The levels of B[a]P measured in the present study (Table 6.2) are within the values reported previously in similar environments. B[a]P concentrations in wood-burning Swedish homes were found to be between 0.09 and 2.2 ng m^{-3}, which was four times higher compared with the reference homes (mean concentrations of 0.63 ng m^{-3} and 0.16 ng m^{-3}) (Gustafson et al., 2008). In Southern Italy, the 12-hour average B[a]P concentration, in six houses heated with wood burning appliances, was 9.4 ng m^{-3} (De Gennaro et al., 2015). Higher B[a]P concentrations were reported by Zhu and Wang (2003) in residential Chinese kitchens (6 to 24 ng m^{-3}). In the present study, B[a]P concentrations were 2.7 and 1.7 times higher indoors than outdoors during the sampling campaign in the fireplace (2.25 ± 0.83 ng m^{-3}) and woodstove (0.382 ± 0.188 ng m^{-3}) equipped homes, respectively. Similar atmospheric B[a]P concentrations were reported in German (0.02 to 7.4 ng m^{-3}) (Bari et al., 2010a) and Finnish (0.32 to 3.4 ng m^{-3}) (Hellén et al., 2008) wood burning residential areas. The carcinogenic potencies of the total PAHs determined for outdoor samples are in the range of values reported at two rural residential areas near Stuttgart in Germany (1.2 to 3.3 ng $B[a]P_{eq}$ m^{-3}) where ambient PM_{10} sampling was performed during two winter seasons (Bari et al., 2011).

Levoglucosan has been extensively used as a chemical tracer for characterisation and quantification of biomass burning emissions worldwide (Vicente and Alves, 2018). This anhydrosugar has been identified in PM emissions from residential biomass combustion (Alves et al., 2017; Vicente et al., 2015), wildfires (e.g. Alves et al., 2011b; Vicente et al., 2011), prescribed fires (e.g. Alves et al., 2010; Zhang et al., 2013) and burning of other cellulose-containing fuels, such as coal (e.g. Yan et al., 2018). The contribution of this anhydrosugar to PM_{10} mass was lower in samples collected during woodstove operation. Levoglucosan emissions are highly dependent on combustion temperature and types of biomass (Bhattarai et al., 2019). Thus, the combustion technology has strong influence on its emissions. Ward et al. (2011) reported a 63% reduction in indoor levoglucosan concentrations after a stove change out programme (from 645 to 238 ng m^{-3}). Outdoors, the levoglucosan concentrations were highly variable which is in accordance with the results from other studies. Bari et al. (2010b) registered levoglucosan ambient concentrations in the range from 35 to 3223 ng m^{-3} in a German residential area during winter. In Belgium, Zdráhal et al. (2002) documented levoglucosan concentrations from 121 to 1133 ng m^{-3} in winter. Higher concentrations were testified by Ward et al. (2006) during the 2003 wildfire season in Montana (860–6091 ng m^{-3}). The L/M ratios (Fig. 6C) of the present study are within the ranges reported in the literature for softwood burning (Fine et al., 2001; Orasche et al., 2012; Schmidl et al., 2011, 2008). Although some eucalypt wood has also been used with the pine logs, the main woody biomass in the experiments was pine, given that it is the dominant forest species in the region. Maenhaut et al. (2012) reported annual L/M ratios for 7 sampling sites in Belgium from 6.2 to 7.1 and highlighted the little variation with season. Bhattarai et al. (2019) summarised L/M ratios in rural areas varying from 11.0 to 15.1. Much higher ratios of anhydrosaccharides (31–92) in source test emissions from lignite combustion were compiled by Fabbri et al. (2009). These researchers reported equal L/(M + G) and L/M ratios since galactosan was not detected in samples. In the present study, the contribution of galactosan to the total mass of anhydrosugars was low. However, its determination may allow differentiation between lignite and biomass burning aerosols (Fabbri et al., 2009).

The presence of phenolic compounds (3-vanillyl propanol, coniferyl aldehyde, acetosyringone, sinapaldehyde and syringaldehyde), diterpenoids (dehydroabietic and abietic acid), triterpenoids (lupeol) and phytosterols (β-sitosterol and stigmasta-3,5-dien-7-one) in samples from the rooms equipped with fireplace and woodstove highlights the input of biomass burning to particulate matter. Most of these organics were only detected in samples collected during fireplace operation. In source characterisation studies, Alves et al. (2017) observed that many of these organic compounds were negatively correlated with combustion temperature, indicating thermal degradation or preferential formation of other classes of organic compounds.

6.4.3. Health risks

In this work, the risks associated with inhalation exposure to particulate-bound trace metals and PAHs were estimated. The indoor/outdoor comparison showed that the carcinogenic potential indoors was greater than the corresponding outdoor value. Regarding the effects of the type of combustion appliance, distinct carcinogenic risks were recorded.

The cancer risk for cobalt, classified as Class 2B carcinogenic element by the IARC (2018), was slightly above the acceptable benchmark level (1.0×10^{-6}) during the woodstove operation. Risks for Cr(VI), classified as Class 1 carcinogenic element by the IARC (2018), were higher than 1.0×10^{-6} during the fireplace operation, both indoors and outdoors, and higher than 1.0×10^{-5} during woodstove operation, also indoors and outdoors (Fig. 6.3). The excess lifetime cancer risks for As, Cd, Ni, and Pb were always lower than the acceptable limit. The global excess lifetime cancer risk for PM_{10}-bound metals was lower than the USEPA guideline of 1.0×10^{-4} but not negligible (>1 ×

10^{-6}) (Fig. 6.3). Total noncarcinogenic risk (sum of all metals) was slightly above the safe level during the woodstove operation. Mn and Al were the most important contributors (>95%) to noncarcinogenic risks.

The increment in the cancer risk due to exposure to particle bond PAHs emitted by the open fireplace is slightly higher than the acceptable level (1×10^{-6}) recommended by USEPA, whereas the use of woodstove led to negligible cancer risks. Outdoors, despite the high variability in carcinogenic risks, these were always negligible ($<1 \times 10^{-6}$).

As discussed above, the differences in the combustion operating conditions resulted in different PM chemical characteristics and consequently in dissimilar health risks. The risk level presented in this study relies on an exposure scenario instead of the typical risk quantification based on continuous exposure. Thus, when comparisons are made with other studies, this aspect should be borne in mind. It should be mentioned that there are no similar studies in the literature with which the exposure risk results of this research can be compared.

6.5. Conclusions

Exposure to airborne particulate matter is recognised as one of the most important environmental risks. Indoor environments deserve special attention given that people spend most of their time in confined spaces. Even though specific indoor activities have been assessed over the years, there is still limited information on the impact of thermal related activities on indoor air quality in developed countries, especially with regard to the characterisation of particulate matter.

The present study evaluated indoor and outdoor concentrations of CO, CO_2 and PM_{10} during the operation of wood burning appliances (open fireplace and woodstove), without any other active source. Although a sharp increase in the CO levels was recorded when using both combustion appliances (11-fold and 3.5-fold in relation to background levels for the fireplace and the woodstove, respectively), the 8-hour average concentration did not exceed the protection limit. The increase in the PM_{10} concentrations due to the use of wood burning appliances, compared to the indoor background air, was noticeable. The ignition and refuelling stages led to peak concentrations of gases and particles. During the operation of both wood burning appliances, indoor levels for most of the measured particulate compounds were higher than those outdoors. The carbonaceous content was dominated by OC, which accounted for 43.9 ± 5.04 wt% and 24.0 ± 7.37 wt% of the PM_{10} mass sampled while using the fireplace and the woodstove, respectively. The chromatographically resolved particulate organic compounds encompassed homologous series of aliphatic compounds, PAHs, monosaccharides, methoxyphenols, sterols and terpenoids, among others. The average concentration of total particulate bond PAHs collected during the operation of the fireplace largely exceeded the one obtained in the experiments with woodstove (10 times, on average). B[a]P, which was present in all samples, including background, was the compound that contributed the most to the carcinogenic potential of the PAH mixture. The cancer risks associated with the inhalation exposure to particulate bound PAHs in the woodstove burning home was found to be negligible. On the other hand, the estimated value of lifetime lung cancer risks in the house equipped with an open fireplace exceeded the health-based guideline levels, demonstrating that long term exposure to PAHs at the respective levels would eventually cause risk of developing cancer. Furthermore, regarding the particulate bound major and trace elements, the excess lifetime cancer risk resulting from Cr(VI) exposure during the fireplace and woodstove operation was higher than 1.0×10^{-6} and 1.0×10^{-5}, respectively. Levoglucosan, used extensively as a chemical tracer for biomass burning, was one of the most abundant organic species, both indoors and outdoors. The presence of guaiacol and syringol type methoxyphenols indicates that smoke emissions resulted from the combustion of mixtures of hard and softwood. The good correlations between PM_{10} concentrations and the organic biomass burning markers highlights the strong impact of this source on indoor and outdoor air quality.

The day-to-day variability in pollutant concentrations is a reflex of the fluctuations in stove operation and weather conditions. Therefore, the findings of this study may not be generalisable and further investigations are necessary to consolidate the conclusions. Larger studies, covering more homes, different combustion appliances and a higher number of measurements, should be carried out to better assess the influence of this source on indoor air quality and health. The characteristics of the dwellings can have a determining effect on the levels of pollutants. Stove design, fuel properties and amounts burned, room features (e.g. dimensions, number of windows and their sizes) and ventilation levels are influential factors to be further assessed.

Despite the limitations, this work provided evidence of the importance of wood combustion as a key indoor source of PM and brought a deeper insight into the characteristics of particulate matter in households with traditional wood burning devices. The effect of this source at local level was also highlighted. Based on the exhaustive PM characterisation, risks and hazards from exposure were estimated for the first time, as far as we know. The results reported here are needed to force the adoption of strategies for reducing exposure to indoor air pollution from household solid fuels. In view of the differences observed in PM composition, both between fireplace and woodstove equipped rooms, and between indoors and outdoors, future investigations should focus on obtaining toxicological profiles, and evaluating different adverse biological outcomes and their relationship with particle-bound chemical constituents.

Effective messaging to homeowners through public information sources (television, radio and printed media) is needed to mobilise communities towards the reduction of environmental threats. A communication strategy that includes a clear link between air quality and health effects, as well as risk mitigation behaviours, is critical to engage the homeowners. Taking into account the results obtained in the present study, the replacement of outdated and inefficient stoves should be encouraged to ensure the air we breathe is cleaner both inside and outside of our homes. Financial incentives (e.g. tax incentives, credit enhancements), applicable to wood-burning appliance replacements, should be created and properly advertised among homeowners.

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References

Abdullahi, K.L., Delgado-Saborit, J.M., Harrison, R.M., 2013. Emissions and indoor concentrations of particulate matter and its specific chemical components from cooking: a review. Atmos. Environ. 71, 260–294. https://doi.org/10.1016/j.atmosenv.2013.01.061.

Abt, E., Suh, H.H., Catalano, P., Koutrakis, P., 2000. Relative contribution of outdoor and indoor particle sources to indoor concentrations. Environ. Sci. Technol. 34, 3579–3587. https://doi.org/10.1021/es990348y.

Allen, R.W., Leckie, S., Millar, G., Brauer, M., 2009. The impact of woodstove technology upgrades on indoor residential air quality. Atmos. Environ. 43, 5908–5915. https://doi.org/10.1016/j.atmosenv.2009.08.016.

Alves, C., Nunes, T., Silva, J., Duarte, M., 2013. Comfort parameters and particulate matter (PM_{10} and $PM_{2.5}$) in school classrooms and outdoor air. Aerosol Air Qual. Res. 13, 1521–1535. https://doi.org/10.4209/aaqr.2012.11.0321.

Alves, C.A., Gonçalves, C., Pio, C.A., Mirante, F., Caseiro, A., Tarelho, L., Freitas, M.C., Viegas, D.X., 2010. Smoke emissions from biomass burning in a Mediterranean shrubland. Atmos. Environ. 44, 3024–3033. https://doi.org/10.1016/j.atmosenv.2010.05.010.

Alves, C., Gonçalves, C., Fernandes, A.P., Tarelho, L., Pio, C., 2011a. Fireplace and woodstove fine particle emissions from combustion of western Mediterranean wood types. Atmos. Res. 101, 692–700.

Alves, C.A., Vicente, A., Monteiro, C., Gonçalves, C., Evtyugina, M., Pio, C., 2011b. Emission of trace gases and organic components in smoke particles from a wildfire in a mixed-evergreen forest in Portugal. Sci. Total Environ. 409, 1466–1475. https://doi.org/ 10.1016/j.scitotenv.2010.12.025.

Alves, C.A., Duarte, M., Nunes, T., Moreira, R., Rocha, S., 2014. Carbonaceous particles emitted from cooking activities in Portugal. Glob. Nest J. 16, 412–420.

Alves, C.A., Vicente, E.D., Rocha, S., Vicente, A.M., 2017. Organic tracers in aerosols from the residential combustion of pellets and agro-fuels. Air Qual. Atmos. Heal. 10. https://doi.org/10.1007/s11869-016-0406-3.

Alves, Vicente, P, A.M., Gomes, J., Nunes, T., Duarte, M., Bandowe, B.A.M., 2016. Polycyclic aromatic hydrocarbons (PAHs) and their derivatives (oxygenated-PAHs, nitrated-PAHs and azaarenes) in size-fractionated particles emitted in an urban road tunnel. Atmos. Res. 180, 128–137. https://doi.org/10.1016/j.atmosres.2016.05.013.

Amato, F., Alastuey, A., Karanasiou, A., Lucarelli, F., Nava, S., Calzolai, G., Severi, M., Becagli, S., Gianelle, V.L., Colombi, C., Alves, C., Custódio, D., Nunes, T., Cerqueira, M., Pio, C., Eleftheriadis, K., Diapouli, E., Reche, C., Minguillón, M.C., Manousakas, M.I., Maggos, T., Vratolis, S., Harrison, R.M., Querol, X., 2016. AIRUSE-LIFE+: a harmonized PM speciation and source apportionment in five southern European cities. Atmos. Chem. Phys. 16, 3289–3309. https://doi.org/10.5194/acp-16-3289-2016.

ASHRAE, 2010. ANSI/ASHRAE standard 55-2010. Thermal Environmental Conditions for Human Occupancy. American society of heating, refrigerating and air-conditioning engineers, Atlanta, USA.

Bari, M.A., Baumbach, G., Kuch, B., Scheffknecht, G., 2010a. Particle-phase concentrations of polycyclic aromatic hydrocarbons in ambient air of rural residential areas in southern Germany. Air Qual. Atmos. Heal. 3, 103–116. https://doi.org/10.1007/s11869- 009-0057-8.

Bari, M.A., Baumbach, G., Kuch, B., Scheffknecht, G., 2010b. Temporal variation and impact of wood smoke pollution on a residential area in southern Germany. Atmos. Environ. 44, 3823–3832. https://doi.org/10.1016/j.atmosenv.2010.06.031.

Bari, M.A., Baumbach, G., Brodbeck, J., Struschka, M., Kuch, B., Dreher, W., Scheffknecht, G., 2011. Characterisation of particulates and carcinogenic polycyclic aromatic hydrocarbons in wintertime wood-fired heating in residential areas. Atmos. Environ. 45, 7627–7634. https://doi.org/10.1016/j.atmosenv.2010.11.053.

Bartington, S.E., Bakolis, I., Devakumar, D., Kurmi, O.P., Gulliver, J., Chaube, G., Manandhar, D.S., Saville, N.M., Costello, A., Osrin, D., Hansell, A.L., Ayres, J.G., 2017. Patterns of domestic exposure to carbon monoxide and particulate matter in households using biomass fuel in Janakpur, Nepal. Environ. Pollut. 220, 38–45. https://doi.org/10.1016/j.envpol.2016.08.074.

Bhattarai, H., Saikawa, E., Wan, X., Zhu, H., Ram, K., Gao, S., Kang, S., Zhang, Q., Zhang, Y., Wu, G., Wang, X., Kawamura, K., Fu, P., Cong, Z., 2019. Levoglucosan as a tracer of biomass burning: recent progress and perspectives. Atmos. Res. 220, 20–33. https://doi. org/10.1016/J.ATMOSRES.2019.01.004.

Bloom, E., Widheden, A., Ekberg, L., Langer, S., Bek, G., 2015. Indoor air quality in passive and conventional new houses in Sweden. Build. Environ. 93, 92–100. https://doi.org/10.1016/j.buildenv.2015.02.004.

Boy, E., Bruce, N., Delgado, H., 2002. Birth weight and exposure to kitchen wood smoke during pregnancy in rural Guatemala. Environ. Health Perspect. 110, 109–114. https://doi.org/10.1289/ehp.02110109.

Brady, M.P., Banta, K., Mizia, J., Lorenz, N., Leonard, D.N., Yamamoto, Y., DeFoort, M., Keiser, J.R., 2017. Alloy corrosion onsiderations in low-cost, clean biomass cook-stoves for the developing world. Energy Sustain. Dev. 37, 20–32. https://doi.org/10.1016/j.esd.2016.12.002.

Brasche, S., Bischof, W., 2005. Daily time spent indoors in German homes – baseline data for the assessment of indoor exposure of German occupants. Int. J. Hyg. Environ. Health 208, 247–253. https://doi.org/10.1016/J.IJHEH.2005.03.003.

Buonanno, G., Giovinco, G., Morawska, L., Stabile, L., 2011. Tracheobronchial and alveolar dose of submicrometer particles for different population age groups in Italy. Atmos. Environ. 45, 6216–6224. https://doi.org/10.1016/j.atmosenv.2011.07.066.

Calvo, A.I., Tarelho, L.A.C., Alves, C.A., Duarte, M., Nunes, T., 2014. Characterization of operating conditions of two residential wood combustion appliances. Fuel Process. Technol. 126, 222–232. https://doi.org/10.1016/j.fuproc.2014.05.001.

Calvo, A.I., Martins, V., Nunes, T., Duarte, M., Hillamo, R., Teinila, K., Pont, V., Castro, A., Fraile, R., Tarelho, L., Alves, C., 2015. Residential wood combustion in two domestic devices: relationship of different parameters throughout the combustion cycle. Atmos. Environ. 116, 72–82. https://doi.org/10.1016/j.atmosenv.2015.06.012.

Castro, A., Calvo, A.I., Blanco-Alegre, C., Oduber, F., Alves, C., Coz, E., Amato, F., Querol, X., Fraile, R., 2018. Impact of the wood combustion in an open fireplace on the air quality of a living room: estimation of the respirable fraction. Sci. Total Environ. 628–629, 169–176. https://doi.org/10.1016/j.scitotenv.2018.02.001.

Chow, J.C., Lowenthal, D.H., Chen, L.W.A., Wang, X., Watson, J.G., 2015. Mass reconstruction methods for $PM_{2.5}$: a review. Air Qual. Atmos. Heal. 8, 243–263. https://doi. org/10.1007/s11869-015-0338-3.

Custódio, D., Pinho, I., Cerqueira, M., Nunes, T., Pio, C., 2014. Indoor and outdoor suspended particulate matter and associated carbonaceous species at residential homes in northwestern Portugal. Sci. Total Environ. 473–474, 72–76. https://doi.org/10.1016/j.scitotenv.2013.12.009.

De Gennaro, G., Dambruoso, P.R., Di Gilio, A., di Palma, V., Marzocca, A., Tutino, M., 2015. Discontinuous and continuous indoor air quality monitoring in homes with fireplaces or wood stoves as heating system. Int. J. Environ. Res. Public Health 13, 1–9. https://doi.org/10.3390/ijerph13010078.

Delgado-Saborit, J.M., Stark, C., Harrison, R.M., 2011. Carcinogenic potential, levels and sources of polycyclic aromatic hydrocarbon mixtures in indoor and outdoor environments and their implications for air quality standards. Environ. Int. 37, 383–392. https://doi.org/10.1016/j.envint.2010.10.011.

Derbez, M., Berthineau, B., Cochet, V., Lethrosne, M., Pignon, C., Riberon, J., Kirchner, S., 2014. Indoor air quality and comfort in seven newly built, energy-efficient houses in France Build. Environ. 72, 173–187. https://doi.org/10.1016/j.buildenv.2013.10.017.

Ezzati, M., Kammen, D.M., 2001. Indoor air pollution from biomass combustion and acute respiratory infections in Kenya: an exposure-response study. Lancet 358, 619–624. https://doi.org/10.1016/S0140-6736(01)05777-4.

Ezzati, M., Kammen, D.M., 2002. The health impacts of exposure to indoor air pollution from solid fuels in developing countries: knowledge, gaps, and data needs. Environ. Health Perspect. 110, 1057–1068. https://doi.org/10.1289/ehp.021101057.

Fabbri, D., Torri, C., Simoneit, B.R.T., Marynowski, L., Rushdi, A.I., Fabiańska, M.J., 2009. Levoglucosan and other cellulose and lignin markers in emissions from burning of Miocene lignites. Atmos. Environ. 43, 2286–2295. https://doi.org/10.1016/j.atmosenv.2009.01.030.

Fine, P.M., Cass, G.R., Simoneit, B.R.T., 2001. Chemical characterization of fine particle emissions from fireplace combustion of woods grown in the northeastern United States. Environ. Sci. Technol. 35, 2665–2675. https://doi.org/10.1021/es001466k.

Fu, P., Kawamura, K., 2010. Ubiquity of bisphenol a in the atmosphere. Environ. Pollut. 158, 3138–3143. https://doi.org/10.1016/j.envpol.2010.06.040.

Fullerton, D.G., Semple, S., Kalambo, F., Suseno, A., Malamba, R., Henderson, G., Ayres, J.G., Gordon, S.B., 2009. Biomass fuel use and indoor air pollution in homes in Malawi. Occup. Environ. Med. 66, 777–783. https://doi.org/10.1136/oem.2008.045013.

Gao, Y., Nelson, E.D., Field, M.P., Ding, Q., Li, H., Sherrell, R.M., Gigliotti, C.L., Van Ry, D.A., Glenn, T.R., Eisenreich, S.J., 2002. Characterization of atmospheric trace elements on $PM_{2.5}$ particulate matter over the New York-New Jersey harbour estuary. Atmos. Environ. 36, 1077–1086. https://doi.org/10.1016/S1352-2310(01)00381-8.

Géhin, E., Ramalho, O., Kirchner, S., 2008. Size distribution and emission rate measurement of fine and ultrafine particle from indoor human activities. Atmos. Environ. 42, 8341–8352. https://doi.org/10.1016/j.atmosenv.2008.07.021.

Glytsos, T., Ondráček, J., Džumbová, L., Kopanakis, I., Lazaridis, M., 2010. Characterization of particulate matter concentrations during controlled indoor activities. Atmos. Environ. 44, 1539–1549. https://doi.org/10.1016/j.atmosenv.2010.01.009.

Gonçalves, C., Alves, C., Pio, C., 2012. Inventory of fine particulate organic compound emissions from residential wood combustion in Portugal. Atmos. Environ. 50, 297–306. https://doi.org/10.1016/j.atmosenv.2011.12.013.

Guo, L., Lewis, J.O., McLaughlin, J.P., 2008. Emissions from Irish domestic fireplaces and their impact on indoor air quality when used as supplementary heating source. Glob. Nest J. 10, 209–216.

Gustafson, P., Ostman, C., Sällsten, G., 2008. Indoor levels of polycyclic aromatic hydrocarbons in homes with or without wood burning for heating. Environ. Sci. Technol. 42, 5074–5080.

He, C., Morawska, L., Hitchins, J., Gilbert, D., 2004. Contribution from indoor sources to particle number and mass concentrations in residential houses. Atmos. Environ. 38, 3405–3415. https://doi.org/10.1016/j.atmosenv.2004.03.027.

He, C., Morawska, L., Gilbert, D., 2005. Particle deposition rates in residential houses. Atmos. Environ. 39, 3891–3899. https://doi.org/10.1016/j.atmosenv.2005.03.016.

Hellén, H., Hakola, H., Haaparanta, S., Pietarila, H., Kauhaniemi, M., 2008. Influence of residential wood combustion on local air quality. Sci. Total Environ. 393, 283–290. https://doi.org/10.1016/j.scitotenv.2008.01.019.

Ho, K.F., Lee, S.C., Chan, C.K., Yu, J.C., Chow, J.C., Yao, X.H., 2003. Characterization of chemical species in $PM_{2.5}$ and PM_{10} aerosols in Hong Kong. Atmos. Environ. 37, 31–39. https://doi.org/10.1016/S1352-2310(02)00804-X.

IARC, 2018. IARC monographs on the identification of carcinogenic hazards to humans, list of classifications, volumes 1-123.Available online. https://monographs.iarc.fr/ list-of-classifications-volumes (accessed on 6 April 19).

Isaxon, C., Gudmundsson, A., Nordin, E.Z., Lönnblad, L., Dahl, A., Wieslander, G., Bohgard, M., Wierzbicka, A., 2015. Contribution of indoor-generated particles to residential exposure. Atmos. Environ. 106, 458–466. https://doi.org/10.1016/j.atmosenv.2014.07.053.

Kajda-Szcześniak, M., 2014. Characteristics of ashes from fireplace. Arch. Waste Manag. Environ. Prot. 16, 73–78.

Kaunelien, V., Prasauskas, T., Krugly, E., Stasiulaitien, I., Ciu, D., Seduikyt, L., 2016. Indoor air quality in low energy residential buildings in Lithuania. Build. Environ. 108, 63–72. https://doi.org/10.1016/j.buildenv.2016.08.018.

Kawamura, K., Bikkina, S., 2016. A review of dicarboxylic acids and related compounds in atmospheric aerosols: molecular distributions, sources and transformation. Atmos. Res. 170, 140–160. https://doi.org/10.1016/j.atmosres.2015.11.018.

Kim, K.H., Jahan, S.A., Kabir, E., 2011. A review of diseases associated with household air pollution due to the use of biomass fuels. J. Hazard. Mater. 192, 425–431. https://doi.org/10.1016/j.jhazmat.2011.05.087.

Kingham, S., Durand, M., Aberkane, T., Harrison, J., Gaines Wilson, J., Epton, M., 2006. Winter comparison of TEOM, MiniVol and DustTrak PM_{10} monitors in a woodsmoke environment. Atmos. Environ. 40, 338–347. https://doi.org/10.1016/j.atmosenv.2005.09.042.

Klepeis, N.E., Nelson, W.C., Ott, W.R., Robinson, J.P., Tsang, A.M., Switzer, P., Behar, J.V., Hern, S.C., Engelmann, W.H., 2001. The National Human Activity Pattern Survey (NHAPS): a resource for assessing exposure to environmental pollutants. J. Expo. Sci. Environ. Epidemiol. 11, 231–252. https://doi.org/10.1038/sj. jea.7500165.

Lamberg, H., Nuutinen, K., Tissari, J., Ruusunen, J., Yli-Pirilä, P., Sippula, O., Tapanainen, M., Jalava, P., Makkonen, U., Teinilä, K., Saarnio, K., Hillamo, R., Hirvonen, M.R., Jokiniemi, J., 2011. Physicochemical characterization of fine particles from small-scale wood combustion. Atmos. Environ. 45, 7635–7643. https://doi.org/10.1016/j.atmosenv.2011.02.072.

Lamberg, H., Tissari, J., Jokiniemi, J., Sippula, O., 2013. Fine particle and gaseous emissions from a small-scale boiler fueled by pellets of various raw materials. Energ. Fuel. 27, 7044–7053. https://doi.org/10.1021/ef401267t.

Leech, J.A., Wilby, K., McMullen, E., Laporte, K., 1996. The Canadian human activity pattern survey: report of methods and population surveyed. Chronic Dis. Can. 17, 118–123.

Leskinen, J., Tissari, J., Uski, O., Virén, A., Torvela, T., Kaivosoja, T., Lamberg, H., Nuutinen, I., Kettunen, T., Joutsensaari, J., Jalava, P.I., Sippula, O., Hirvonen, M.R., Jokiniemi, J., 2014. Fine particle emissions in three different combustion conditions of a wood chip-fired appliance - particulate physico-chemical properties and induced cell death. Atmos. Environ. 86, 129–139. https://doi.org/10.1016/j.atmosenv.2013.12.012.

Long, C.M., Suh, H.H., Koutrakis, P., 2000. Characterization of indoor particle sources using continuous mass and size monitors. J. Air Waste Manag. Assoc. 50, 1236–1250.

Long, C.M., Suh, H.H., Catalano, P.J., Koutrakis, P., 2001. Using time- and size-resolved particulate data to quantify indoor penetration and deposition behavior. Environ. Sci. Technol. 35, 2089–2099. https://doi.org/10.1021/es001477d.

Maenhaut, W., Vermeylen, R., Claeys, M., Vercauteren, J., Matheeussen, C., Roekens, E., 2012. Assessment of the contribution from wood burning to the PM_{10} aerosol in Flanders, Belgium. Sci. Total Environ. 437, 226–236. https://doi.org/10.1016/j.scitotenv.2012.08.015.

Massey, D.D., Kulshrestha, A., Taneja, A., 2013. Particulate matter concentrations and their related metal toxicity in rural residential environment of semi-arid region of India. Atmos. Environ. 67, 278–286. https://doi.org/10.1016/j.atmosenv.2012.11.002.

McCormack, M.C., Breysse, P.N., Hansel, N.N., Matsui, E.C., Tonorezos, E.S., Curtin-Brosnan, J., Williams, D.L., Buckley, T.J., Eggleston, P.A., Diette, G.B., 2008. Common household activities are associated with elevated particulate matter concentrations in bedrooms of inner-city Baltimore pre-school children. Environ. Res. 106, 148–155. https://doi.org/10.1016/j.envres.2007.08.012.

McNamara, M., Thornburg, J., Semmens, E., Ward, T., Noonan, C., 2013. Coarse particulate matter and airborne endotoxin within wood stove homes. Indoor Air 23, 498–505. https://doi.org/10.1111/ina.12043.

McNamara, M.L., Noonan, C.W., Ward, T.J., 2011. Correction factor for continuous monitoring of wood smoke fine particulate matter. Aerosol Air Qual. Res. 11, 315–322. https://doi.org/10.1039/b800799c.O.

McNamara, M.L., Thornburg, J., Semmens, E.O., Ward, T.J., Noonan, C.W., 2017. Reducing indoor air pollutants with air filtration units in wood stove homes. Sci. Total Environ. 592, 488–494. https://doi.org/10.1016/j.scitotenv.2017.03.111.

Molloy, S.B., Cheng, M., Galbally, I.E., Keywood, M.D., Lawson, S.J., Powell, J.C., Gillett, R., Dunne, E., Selleck, P.W., 2012. Indoor air quality in typical temperate zone Australian dwellings. Atmos. Environ. 54, 400–407. https://doi.org/10.1016/j.atmosenv.2012.02.031.

Molnár, P., Gustafson, P., Johannesson, S., Boman, J., Barregård, L., Sällsten, G., 2005. Domestic wood burning and $PM_{2.5}$ trace elements: personal exposures, indoor and outdoor levels. Atmos. Environ. 39, 2643–2653. https://doi.org/10.1016/j.atmosenv.2005.01.016.

Morawska, L., Afshari, A., Bae, G.N., Buonanno, G., Chao, C.Y.H., Hänninen, O., Hofmann, W., Isaxon, C., Jayaratne, E.R., Pasanen, P., Salthammer, T., Waring, M., Wierzbicka, A., 2013. Indoor aerosols: from personal exposure to risk assessment. Indoor Air 23, 462–487. https://doi.org/10.1111/ina.12044.

Morawska, L., Ayoko, G.A., Bae, G.N., Buonanno, G., Chao, C.Y.H., Clifford, S., Fu, S.C., Hänninen, O., He, C., Isaxon, C., Mazaheri, M., Salthammer, T., Waring, M.S., Wierzbicka, A., 2017. Airborne particles in indoor environment of homes, schools, offices and aged care facilities: the main routes of exposure. Environ. Int. 108, 75–83. https://doi.org/10.1016/J.ENVINT.2017.07.025.

Morawska, L., Salthammer (Eds), T., 2003. Indoor Environment. Airborne Particles and Settled Dust. Wiley-VCH GmbH & Co. KGaA.

Nasir, Z.A., Colbeck, I., 2013. Particulate pollution in different housing types in a UK suburban location. Sci. Total Environ. 445–446, 165–176. https://doi.org/10.1016/j.scitotenv.2012.12.042.

Nisbet, I.C.T., LaGoy, P.K., 1992. Toxic equivalency factors (TEFs) for polycyclic aromatic hydrocarbons (PAHs). Regul. Toxicol. Pharmacol. 16, 290–300.

Noonan, C.W., Navidi, W., Sheppard, L., Palmer, C.P., Bergauff, M., Hooper, K., Ward, T.J., 2012. Residential indoor $PM_{2.5}$ in wood stove homes: follow-up of the Libby changeout program. Indoor Air 22, 492–500. https://doi.org/10.1111/j.1600-0668.2012.00789.x.

Nzihou, A., Stanmore, B., 2013. The fate of heavy metals during combustion and gasification of contaminated biomass-a brief review. J. Hazard. Mater. 256–257, 56–66. https://doi.org/10.1016/j.jhazmat.2013.02.050.

Oeder, S., Dietrich, S., Weichenmeier, I., Schober, W., Pusch, G., Jörres, R.A., Schierl, R., Nowak, D., Fromme, H., Behrendt, H., Buters, J.T.M., 2012. Toxicity and elemental composition of particulate matter from outdoor and indoor air of elementary schools in Munich, Germany. Indoor Air 22, 148–158. https://doi.org/10.1111/j.1600-0668.2011.00743.x.

Oliveira, T.S., Pio, C.A., Alves, C.A., Silvestre, A.J.D., Evtyugina, M., Afonso, J.V., Fialho, P., Legrand, M., Puxbaum, H., Gelencsér, A., 2007. Seasonal variation of particulate lipophilic organic compounds at nonurban sites in Europe. J. Geophys. Res. Atmos. 112. https://doi.org/10.1029/2007JD008504.

Orasche, J., Seidel, T., Hartmann, H., Schnelle-Kreis, J., Chow, J.C., Ruppert, H., Zimmermann, R., 2012. Comparison of emissions from wood combustion. Part 1: emission factors and characteristics from different small-scale residential heating appliances considering particulate matter and polycyclic aromatic hydrocarbon (PAH) related toxicological potential of particle-bound organic species. Energ. Fuel. 26, 6695–6704. https://doi.org/ 10.1021/ef301295k.

Ordinance Nº. 353-A/2013 (Portaria nº 353-A/2013). Regulamento de Desempenho Energético dos Edifícios de Comércio e Serviços (RECS)—Requisitos de Ventilação e Qualidade do ar Interior. Ministério do Ambiente Ordenamento do Território e Energia da Saúde e da Solidariedade Emprego e Segurança Social, Lisboa, Portugal.

Oros, D.R., Simoneit, B.R., 2001a. Identification and emission factors of molecular tracers in organic aerosols from biomass burning part 2. Deciduous trees. Appl. Geochem. 16, 1545–1565. https://doi.org/10.1016/S0883-2927(01)00022-1.

Oros, D.R., Abas, M.R. bin, Omar, N.Y.M.J., Rahman, N.A., Simoneit, B.R.T., 2006. Identification and emission factors of molecular tracers in organic aerosols from biomass burning: Part 3. Grasses. Appl. Geochem. 21, 919–940. https://doi.org/10.1016/J.APGEOCHEM.2006.01.008.

Oros, D.R., Simoneit, B.R.T., 2001. Identification and emission factors of molecular tracers in organic aerosols from biomass burning part 1. Temperate climate conifers. Appl. Geochem. https://doi.org/10.1016/S0883-2927(01)00021-X.

Parajuli, I., Lee, H., Shrestha, K.R., 2016. Indoor air quality and ventilation assessment of rural mountainous households of Nepal. Int. J. Sustain. Built Environ. 5, 301–311. https://doi.org/10.1016/j.ijsbe.2016.08.003.

Pastorello, C., Caserini, S., Galante, S., Dilara, P., Galletti, F., 2011. Importance of activity data for improving the residential wood combustion emission inventory at regional level. Atmos. Environ. 45, 2869–2876. https://doi.org/10.1016/j.atmosenv.2011.02.070.

Pegas, P.N., Nunes, T., Alves, C.A., Silva, J.R., Vieira, S.L.A., Caseiro, A., Pio, C.A., 2012. Indoor and outdoor characterisation of organic and inorganic compounds in city centre and suburban elementary schools of Aveiro, Portugal. Atmos. Environ. 55, 80–89. https://doi.org/10.1016/J.ATMOSENV.2012.03.059.

Pokhrel, A.K., Bates, M.N., Verma, S.C., Joshi, H.S., Sreeramareddy, C.T., Smith, K.R., 2010. Tuberculosis and indoor biomass and kerosene use in Nepal: a case-control study. Environ. Health Perspect. 118, 558–564. https://doi.org/10.1289/ehp.0901032.

Polidori, A., Arhami, M., Sioutas, C., Delfino, R.J., Allen, R., 2007. Indoor/outdoor relationships, trends, and carbonaceous content of fine particulate matter in retirement homes of the Los Angeles basin. J. Air Waste Manag. Assoc. 57, 366–379. https://doi.org/10.1080/10473289.2007.10465339.

Querol, X., Alastuey, A., Rodriguez, S., Plana, F., Ruiz, C.R., Cots, N., Massagué, G., Puig, O., 2001. PM_{10} and $PM_{2.5}$ source apportionment in the Barcelona metropolitan area, Catalonia, Spain. Atmos. Environ. 35, 6407–6419. https://doi.org/10.1016/S1352-2310 (01)00361-2.

Raspanti, G.A., Hashibe, M., Siwakoti, B., Wei, M., Thakur, B.K., Pun, C.B., Al-Temimi, M., Lee, Y.C.A., Sapkota, A., 2016. Household air pollution and lung cancer risk among never-smokers in Nepal. Environ. Res. 147, 141–145. https://doi.org/10.1016/j.envres.2016.02.008.

Regalado, J., Pérez-Padilla, R., Sansores, R., Ramirez, J.I.P., Brauer, M., Paré, P., Vedal, S., 2006. The effect of biomass burning on respiratory symptoms and lung function in rural Mexican women. Am. J. Respir. Crit. Care Med. 174, 901–905. https://doi.org/10.1164/rccm.200503-479OC.

Rivas, I., Viana, M., Moreno, T., Bouso, L., Pandolfi, M., Alvarez-Pedrerol, M., Forns, J., Alastuey, A., Sunyer, J., Querol, X., 2015. Outdoor infiltration and indoor contribution of UFP and BC, OC, secondary inorganic ions and metals in $PM_{2.5}$ in schools. Atmos. Environ. 106, 129–138. https://doi.org/10.1016/J.ATMOSENV.2015.01.055.

Rohra, H., Tiwari, R., Khandelwal, N., Taneja, A., 2018. Mass distribution and health risk assessment of size segregated particulate in varied indoor microenvironments of Agra, India - a case study. Urban Clim. 24, 139–152. https://doi.org/10.1016/j.uclim.2018.01.002.

Salthammer, T., Schripp, T., Wientzek, S., Wensing, M., 2014. Impact of operating wood burning fireplace ovens on indoor air quality. Chemosphere 103, 205–211. https://doi.org/10.1016/j.chemosphere.2013.11.067.

Saraga, D.E., Makrogkika, A., Karavoltsos, S., Sakellari, A., Diapouli, E., Eleftheriadis, K., Vasilakos, C., Helmis, C., Maggos, T., 2015. A pilot investigation of PM indoor/outdoor mass concentration and chemical analysis during a period of extensive fireplace use in Athens. Aerosol Air Qual. Res. 15, 2485–2495. https://doi.org/10.4209/ aaqr.2015.02.0100.

Schmidl, C., Marra, I.L., Caseiroa, A., Kotianová, P., Berner, A., Bauer, H., Kasper-Giebl, A., Puxbaum, H., 2008. Chemical characterisation of fine particle emissions from wood stove combustion of common woods growing in mid-European Alpine regions. Atmos. Environ. 42, 126–141. https://doi.org/10.1016/j.atmosenv.2007.09.028.

Schmidl, C., Luisser, M., Padouvas, E., Lasselsberger, L., Rzaca, M., Ramirez-Santa Cruz, C., Handler, M., Peng, G., Bauer, H., Puxbaum, H., 2011. Particulate and gaseous emissions from manually and automatically fired small scale combustion systems. Atmos. Environ. 45, 7443–7454. https://doi.org/10.1016/j.atmosenv.2011.05.006.

Schweizer, C., Edwards, R.D., Bayer-Oglesby, L., Gauderman, W.J., Ilacqua, V., Juhani Jantunen, M., Lai, H.K., Nieuwenhuijsen, M., Künzli, N., 2007. Indoor time– microenvironment–activity patterns in seven regions of Europe. J. Expo. Sci. Environ. Epidemiol. 17, 170–181. https://doi.org/10.1038/sj.jes.7500490.

Semmens, E.O., Noonan, C.W., Allen, R.W., Weiler, E.C., Ward, T.J., 2015. Indoor particulate matter in rural, wood stove heated homes. Environ. Res. 138, 93–100. https://doi.org/10.1016/j.envres.2015.02.005.

Semple, S., Garden, C., Coggins, M., Galea, K.S., Whelan, P., Cowie, H., Sánchez- Jiménez, A., Thorne, P.S., Hurley, J.F., Ayres, J.G., 2012. Contribution of solid fuel, gas combustion, or tobacco smoke to indoor air pollutant concentrations in Irish and Scottish homes. Indoor Air 22, 212–223. https://doi.org/10.1111/ j.1600-0668.2011.00755.x.

Shen, G., Tao, S., Wei, S., Zhang, Y., Wang, R., Wang, B., Li, W., Shen, H., Huang, Y., Yang, Y., Wang, W., Wang, X., Simonich, S.L.M., 2012. Retene emission from residential solid fuels in China and evaluation of retene as a unique marker for soft wood combustion. Environ. Sci. Technol. 46, 4666–4672. https://doi.org/10.1021/es300144m.

Sigsgaard, T., Forsberg, B., Annesi-Maesano, I., Blomberg, A., Bølling, A., Boman, C., Bønløkke, J., Brauer, M., Bruce, N., Héroux, M.-E., Hirvonen, M.-R., Kelly, F., Künzli, N., Lundbäck, B., Moshammer, H., Noonan, C., Pagels, J., Sallsten, G., Sculier, J.-P., Brunekreef, B., 2015. Health impacts of anthropogenic biomass burning in the developed world. Eur. Respir. J. 46, 1577–1588. https://doi.org/10.1183/13993003.01865- 2014.

Simoneit, B.R.T., Medeiros, P.M., Didyk, B.M., 2005. Combustion products of plastics as indicators for refuse burning in the atmosphere. Environ. Sci. Technol. 39, 6961–6970. https://doi.org/10.1021/es050767x.

Slezakova, K., Castro, D., Delerue-Matos, C., Morais, S., Pereira, M.D.C., 2014. Levels and risks of particulate-bound PAHs in indoor air influenced by tobacco smoke: a field measurement. Environ. Sci. Pollut. Res. 21, 4492–4501. https://doi.org/10.1007/s11356-013-2391-5.

Smith, K.R., McCracken, J.P., Weber, M.W., Hubbard, A., Jenny, A., Thompson, L.M., Balmes, J., Diaz, A., Arana, B., Bruce, N., 2011. Effect of reduction in household air pollution on childhood pneumonia in Guatemala (RESPIRE): a randomised controlled trial. Lancet 378, 1717–1726. https://doi.org/10.1016/S0140-6736(11)60921-5.

Srivastava, D., Favez, O., Perraudin, E., Villenave, E., Albinet, A., 2018. Comparison of measurement-based methodologies to apportion Secondary Organic Carbon (SOC) in $PM_{2.5}$: a review of recent studies. Atmosphere (Basel) 9. https://doi.org/10.3390/atmos9110452.

Taneja, A., Saini, R., Masih, A., 2008. Indoor air quality of houses located in the urban environment of Agra, India. Ann. N. Y. Acad. Sci. 1140, 228–245. https://doi.org/10.1196/annals.1454.033.

Tang, R., Wang, Z., 2018. Field study on indoor air quality of urban apartments in severe cold region in China. Atmos. Pollut. Res. 9, 552–560. https://doi.org/10.1016/j.apr.2017.12.004.

Tissari, J., Sippula, O., Kouki, J., Vuorio, K., Jokiniemi, J., 2008. Fine particle and gas emissions from the combustion of agricultural fuels fired in a 20 kW burner. Energ. Fuel. 22, 2033–2042. https://doi.org/10.1021/ef700766y.

USEPA, 1993. Provisional Guidance for Quantitative Risk Assessment of Polycyclic Aromatic Hydrocarbons. EPA/600/R-93/089. US Environmental Protection Agency, Office of Research and Development, Washington DC, USA.

USEPA, 2005. Guidelines for Carcinogen Risk Assessment. EPA/630/P-03/001B. US Environmental Protection Agency, Risk Assessment Forum, Washington DC, USA.

USEPA, 2009. Assessment Guidance for Superfund Volume I: Human Health Evaluation Manual (Part F, Supplemental Guidance for Inhalation Risk Assessment). EPA/540/ R/070/002. US Environmental Protection Agency, Office of Emergency and Remedial Response, Washington DC, USA.

USEPA, 2013. Users' guide and background technical document for USEPA region 9 - preliminary remediation goals (PRG) table. Available online: https://semspub.epa.gov/work/02/103453.pdf (accessed on 3 June 2019).

USEPA, 2017. Regional Screening Level (RSL) summary table. Available online. https://semspub.epa.gov/work/03/2245073.pdf. (accessed on 10 June 2019).

USEPA, 2019. Integrated Risk Information System (IRIS) Assessments. Available online. https://cfpub.epa.gov/ncea/iris_drafts/AtoZ.cfm.

Van Lith, S.C., Alonso-Ramírez, V., Jensen, P.A., Frandsen, F.J., Glarborg, P., 2006. Release to the gas phase of inorganic elements during wood combustion. Part 1: development and evaluation of quantification methods. Energy Fuel 20, 964–978. https://doi.org/10.1021/ef050131r.

Varshney, P., Saini, R., Taneja, A., 2016. Trace element concentration in fine particulate matter ($PM_{2.5}$) and their bioavailability in different microenvironments in Agra, India: a case study. Environ. Geochem. Health 38, 593–605. https://doi.org/10.1007/s10653-015-9745-5.

Vette, A.F., Rea, A.W., Lawless, P.A., Rodes, C.E., Evans, G., Highsmith, V.R., Sheldon, L., Carolina, N., 2001. Characterization of indoor-outdoor aerosol concentration relationships during the Fresno PM exposure studies. Aerosol Sci. Technol. 34, 118–126.

Vicente, A., Alves, C., Monteiro, C., Nunes, T., Mirante, F., Evtyugina, M., Cerqueira, M., Pio, C., 2011. Measurement of trace gases and organic compounds in the smoke plume from a wildfire in Penedono (central Portugal). Atmos. Environ. 45, 5172–5182. https://doi.org/10.1016/j.atmosenv.2011.06.021.

Vicente, E.D., Alves, C.A., 2018. An overview of particulate emissions from residential biomass combustion. Atmos. Res. 199. https://doi.org/10.1016/j.atmosres.2017.08.027.

Vicente, E.D., Duarte, M.A., Calvo, A.I., Nunes, T.F., Tarelho, L.A.C., Custódio, D., Colombi, C., Gianelle, V., Sanchez de la Campa, A., Alves, C.A., 2015. Influence of operating conditions on chemical composition of particulate matter emissions from residential combustion. Atmos. Res. 166, 92–100. https://doi.org/10.1016/j.atmosres.2015.06.016.

Vu, T.V., Harrison, R.M., 2019. Chemical and physical properties of indoor aersols. In: Harrison, R.M., Hester, R.E. (Eds.), Indoor Air Pollution, Issues in Environmental Science and Technology. Royal Society of Chemistry, Cambridge. https://doi.org/10.1039/9781788016179.

Wallace, L., 2006. Indoor sources of ultrafine and accumulation mode particles: size distributions, size-resolved concentrations, and source strengths. Aerosol Sci. Technol. 40, 348–360. https://doi.org/10.1080/02786820600612250.

Ward, T., Noonan, C., 2008. Results of a residential indoor $PM_{2.5}$ sampling program before and after a woodstove changeout. Indoor Air 18, 408–415. https://doi.org/10.1111/j.1600-0668.2008.00541.x.

Ward, T., Boulafentis, J., Simpson, J., Hester, C., Moliga, T., Warden, K., Noonan, C., 2011. Lessons learned from a woodstove changeout on the Nez Perce Reservation. Sci. Total Environ. 409, 664–670. https://doi.org/10.1016/j.scitotenv.2010.11.006.

Ward, T. J., Hamilton, R.F., Dixon, R.W., Paulsen, M., Simpson, C.D., 2006. Characterization and evaluation of smoke tracers in PM: results from the 2003 Montana wildfire season. Atmos. Environ. 40, 7005–7017. https://doi.org/10.1016/j.atmosenv.2006.06.034.

Ward, T.J., Semmens, E.O., Weiler, E., Harrar, S., Noonan, C.W., 2017. Efficacy of interventions targeting household air pollution from residential wood stoves. J. Expo. Sci. Environ. Epidemiol. 27, 64–71. https://doi.org/10.1038/jes.2015.73.

Wedepohl, K.H., 1995. The composition of the continental crust. Geochim. Cosmochim. Acta 59, 1217–1232.

Weisel, C.P., Alimokhtari, S., Sanders, P.F., 2008. Indoor air VOC concentrations in suburban and rural New Jersey. Environ. Sci. Technol. 42, 8231–8238. https://doi.org/10.1021/es8005223.

WHO, 2010. Guidelines for Indoor Air Quality, WHO Guidelines. World Health Organization, Geneva, Switzerland https://doi.org/10.1186/2041-1480-2-S2-I1.

WHO, 2014. WHO Guidelines for Indoor Air Quality: Household Fuel Combustion. World Health Organization, Geneva, Switzerland.

WHO, 2016. Ambient Air Pollution: a Global Assessment of Exposure and Burden of Disease. World Health Organization, Geneva, Switzerland.

Wöhler, M., Andersen, J.S., Becker, G., Persson, H., Reichert, G., Schön, C., Schmidl, C., Jaeger, D., Pelz, S.K., 2016. Investigation of real life operation of biomass room heating appliances - results of a European survey. Appl. Energy 169, 240–249. https://doi.org/10.1016/j.apenergy.2016.01.119.

Wylie, B.J., Coull, B. a, Hamer, D.H., Singh, M.P., Jack, D., Yeboah-Antwi, K., Sabin, L., Singh, N., MacLeod, W.B., 2014. Impact of biomass fuels on pregnancy outcomes in central East India. Environ. Health 13 (1). https://doi.org/10.1186/1476-069X-13-1.

Yan, C., Zheng, M., Sullivan, A.P., Shen, G., Chen, Y., Wang, S., Zhao, B., Cai, S., Desyaterik, Y., Li, X., Zhou, T., Gustafsson, Ö., Collett, J.L., 2018. Residential coal combustion as a source of levoglucosan in China. Environ. Sci. Technol. 52, 1665-1674. https://doi.org/10.1021/acs.est.7b05858.

Zdráhal, Z., Oliveira, J., Vermeylen, R., Claeys, M., Maenhaut, W., 2002. Improved method for quantifying levoglucosan and related monosaccharide anhydrides in atmospheric aerosols and application to samples from urban and tropical locations. Environ. Sci. Technol. 36, 747–753. https://doi.org/10.1021/ES015619V.

Zhang, L., Cheng, Y., Zhang, Y., He, Y., Gu, Z., Yu, C., 2017. Impact of air humidity fluctuation on the rise of PM mass concentration based on the high-resolution monitoring data. Aerosol Air Qual. Res. 17, 543–552. https://doi.org/10.4209/aaqr.2016.07.0296.

Zhang, Q., Gangupomu, R.H., Ramirez, D., Zhu, Y., 2010. Measurement of ultrafine particles and other air pollutants emitted by cooking activities. Int. J. Environ. Res. Public Health 7, 1744–1759. https://doi.org/10.3390/ijerph7041744.

Zhang, Y., Obrist, D., Zielinska, B., Gertler, A., 2013. Particulate emissions from different types of biomass burning. Atmos. Environ. 72, 27–35. https://doi.org/10.1016/j.atmosenv.2013.02.026.

Zhu, L., Wang, J., 2003. Sources and patterns of polycyclic aromatic hydrocarbons pollution in kitchen air, China. Chemosphere 50, 611–618. https://doi.org/10.1016/ S0045-6535(02)00668-9.

Chapter 7

Chapter 7. Lung-deposited dose of particulate matter from residential exposure to smoke from wood burning

Chapter section submitted as original article:

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Abstract

The dosimetry model ExDoM2 was applied to determine the deposited dose of inhaled particulate matter (PM_{10}) from residential biomass combustion in the human respiratory tract (HRT) of adults and children. The dose was estimated using PM_{10} exposure concentrations obtained from a field campaign carried out in two households during the operation of distinct combustion appliances (open fireplace and woodstove). Simultaneously, PM_{10} levels were monitored outside to investigate the outdoor dose in a rural area strongly impacted by biomass burning emissions. The highest amount of the deposited particles was recorded in the extrathoracic region (68-79%), whereas the deposition was much lower in the tracheobronchial tree (5-6%) and alveolar–interstitial region (16-21%). The total dose received while using the fireplace was more than twofold the one received in the room with a woodstove and more than 10 times higher than in the absence of the source. Overall, indoor doses were higher than the ones received by a subject exposed outdoors, especially at the alveolar–interstitial region. After 24 h of exposure, it was observed that approximately 35 to 37% of the particles deposited in the HRT were transferred to the gastrointestinal tract, while approximately 2.0-2.5% were absorbed into the blood. This study provides biologically relevant results on the lung deposition of particles from residential biomass burning that can be used as a reference for future research.

Keywords: Dose, Human respiratory tract, Lung deposition, Indoor air pollution, PM_{10}, Residential wood combustion.

7.1. Introduction

Residential biomass combustion is well-known as a major source of particulate matter (PM) worldwide (Vicente and Alves, 2018; Olsen et al., 2020). In Portugal, the high contribution of this source to the primary $PM_{2.5}$ emissions, more than 30% in 2005 (Amann et al., 2018), can be mainly assigned to the extensive use of batch mode operated traditional combustion appliances, which generate higher PM emissions than automatically fed combustion appliances (Vicente and Alves, 2018; Olsen et al., 2020). In addition to its contribution to ambient PM levels, this source also greatly affects household air quality (Guo et al., 2008; McNamara et al., 2013; Salthammer et al., 2014; de Gennaro et al., 2015; Saraga et al., 2015; Parajuli et al., 2016; Bartington et al., 2017; Castro et al., 2018). Smoke from biomass combustion has been associated with an array of respiratory health outcomes, including increase in the incidence of pneumonia, tuberculosis, asthma, and chronic obstructive pulmonary disease (COPD) (Naeher et al., 2007; Fullerton et al., 2008; Kim et al., 2011; Laumbach and Kipen, 2012; Sood, 2012; Sigsgaard et al., 2015; Wolff et al., 2020; Pial et al., 2020). Studies conducted in the United States found evidence of respiratory symptoms in children living in wood burning households (reviewed by Naeher et al., 2007). Moreover, the use of a fireplace for 4 h was associated with increased risk of respiratory symptoms by about 16–20% of women living in tobacco-free homes (Naeher et al., 2007, and references therein). The inhalation and particle deposition in the human respiratory tract (HRT) are behind the PM-related health effects. However, the actual dose is seldom considered in epidemiological and toxicological studies, and frequently exposure is used as a measure for dose (Schlesinger et al., 2006; Paur et al., 2011; Schmid and Cassee, 2017). Particle deposition in the HRT occur by the action of three main mechanisms (impaction, settling and diffusion) and two secondary mechanisms (interception and electrostatic deposition) (Lippmann et al., 1980; Hinds, 1999; Hofmann, 2011). Deposition is governed by the particle properties (e.g. size, shape, chemical characteristics), physiological and respiration parameters (e.g. breathing pattern, ventilation rate, exercise level, health condition, age, gender) (Lippmann et al., 1980; Hinds, 1999; Hofmann, 2011). The deposited dose within the HRT is critical to determine the particle-induced biological response in toxicological studies and to assess the health risk of aerosols in epidemiological studies (Schmid and Cassee, 2017).

In previous studies, the total lung dose of biomass combustion-generated aerosols was measured directly *in vivo*, monitoring the inhaled and exhaled particle concentrations (Löndahl et al., 2008; Muala et al., 2015). For example, Löndahl et al. (2008) measured the total lung deposition dose in never-smoking healthy subjects breathing by mouth and found that the total deposited fraction of particles from two types of biomass combustion (efficient combustion and low-temperature incomplete combustion) was 0.24, by mass. Despite the valuable information provided by total dose estimations, knowledge regarding regional deposition in the HRT is crucial to assess the potential hazard of inhaled particles (Hinds, 1999). The regional dose in the respiratory system is difficult to be determined experimentally, although some methods are available (Kim, 2009; Löndahl et al., 2014). Therefore, the regional dose is typically estimated by means of mathematical models (ICRP, 1994; Hussain et al., 2011; Hofmann, 2011; Aleksandropoulou and Lazaridis, 2013).

Few research studies have been conducted to characterise the exposure and lung burden arising from biomass combustion in indoor microenvironments. In Italian households, Stabile et al. (2018) carried out on-site measurements to evaluate the exposure and dose of particles received by the population living in dwellings where biomass-burning systems (open fireplace, woodstove and pellet stove) were used for heating. The researchers estimated the alveolar and tracheobronchial dose considering the measured exposure concentrations, the exposed individual's inhalation rate and assuming a constant value of 0.2 for the PM_{10} deposition fraction in the lungs. Recently, Nicolaou et al. (2020) characterised the exposure of household biomass-related pollution in the Peru Andean region. The researchers measured daily $PM_{2.5}$ levels in the kitchen and near the Andean women's breathing zone and performed lung deposition modelling to determine the lung-deposited dose and regional deposition fractions of inhaled PM. A mean total deposition in the respiratory airways for the adult Andean women of 33.0 ± 0.75% of the inhaled mass, with 14.9 ± 0.76% depositing in the intrathoracic airways, was reported.

Studies on exposure and dose in indoor environments with biomass heating systems are scarce. Given the lack of information, as well as the impact that a residential combustion appliance can have on indoor air quality (e.g. Salthammer et al., 2014; Stabile et al., 2018; Vicente et al., 2020), the goal of the present study was to estimate the total and regional doses in the HRT based on the indoor exposure to PM_{10} when using wood burning appliances. Additionally, through modelling, this study aimed to compare the doses obtained indoors with those associated with exposure to outdoor particles in a rural area highly impacted by residential biomass burning.

7.2. Methodology

7.2.1. Site description and PM_{10} measurements

A winter sampling campaign was carried out in January 2017 in a small village in central Portugal. The weather was typical for the season, with mean diurnal temperatures between 7 and 14

°C. Wood burning for residential heating is common in this area. There are no major industries nearby or major roads close to the village, where traffic is limited.

To assess the exposure to PM from residential wood burning indoors, two dwellings were selected. One household was equipped with an open fireplace in the kitchen (about 38 m^3) and the other with a woodstove, also installed in the kitchen (about 67 m^3). The monitoring programme was carried out under controlled conditions, meaning that during the weeks of experiments no other activities took place in the houses and only the person responsible for the measurements was allowed in the residences. The experiments were conducted under minimum ventilation conditions (doors and windows closed) with an average air exchange of 0.78 ± 0.12 and 0.72 ± 0.13 h^{-1} in the rooms equipped with fireplace and woodstove, respectively. Three (woodstove) to four (fireplace) experiments of 8-h each were performed in different days, mimicking the rural resident’s behaviour. To start the combustion experiments, pinecones were ignited and used to lit pine and eucalyptus split logs, two abundant tree species in the region. Throughout the burning period, the combustion appliance was refuelled several times: three and five times for the fireplace and woodstove, respectively. The duration of the experiments and number of batches to refuel the combustion chambers tried to mimic common European burning practices (Gustafson et al., 2008; Wöhler et al., 2016; Reichert et al., 2016). Additionally, background measurements, in the absence of indoor sources of PM, were carried out in each residence.

PM_{10} mass concentrations were continuously measured by a light-scattering laser photometer (DustTrak DRX 8533, TSI,) with a 1-minute resolution, in the indoor and outdoor environments, simultaneously. Additionally, concurrent indoor and outdoor PM_{10} samples were collected on quartz filters using two high volume air samplers (CAV-A/mb, MCV). After gravimetric quantification of PM_{10} mass concentrations (XPE105 DeltaRange®, Mettler Toledo), the chemical composition was determined (organic and elemental carbon, water soluble ions, speciated organic compounds, metals). The detailed description of the analytical techniques and the PM_{10} chemical composition can be found in a previous work (Vicente et al., 2020). The concentrations recorded by the DustTrak monitor were corrected using the gravimetric measurements.

7.2.2. Particle dosimetry model

The particle deposition in the HRT was estimated by the dosimetry model ExDoM2, a revised version of ExDoM (Aleksandropoulou and Lazaridis, 2013), which is based on the International Commission on Radiological Protection model (ICRP, 1994, 2015). A full description of the model has been reported by Aleksandropoulou and Lazaridis (2013) and Chalvatzaki and

Lazaridis (2015). The ExDoM2 model simulates the dynamics of inhaled particulate matter in human airways and estimates the dose, based upon empirical equations (ICRP, 1994), in the five regions of the HRT: extrathoracic (ET1: anterior nose and ET2: posterior nasal passages), tracheobronchial (BB: trachea and bb: bronchiolar), and alveolar interstitial (AI). To model particle deposition, the regions were treated as a series of filters during both inhalation and exhalation. The two sub-compartments of the extrathoracic compartment (ET), ET1 and ET2, receive approximately 65% and 35% of the ET deposits of inhaled aerosols, respectively (ICRP, 2015).

The model takes into account the particle's inhalability, fraction of particles that effectively enter the human body, considering the aerodynamic diameter of the particles and the air velocity at the exposure site (Aleksandropoulou and Lazaridis, 2013). The deposition pattern of particles in the HRT is closely related to the particle size and to the breathing pattern and the anatomical and physiological characteristics of the exposed subject. The ventilation rate depends on the activity level of the exposed subject, age and gender (ICRP, 1994). Age- and gender-specific standardised values for different physical activity levels (sleeping, sitting awake, light exercise, and heavy exercise) are listed in the ICRP (1994) report. The model allows to estimate the retention of particles in the HRT and the mass transferred to the gastrointestinal (GI) tract, the lymph nodes, and absorbed into blood. The mechanical clearance of particles is calculated by the ICRP compartment model (ICRP, 2015). In the present work, the absorption of PM_{10} into blood was assumed to be moderate and to occur at the same rate in all regions (except in ET1 for which it was assumed that no absorption takes place) (ICRP, 2015). Absorption is treated as a two stage process consisting of dissociation and absorption (ICRP, 2015).

7.2.3. Exposure scenario

Input parameters of the model cover the exposed subject (age and gender), PM exposure concentrations (hourly average), breathing mode (nose or mouth breathing), activity level (sleep, sitting/resting and light activity, heavy activity), wind speed and particle size distributions (Table 7.1). In the present study, PM_{10} deposition in the HRT was modelled for three different healthy subjects, male, female and 10 years male child exposed to biomass burning particles indoors 8 hours per day. The burning period defined in the present study is similar to the daily average time reported previously for residential heating in Europe (Gustafson et al., 2008; Stabile et al., 2018). It was assumed that the subjects were under light physical activity and breathing through the nose. For comparison purposes, the same assumption was made to assess exposure to outdoor PM_{10} and indoor PM_{10} in the absence of sources (background). Particles were considered spherical (shape factor of 1)

(Martins et al., 2015; Sánchez-Soberón et al., 2015; Mammi-Galani et al., 2017). The particle density was calculated based on their chemical composition at each sampling site (indoor fireplace, indoor woodstove and outdoor) (Vicente et al., 2020) (Table 7.1).

Table 7.1. Input data for ExDoM2 model.

	Indoor				Outdoor	
	Fireplace	Background	Woodstove	Background	Fireplace	Woodstove
Particle properties						
PM_{10} Concentration ($\mu g\ m^{-3}$) [a]	88 - 489	14 - 17	69 - 122	21 - 24	49 - 94	17 - 72
PM_1/PM_{10}	0.97	0.97	0.84	0.97	0.89	
Density (g cm^{-3})	1.5	1.5	2.0	1.5	1.9	
MMAD (µm)	0.7	1.0	0.7	1.0	0.87	
GSD (µm)	1.8	2.3	1.8	2.3	4.0	
Exposure scenario						
Breathing scenario	Nose					
Exposure duration (h)	8					
PM_{10} concentration	Hourly average					
Activity level	Light exercise					

[a] 8-h average (minimum-maximum concentrations); MMAD: Mass median aerodynamic diameter; GSD: Geometric standard deviation.

The size distribution of the indoor and outdoor PM_{10} was considered monodisperse with a mass median aerodynamic diameter (MMAD) of 0.87 µm (Castro et al., 2018) and 0.66 µm (Bari et al., 2011a) indoors and outdoors, respectively (Table 7.1). The density of the particles indoors in the absence of activity (background) was considered 1.5 g cm^{-3} and the MMAD of the particles equal to 1.0 µm (Castro et al., 2018).

7.3. Results

7.3.1. Exposure concentrations

The range and average PM_{10} concentrations indoors and outdoors, as well as the daily profiles, during the operation of the woodstove and fireplace, have been reported in detail in a previous manuscript (Vicente et al., 2020). Regarding the daily profiles (Fig. 7.1A), the lighting and refuelling were found to be the main polluting phases. In general, during the wood burning periods, indoor concentrations were higher than those outdoors. Fig. 7.1B displays the average exposure concentrations obtained with the DustTrak for an 8-h period for each measurement day, which include four monitoring periods with the fireplace in use, three periods with the woodstove in operation, and the respective outdoor data.

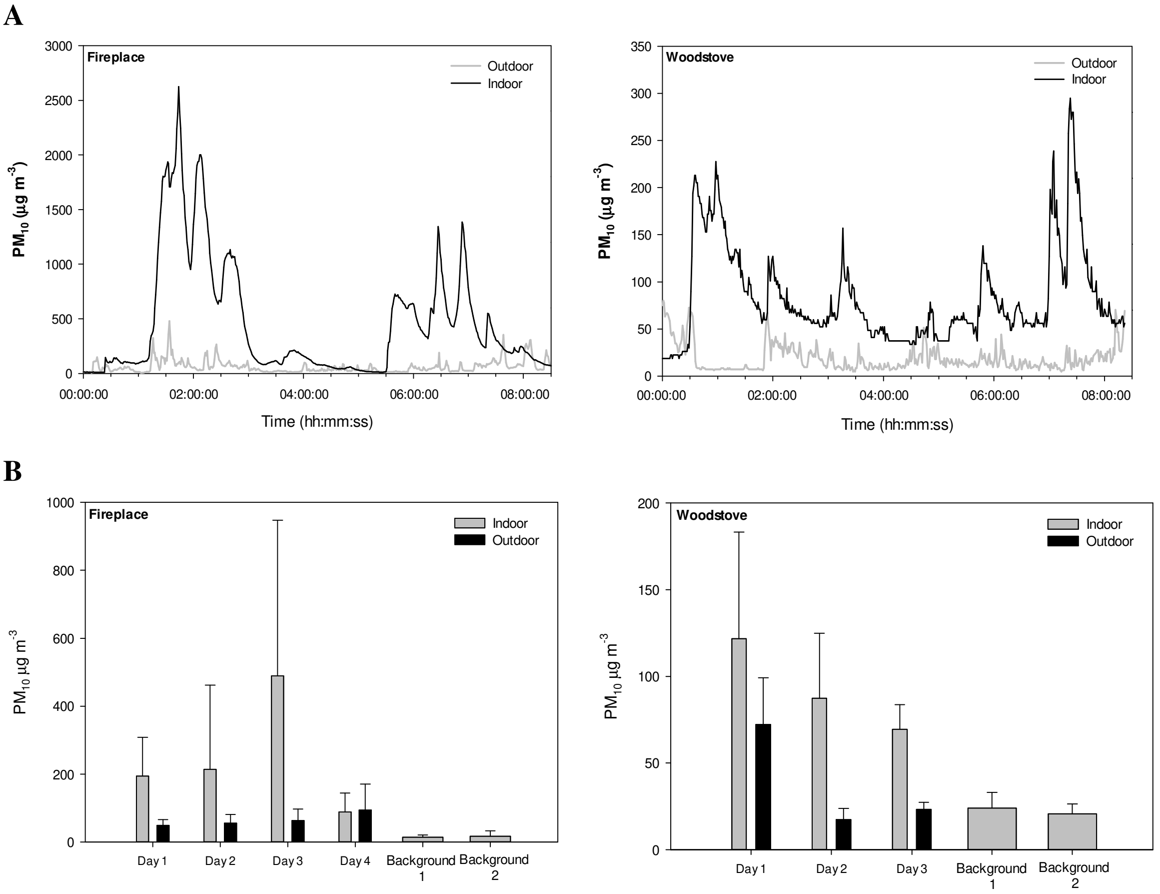

Figure 7.1. Example of PM_{10} profiles (µg m^{-3}) (A) and 8-h average concentrations (B) for wood burning experiments and background measurements.

Additionally, measurements of background levels in the rooms for an equivalent period (8-h) were also included. The results showed a 16- (fireplace) and 4-fold (woodstove) increase, on average, in exposure concentrations during the operation of wood burning appliances in comparison with levels in the absence of indoor activity (background measurements). During the operation of the fireplace, indoor PM_{10} levels (8-h average) were in the range from 88.3 to 489 µg m^{-3}. In the room equipped with woodstove, PM_{10} concentrations (8-h average) were lower but still high, in the range from 69.4 to 122 µg m^{-3}. The door in the woodstove allows sealing off the combustion chamber from the room, however, it is periodically open to refuel which might lead to smoke leakage into the room. The impact of the refuelling operations on the indoor PM levels was also highlighted in a recent study conducted in twenty English households using low cost air quality monitors (Chakraborty et al., 2020). Under real life conditions, Stabile et al. (2018) investigated the indoor exposure to particles emitted by biomass-burning heating systems in private Italian households. During the combustion periods, the researchers found particle concentrations in the range from 24-552 µg m^{-3}, 29-227 µg m^{-3} and 16-70 µg m^{-3} for open fireplaces, woodstoves and pellet stoves, respectively. As observed in the present study, the greatest particle concentration increase was recorded for wood combustion in open fireplace while a smaller, but still clear increase was observed for the woodstove. The researchers found a minor increase in indoor PM levels when operating pellet stoves. Similarly, Salthammer et al. (2014) investigated the effects of wood-burning appliances on indoor air quality on-site, in private German households. The study comprised seven households, six with closed combustion appliances and one with an open device. The 24-h average $PM_{2.5}$ concentrations were in the range from 6 to 55 µg m^{-3}.

In the present study, the outdoor PM_{10} concentrations during the indoor burning periods ranged from 49.4 ± 19.9 to 94.2 ± 76.5 µg m^{-3} and from 17.3 ± 6.44 to 72.3 ± 27.0 µg m^{-3} for the operation of the fireplace and the woodstove, respectively. In the winter of 2006, the daily average $PM_{2.5}$ concentrations in a residential area of Kurkimäki (Finland), where there are no major roads or other emission sources, ranged from 5 µg m^{-3} to over 40 µg m^{-3}. In this area, the researchers recorded short-time concentration peaks up to 1000 µg m^{-3} (minute averages), which were ascribed to local wood combustion (Hellén et al., 2008). In a Danish small rural town with widespread use of wood combustion for heating, Glasius et al. (2006) measured $PM_{2.5}$ concentrations about 4 µg m^{-3} higher than at a nearby background site. The average $PM_{2.5}$ concentration in the residential area during the intensive measuring period was 16 µg m^{-3}. In Germany, at a residential site in Dettenhausen, Bari et al. (2011b) reported that at the beginning of winter months (November, December), the average PM_{10} concentrations varied from 10 to 40 µg m^{-3}, while the highest peak concentrations were observed from middle of January to the early February, which the researchers attributed to the limited dispersion of air pollutants caused by surface inversions.

7.3.2. Total and regional doses

The 8-h PM_{10} doses in the regions of the HRT for each subject are shown in Fig. 7.2 for indoor exposure during the operation of the fireplace and woodstove and the corresponding outdoor values.

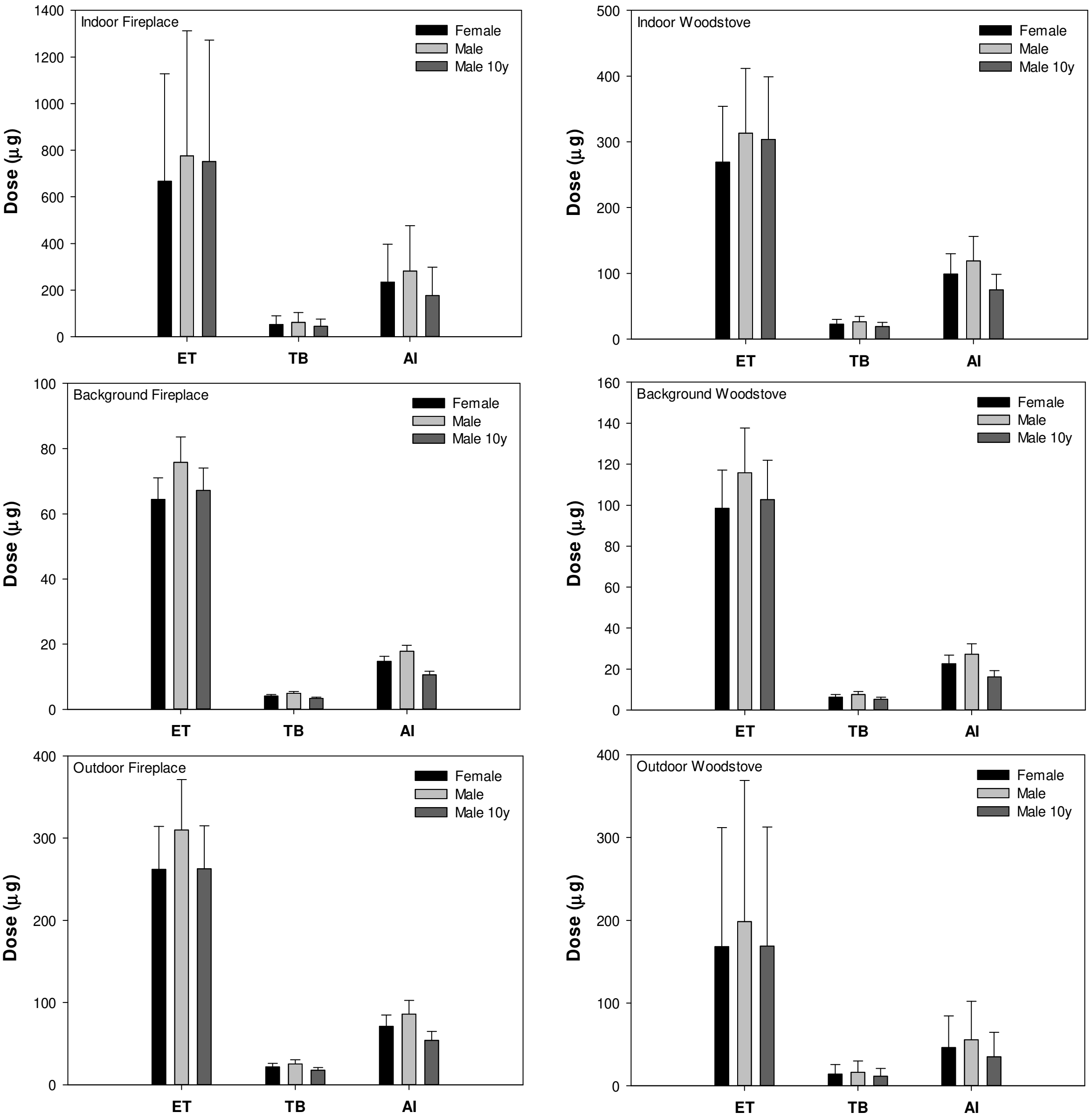

Figure 7.2. Particulate matter 8-h dose in the different regions of the HRT tract (ET – extrathoracic, TB – tracheobronchial and AI – alveolar–interstitial) for different subjects.

Overall, small differences were recorded in the cumulative deposited dose between different genders and ages. Nevertheless, children inhale more air per unit of body weight than adults and are more susceptible to respiratory risks than adults due to their immature immune system. Respiratory disease is a leading cause of childhood mortality globally (Xi et al., 2015). The inter-subject variability in the particle doses can be substantial, as observed by Löndahl et al. (2008). The researchers experimentally determined the deposition fraction of aerosol from efficient and low temperature biomass combustion in 10 healthy subjects (4 men and 6 women) aged 21–31. It was reported that there was more than a factor of 2 in difference between the subjects with the highest deposition fraction and those with the lowest (Löndahl et al., 2008).

Indoors, the highest deposited dose was received by subjects exposed to particles produced during wood combustion in the open fireplace with an average 8-h cumulative dose of 954 ± 660 µg, 1119 ± 773 µg and 974 ± 673 µg for females, males and 10-year male children, respectively. The corresponding values for a subject in the room equipped with a woodstove were 391 ± 123 µg, 459 ± 144 µg and 398 ± 125 µg for females, males and 10-year male children, respectively. The total dose received by a subject in the room where the fireplace was in operation was more than twice the one received in the room with a woodstove and 11 to 12-fold higher than the total dose received by a subject in the room without indoor pollution sources. A lower increase (3-fold) in the total dose received by a subject exposed to particles from the woodstove operation in comparison with the one received in the absence of indoor sources was recorded. As displayed in Fig. 7.3, high variability in the hourly dose was recorded during the 8-h measurement period, especially when the open fireplace was in use. As explored in Vicente et al. (2020), the daily profiles revealed high PM_{10} peak concentrations during the start-up phase, as well as during refuelling periods. In the periods when the stove was active, the dose was lower but still noticeable. Similarly, Stabile et al. (2018) reported larger doses from exposure to particles from wood combustion in open fireplaces in comparison with woodstoves and automatically fed appliances (pellet stove). Outdoors, the received dose for a male subject ranged from 77 to 413 µg and from 111 to 535 µg for 8-h exposure during the campaign with the fireplace and the woodstove, respectively. The variability found in outdoor doses might be ascribed to the distinct weather conditions in different monitoring days.

Regarding the regional deposition of inhaled particles, the results showed that the ET airways received the highest amount of the particulate mass deposited in the HRT (68–79%) whilst the lowest was recorded in the TB region (5-6%) (Fig. 7.2). The nose has an important role as an air conditioner and a defender of the lower HRT since it is responsible for filtering, humidifying, and heating the inhaled air, as well as for trapping inhaled particles, protecting the gas-exchange regions of the lung (Hinds, 1999; Harkema et al., 2013). The AI region received from 18 to 26 % and from 16 to 21 % of the total particulate mass deposited in the HRT indoors and outdoors, respectively. Globally, indoor doses were higher than the ones received by a subject exposed outdoors, especially at the AI region.

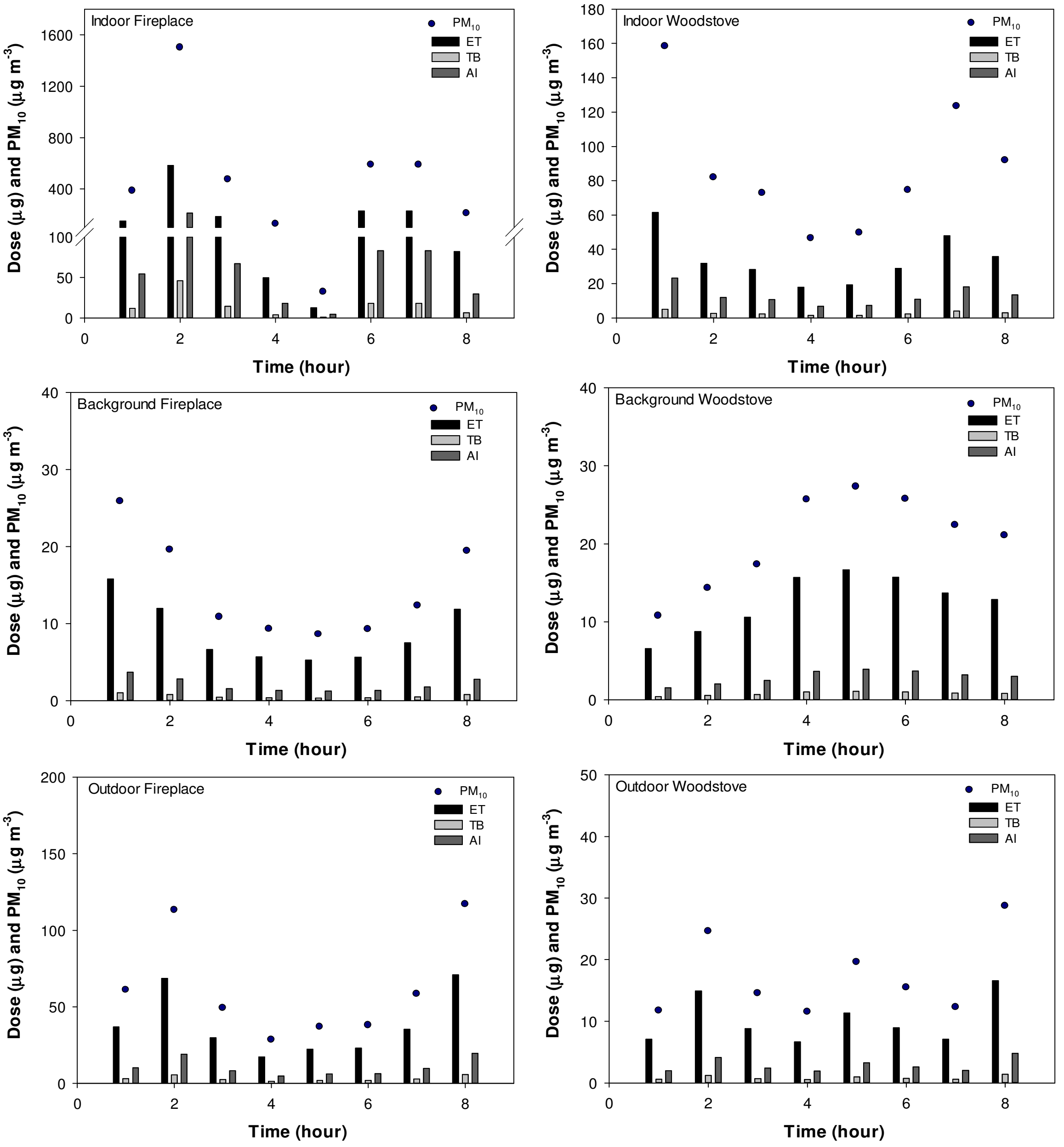

Figure 7.3. Example of hourly PM_{10} exposure concentration and dose in the different regions of the HRT (ET – extrathoracic, TB – tracheobronchial and AI – alveolar–interstitial) estimated for an adult male.

Doses at the AI region for a subject exposed to indoor particles from woodstove operation were, on average, 2.8 times higher than those received outdoors. Indoors, the operation of the fireplace led to doses at the AI region 3.5 times higher, on average, than outdoors. The dose received by a subject at the AI region in the absence of indoor sources of PM was 16-17 and 3-4 times lower than during the operation of the fireplace and woodstove, respectively.

The dose per surface area or mass of lung/tissue plays a crucial role in a toxicological dose-response analysis with significance for human risk assessment (Schmid and Cassee, 2017).

Considering the age and gender specific superficial area of the HRT regions (ET, TB, AI) reported by Sarangapani et al. (2003), it was observed that, although the mass received at the AI region was greater than the one recorded in the TB region, the deposited mass of particles per square centimetre of tissue surface area was higher at the latter region (Fig. 7.4). In fact, the alveoli account for more than 90% of the lung surface area. The alveolar region, where the air-blood barrier is thinner, represents the potentially most vulnerable site of deposition due to the easier access to the blood stream. Additionally, considering that clearance mechanisms are slower in the lower RT, the probability of adverse health effects due to particle–cell/tissue interactions is higher in this region of the HRT (Paur et al., 2011).

For *in vitro* toxicological studies, target tissue/site dose reflect more accurately the amount of material coming in contact with the cells than measures of exposure (Paur et al., 2011; Schmid and Cassee, 2017). Thus, this metric yields important information about the dosage to be tested in *in vitro* assays. Considering the exposure scenario evaluated in the present study, a realistic alveolar dose ranging from 1.1 to 6.5×10^{-4} µg PM_{10} cm^{-2} could be used to evaluate the toxicological potential on confluent alveolar epithelial cell cultures *in vitro*.

It should be borne in mind that the doses obtained in the present study, for healthy subjects, might be increased in subjects with pre-existing respiratory diseases (Bennett et al., 1997; Kim and Kang, 1997; Brown et al., 2002; Chalupa et al., 2004; Löndahl et al., 2012). The differences in doses have been ascribed to increased deposition efficiency, less even distribution of inhaled air, and decreased particle clearance rates in individuals with pre-existing lung diseases (Phalen et al., 2006). Studies performed to assess the dose received by individuals with COPD found an increased particle deposition rate in comparison to healthy subjects as result of the higher minute ventilation (Bennett et al., 1997; Kim and Kang, 1997; Brown et al., 2002; Löndahl et al., 2012). For example, Bennett et al. (1997) reported deposition rates 2.5 times higher in COPD patients compared to healthy subjects. Pre-existing lung disease along with other factors, such as the effects of exercise, oral breathing and unusual anatomy, can produce doses that exceed those of the average resting person by factors of about 33–67 (Phalen et al., 2006). Additionally, considering spatially non-uniform deposition regions and clearance, Paur et al. (2011) assumed a factor of 10 to account for high-dose regions, or hot spots. Taking into account these factors, particle doses ranging from about 0.07 to 0.44 µg PM_{10} cm^{-2} could be considered to expose alveolar epithelial cell cultures *in vitro* for the worst-case exposure scenario.

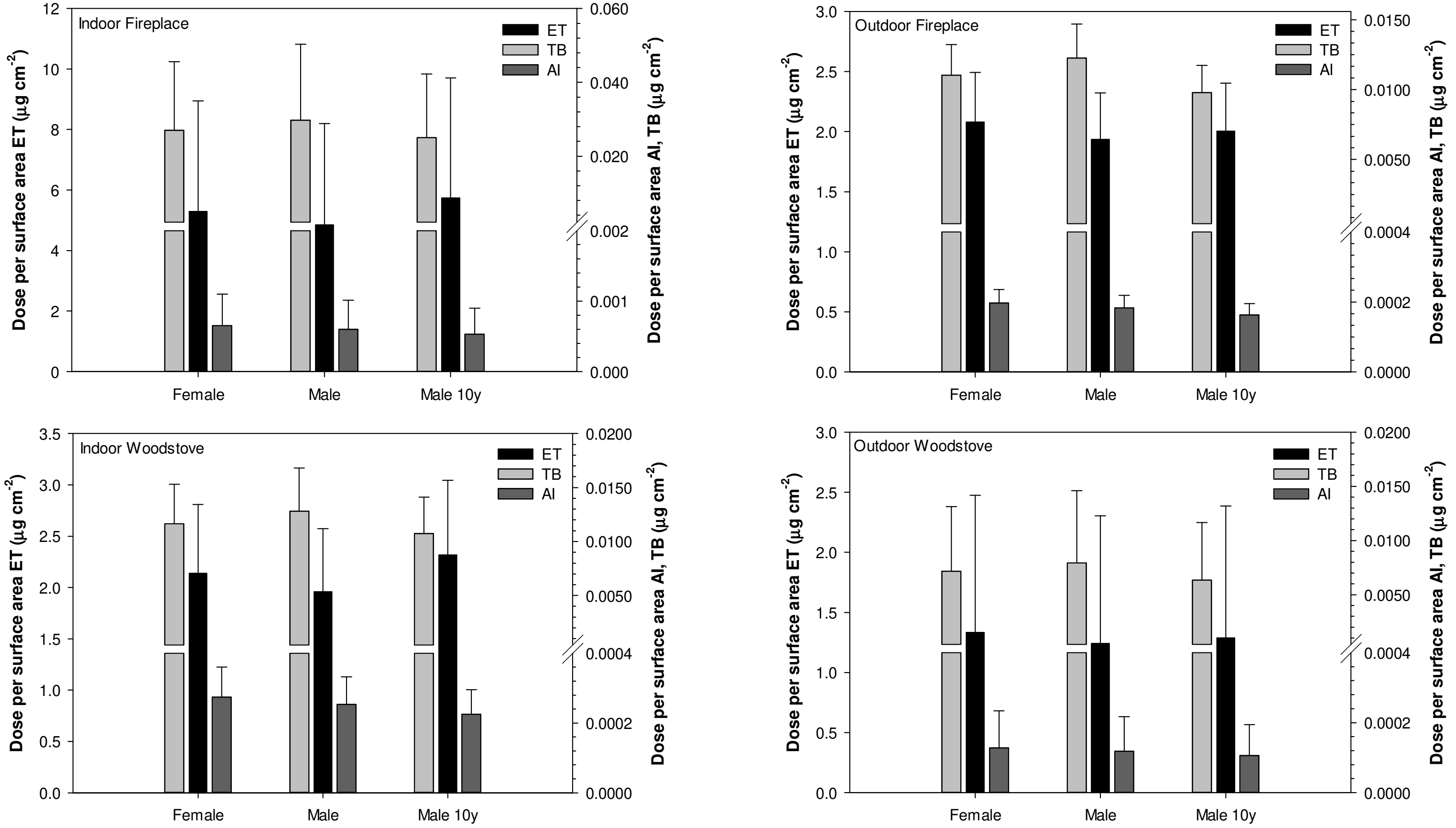

Figure 7.4. Dose per surface area of the target tissue considering 8-h exposure (ET – extrathoracic, TB – tracheobronchial and AI – alveolar–interstitial).

7.3.3. PM retention and clearance

The PM_{10} retention in the HRT and the mass transferred to the gastro-intestinal tract (oesophagus), lymph nodes and blood (absorption into the blood) 24-h after exposure are displayed in Table 7.2. Indoors, 49 to 67% and 53 to 61% of the particles deposited in the HRT remained in the RT of a subject exposed to wood smoke from the fireplace and woodstove, respectively. Outdoors, 49 to 60% of the deposited particles were retained in the HRT.

After 24-h of exposure, the highest dose of particles was recorded in the oesophagus (Table 7.2), which derives from the higher deposited dose in the ET region. Particles deposited in the ET2 region, or transferred to this region from the anterior nasal passage and trachea, are cleared rapidly by mucociliary action to the throat and swallowed, transferring the particles to the GI tract (ICRP, 2015). The particulate fraction that deposits in the tracheobronchial region, consisting of trachea, bronchi and terminal bronchioles, can be trapped in the mucus produced by the bronchial epithelial cells and cleared by mucociliary transport into the throat, and then swallowed to the GI tract. The ICRP (2015) assumes that a fraction of particles deposited in the bronchial tree clears slowly, with mucus velocities generally increasing towards the trachea. The association between the exposure to biomass burning smoke and the development of gastrointestinal cancers has been reported in previous studies (Kayamba et al., 2017; Sheikh et al., 2020). Of the particles deposited to the RT, about 2% were absorbed into the blood (assuming moderate blood absorption) after 24-h of exposure. More than 90% of the particles deposited in the AI region remained deposited after 24-h of exposure. As mentioned above, particles deposited deeper in the lung take longer to be cleared, increasing the probability of adverse health effects in this region of the HRT (Paur et al., 2011). In the AI region, particles can induce local inflammation and leak into the systemic circulation, inducing adverse reactions in extra pulmonary sites, which can lead to the onset of, for example, cardiovascular diseases. Additionally, direct translocation of particles from the respiratory epithelium towards circulation can also provoke adverse effects on different extra pulmonary sites (Schwarze et al., 2006; Nemmar et al., 2013; Du et al., 2016; Fiordelisi et al., 2017; Corsini et al., 2019).

Table 7.2. Retention of particles in the HRT, mass of PM_{10} (μg) transferred to the gastrointestinal tract, lymph nodes and absorbed into the blood after 24-h exposure (ET – extrathoracic, TB – tracheobronchial and AI – alveolar–interstitial).

	ET	TB	AI	Oesophagus	Lymph nodes	Blood Absorption
Fireplace						
Indoor						
Female	318 ± 205	35.1 ± 23.1	217 ± 148	326 ± 239	$(9.02 \pm 7.61) \times 10^{-5}$	23.1 ± 18.8
Male	370 ± 239	39.7 ± 26.0	260 ± 177	380 ± 279	$(10.5 \pm 8.84) \times 10^{-5}$	27.5 ± 22.3
Male 10y	358 ± 232	27.7 ± 18.1	163 ± 111	366 ± 269	$(9.70 \pm 8.18) \times 10^{-5}$	18.3 ± 14.8
Background						
Female	28.0 ± 0.771	2.28 ± 0.0560	13.4 ± 1.10	33.6 ± 6.45	$(1.04 \pm 0.328) \times 10^{-5}$	1.84 ± 0.524
Male	32.9 ± 0.908	2.66 ± 0.0813	16.2 ± 1.33	39.6 ± 7.62	$(1.23 \pm 0.386) \times 10^{-5}$	2.21 ± 0.630
Male 10y	29.2 ± 0.801	1.74 ± 0.0798	9.62 ± 0.794	34.8 ± 6.68	$(1.05 \pm 0.330) \times 10^{-5}$	1.41 ± 0.394
Outdoor						
Female	124 ± 21.7	14.5 ± 2.48	65.3 ± 12.7	128 ± 28.9	$(3.66 \pm 0.877) \times 10^{-5}$	7.71 ± 1.94
Male	147 ± 25.7	16.5 ± 2.80	79.0 ± 15.3	152 ± 34.3	$(4.32 \pm 1.03) \times 10^{-5}$	9.22 ± 2.33
Male 10y	124 ± 21.8	11.4 ± 1.92	50.0 ± 9.71	128 ± 28.8	$(3.51 \pm 0.877) \times 10^{-5}$	6.07 ± 1.57
Woodstove						
Indoor						
Female	122 ± 33.5	14.9 ± 4.22	90.5 ± 27.8	136 ± 47.1	$(4.23 \pm 1.71) \times 10^{-5}$	10.8 ± 4.25
Male	142 ± 39.0	16.7 ± 4.72	109 ± 33.3	159 ± 54.9	$(4.91 \pm 1.99) \times 10^{-5}$	12.9 ± 5.05
Male 10y	138 ± 37.8	11.7 ± 3.25	68.5 ± 21.0	153 ± 52.8	$(4.53 \pm 1.84) \times 10^{-5}$	8.58 ± 3.35
Background						
Female	47.3 ± 0.842	3.84 ± 0.126	21.8 ± 1.89	52.7 ± 8.38	$(1.54 \pm 0.434) \times 10^{-5}$	2.76 ± 0.650
Male	55.6 ± 0.990	4.49 ± 0.135	26.3 ± 2.28	62.1 ± 9.89	$(1.82 \pm 0.512) \times 10^{-5}$	3.32 ± 0.780
Male 10y	49.2 ± 0.879	2.95 ± 0.0678	15.7 ± 1.36	54.7 ± 8.68	$(1.56 \pm 0.438) \times 10^{-5}$	2.12 ±0.489
Outdoor						
Female	81.4 ± 69.6	9.62 ± 8.06	42.5 ± 35.5	80.6 ± 69.1	$(2.30 \pm 1.99) \times 10^{-5}$	4.81 ± 4.05
Male	96.2 ± 82.3	11.0 ± 9.21	51.4 ± 42.9	95.4 ± 81.9	$(2.71 \pm 2.34) \times 10^{-5}$	5.76 ± 4.85
Male 10y	81.7 ± 69.6	7.58 ± 6.35	32.5 ± 27.1	80.5 ± 68.9	$(2.22 \pm 1.92) \times 10^{-5}$	3.82 ± 3.22

7.4. Conclusions

Particulate matter dosimetry provides the crucial link between exposure and dose reaching various regions of the HRT, which is a key factor with regard to the triggered health effects.

The dose received by different subjects in indoor environments, where biomass heating systems (fireplace and woodstove) were in operation, was evaluated by means of the concentration levels measured during an experimental campaign using the dosimetry model ExDoM2. Measurements were performed in the periods of use of the wood combustion appliances (8 hours) simultaneously indoors and outdoors. Background measurements, in the absence of indoor PM sources were also conducted. Data on exposure to airborne particulate matter was used to evaluate the dose received by different subjects (male, female and 10-year male children) who were assumed to be under light level of exertion.

The results of the dosimetry model revealed that the age and gender of the exposed subject played a minor role in the estimated deposited dose, being slightly higher for male adults. Higher deposited PM_{10} doses in the HRT were registered indoors during the operation of the open fireplace (up to twofold) in relation to those obtained for the woodstove. When compared with the total dose received by a subject indoors in the absence of activity, a 3-fold increase (woodstove) up to 10 times (fireplace) in the dose was observed in the presence of wood burning appliances. Despite the contribution of biomass burning emissions to the PM_{10} outdoor levels, indoor doses were in general higher than those received by a subject exposed outside the home. At the AI region, indoor doses were, on average, 2.8 and 3.5 times higher than the ones received outdoors during the operation of the woodstove and fireplace, respectively.

Taking into consideration the potential health effects, the regional dose was assessed. The results indicated that the highest mass of particles was deposited in the extrathoracic airways. However, the particles deposited in this region are removed much more rapidly to the gastrointestinal tract than those in the deeper regions of the respiratory system. On the contrary, it was observed that more than 90% of the particles deposited in the AI region remained deposited after 24 h of exposure.

The findings of the present study demonstrate that exposure to household particulate matter arising from the operation of wood burning appliances can have major impacts on human health. Considering that the deposition of inhaled particles in the HRT is one of the key factors for assessing toxic effects of airborne particles, the results of this work provide novel data on PM regional deposition, which can be employed in future research on toxicological assessment of particles arising from biomass burning.

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References

Aleksandropoulou, V., Lazaridis, M., 2013. Development and application of a model (ExDoM) for calculating the respiratory tract dose and retention of particles under variable exposure conditions. Air Qual. Atmos. Health 6, 13–26. https://doi.org/10.1007/s11869-010-0126-z

Amann, M., Cofala, J., Klimont, Z., Nagl, C., Schieder, W., 2018. Measures to address air pollution from small combustion sources. Amann M. (Ed.). International Institute for Applied Systems Analysis (IIASA) and Environment Agency, Austria

Bari, M.A., Baumbach, G., Brodbeck, J., Struschka, M., Kuch, B., Dreher, W., Scheffknecht, G., 2011a. Characterisation of particulates and carcinogenic polycyclic aromatic hydrocarbons in wintertime wood-fired heating in residential areas. Atmos. Environ. 45, 7627–7634. https://doi.org/10.1016/j.atmosenv.2010.11.053

Bari, M.A., Baumbach, G., Kuch, B., Scheffknecht, G., 2011b. Air pollution in residential areas from wood-fired heating. Aerosol Air Qual. Res. 11, 749–757. https://doi.org/10.4209/aaqr.2010.09.0079

Bartington, S.E., Bakolis, I., Devakumar, D., Kurmi, O.P., Gulliver, J., Chaube, G., Manandhar, D.S., Saville, N.M., Costello, A., Osrin, D., Hansell, A.L., Ayres, J.G., 2017. Patterns of domestic exposure to carbon monoxide and particulate matter in households using biomass fuel in Janakpur, Nepal. Environ. Pollut. 220, 38–45. https://doi.org/10.1016/j.envpol.2016.08.074

Bennett, W.D., Zeman, K.L., Kim, C., Mascarella, J., 1997. Enhanced deposition of fine particles in COPD patients spontaneously breathing at rest. Inhal. Toxicol. 9, 1–14. https://doi.org/10.1080/089583797198376

Brown, J.S., Zeman, K.L., Bennett, W.D., 2002. Ultrafine particle deposition and clearance in the healthy and obstructed lung. Am. J. Respir. Crit. Care Med. 166, 1240–1247. https://doi.org/10.1164/rccm.200205-399OC

Castro, A., Calvo, A.I., Blanco-Alegre, C., Oduber, F., Alves, C., Coz, E., Amato, F., Querol, X., Fraile, R., 2018. Impact of the wood combustion in an open fireplace on the air quality of a living room: Estimation of the respirable fraction. Sci. Total Environ. 628–629, 169–176. https://doi.org/10.1016/j.scitotenv.2018.02.001

Chakraborty, R., Heydon, J., Mayfield, M., Mihaylova, L., 2020. Indoor air pollution from residential stoves: examining the flooding of particulate matter into homes during real-world use. Atmosphere (Basel). 11, 1326. https://doi.org/10.3390/atmos11121326

Chalupa, D.C., Morrow, P.E., Oberdörster, G., Utell, M.J., Frampton, M.W., 2004. Ultrafine particle deposition in subjects with asthma. Environ. Health Perspect. 112, 879–882. https://doi.org/10.1289/ehp.6851

Chalvatzaki, E., Lazaridis, M., 2015. Development and application of a dosimetry model (ExDoM2) for calculating internal dose of specific particle-bound metals in the human body. Inhal. Toxicol. 27, 308–320. https://doi.org/10.3109/08958378.2015.1046201

Corsini, E., Marinovich, M., Vecchi, R., 2019. Ultrafine particles from residential biomass combustion: a review on experimental data and toxicological response. Int. J. Mol. Sci. 20. https://doi.org/10.3390/ijms20204992

de Gennaro, G., Dambruoso, P.R., Di Gilio, A., di Palma, V., Marzocca, A., Tutino, M., 2015. Discontinuous and continuous indoor air quality monitoring in homes with fireplaces or wood stoves as heating system. Int. J. Environ. Res. Public Health 13, 1–9. https://doi.org/10.3390/ijerph13010078

Du, Y., Xu, X., Chu, M., Guo, Y., Wang, J., 2016. Air particulate matter and cardiovascular disease: the epidemiological, biomedical and clinical evidence. J Thorac Dis 8, 8–19. https://doi.org/10.3978/j.issn.2072-1439.2015.11.37

Fiordelisi, A., Piscitelli, P., Trimarco, B., Coscioni, E., Iaccarino, G., Sorriento, D., 2017. The mechanisms of air pollution and particulate matter in cardiovascular diseases. Hear. Fail Rev 22, 337–347. https://doi.org/10.1007/s10741-017-9606-7

Fullerton, D.G., Bruce, N., Gordon, S.B., 2008. Indoor air pollution from biomass fuel smoke is a major health concern in the developing world. Trans. R. Soc. Trop. Med. Hyg. 102, 843–851. https://doi.org/10.1016/j.trstmh.2008.05.028

Glasius, M., Ketzel, M., Wåhlin, P., Jensen, B., Mønster, J., Berkowicz, R., Palmgren, F., 2006. Impact of wood combustion on particle levels in a residential area in Denmark. Atmos. Environ. 40, 7115–7124. https://doi.org/10.1016/j.atmosenv.2006.06.047

Guo, L., Lewis, J.O., McLaughlin, J.P., 2008. Emissions from Irish domestic fireplaces and their impact on indoor air quality when used as supplementary heating source. Glob. Nest J. 10, 209–216.

Gustafson, P., Ostman, C., Sällsten, G., 2008. Indoor levels of polycyclic aromatic hydrocarbons in homes with or without wood burning for heating. Environ. Sci. Technol. 42, 5074–80.

Harkema, J.R., Nikula, K.J., Haschek, W.M., 2013. Respiratory System, in: Haschek, W.M., Wallig, M.A., Rousseaux, C.G. (Eds.), Haschek and Rousseaux's Handbook of Toxicologic Pathology. Elsevier Inc., pp. 1935–2003. https://doi.org/10.1016/B978-0-12-415759-0.00051-0

Hellén, H., Hakola, H., Haaparanta, S., Pietarila, H., Kauhaniemi, M., 2008. Influence of residential wood combustion on local air quality. Sci. Total Environ. 393, 283–290. https://doi.org/10.1016/j.scitotenv.2008.01.019

Hinds, W.C., 1999. Aerosol Technology: Properties, Behavior, ans Measurement of Airborne Particles, second edition, John Wiley and Sons.

Hofmann, W., 2011. Modelling inhaled particle deposition in the human lung-A review. J. Aerosol Sci. https://doi.org/10.1016/j.jaerosci.2011.05.007

Hussain, M., Madl, P., Khan, A., 2011. Lung deposition predictions of airborne particles and the emergence of contemporary diseases Part I. theHealth 2, 51–59.

ICRP, 2015. Occupational Intakes of Radionuclides: Part 1. ICRP Publication 130. Ann. ICRP 44(2).

ICRP, 1994. Human Respiratory Tract Model for Radiological Protection. Publication 66. Volume 24. Pergamon.

Kayamba, V., Heimburger, D.C., Morgan, D.R., Atadzhanov, M., Kelly, P., 2017. Exposure to biomass smoke as a risk factor for oesophageal and gastric cancer in low-income populations: A systematic review. Malawi Med. J. 29, 212–217. https://doi.org/10.4314/mmj.v29i2.25

Kim, C.S., 2009. Deposition of aerosol particles in human lungs: *in vivo* measurement and modelling. Biomarkers 14, 54–58. https://doi.org/10.1080/13547500902965286

Kim, C.S., Kang, T.C., 1997. Comparative measurement of lung deposition of inhaled fine particles in normal subjects and patients with obstructive airway disease. Am. J. Respir. Crit. Care Med. 155, 899–905. https://doi.org/10.1164/ajrccm.155.3.9117024

Kim, K.H., Jahan, S.A., Kabir, E., 2011. A review of diseases associated with household air pollution due to the use of biomass fuels. J. Hazard. Mater. 192, 425–431. https://doi.org/10.1016/j.jhazmat.2011.05.087

Laumbach, R.J., Kipen, H.M., 2012. Respiratory health effects of air pollution: Update on biomass smoke and traffic pollution. J. Allergy Clin. Immunol. https://doi.org/10.1016/j.jaci.2011.11.021

Lippmann, M., Yeates, D.B., Albert, R.E., 1980. Deposition, retention, and clearance of inhaled particles. Br. J. Ind. Med. https://doi.org/10.1136/oem.37.4.337

Löndahl, J., Möller, W., Pagels, J.H., Kreyling, W.G., Swietlicki, E., Schmid, O., 2014. Measurement techniques for respiratory tract deposition of airborne nanoparticles: A critical review. J. Aerosol Med. Pulm. Drug Deliv. 27, 229–254. https://doi.org/10.1089/jamp.2013.1044

Löndahl, J., Pagels, J.H., Boman, C., Swietlicki, E., Massling, A., Rissler, J., Blomberg, A., Bohgard, M., Sandstrom, T., 2008. Deposition of biomass combustion aerosol particles in the human respiratory tract. Inhal. Toxicol. 20, 923–933. https://doi.org/10.1080/08958370802087124

Löndahl, J., Swietlicki, E., Rissler, J., Bengtsson, A., Boman, C., Blomberg, A., Sandström, T., 2012. Experimental determination of the respiratory tract deposition of diesel combustion particles in patients with chronic obstructive pulmonary disease. Part. Fibre Toxicol. 9, 30. https://doi.org/10.1186/1743-8977-9-30

Mammi-Galani, E., Eleftheriadis, K., Mendes, L., Lazaridis, M., 2017. Exposure and dose to particulate matter inside the subway system of Athens, Greece. Air Qual. Atmos. Health 10, 1015–1028. https://doi.org/10.1007/s11869-017-0490-z

Martins, V., Cruz Minguillón, M., Moreno, T., Querol, X., de Miguel, E., Capdevila, M., Centelles, S., Lazaridis, M., 2015. Deposition of aerosol particles from a subway microenvironment in the human respiratory tract. J. Aerosol Sci. 90, 103–113. https://doi.org/10.1016/j.jaerosci.2015.08.008

McNamara, M., Thornburg, J., Semmens, E., Ward, T., Noonan, C., 2013. Coarse particulate matter and airborne endotoxin within wood stove homes. Indoor Air 23, 498–505. https://doi.org/10.1111/ina.12043

Muala, A., Nicklasson, H., Boman, C., Swietlicki, E., Nyström, R., Pettersson, E., Bosson, J.A., Rissler, J., Blomberg, A., Sandström, T., Löndahl, J., 2015. respiratory tract deposition of inhaled wood smoke particles in healthy volunteers. J. Aerosol Med. Pulm. Drug Deliv. 28, 237–246. https://doi.org/10.1089/jamp.2014.1122

Naeher, L.P., Brauer, M., Lipsett, M., Zelikoff, J.T., Simpson, C.D., Koenig, J.Q., Smith, K.R., 2007. Woodsmoke health effects: A review. Inhal. Toxicol. 19, 67–106. https://doi.org/10.1080/08958370600985875

Nemmar, A., Holme, J.A., Rosas, I., Schwarze, P.E., Alfaro-moreno, E., 2013. Recent advances in particulate matter and nanoparticle toxicology: A review of the *in vivo* and *in vitro* studies. Biomed Res. Int. 2013.

Nicolaou, L., Fandiño-Del-Rio, M., Koehler, K., Checkley, W., 2020. Size distribution and lung-deposited doses of particulate matter from household exposure to biomass smoke. Indoor Air ina.12710. https://doi.org/10.1111/ina.12710

Olsen, Y., Nøjgaard, J.K., Olesen, H.R., Brandt, J., Sigsgaard, T., Pryor, S.C., Ancelet, T., Viana, M. del M., Querol, X., Hertel, O., 2020. Emissions and source allocation of carbonaceous air pollutants from wood stoves in developed countries: A review. Atmos. Pollut. Res. https://doi.org/10.1016/j.apr.2019.10.007

Parajuli, I., Lee, H., Shrestha, K.R., 2016. Indoor Air Quality and ventilation assessment of rural mountainous households of Nepal. Int. J. Sustain. Built Environ. 5, 301–311. https://doi.org/10.1016/j.ijsbe.2016.08.003

Paur, H.R., Cassee, F.R., Teeguarden, J., Fissan, H., Diabate, S., Aufderheide, M., Kreyling, W.G., Hänninen, O., Kasper, G., Riediker, M., Rothen-Rutishauser, B., Schmid, O., 2011. *In-vitro* cell exposure studies for the assessment of nanoparticle toxicity in the lung-A dialog between aerosol science and biology. J. Aerosol Sci. 42, 668–692. https://doi.org/10.1016/j.jaerosci.2011.06.005

Phalen, R.F., Oldham, M.J., Nel, A.E., 2006. Tracheobronchial particle dose considerations for *in vitro* toxicology studies. Toxicol. Sci. 92, 126–132. https://doi.org/10.1093/toxsci/kfj182

Pial, R.H., Hashan, M.R., Ghozy, S., Dibas, M., El-Qushayri, A.E., Abdel-Daim, M.M., 2020. Comparative study on respiratory function among rural women using biomass fuel and non-biomass fuel: Evidence of a cross-sectional survey in Bangladesh. Environ. Sci. Pollut. Res. 27, 24039–24047. https://doi.org/10.1007/s11356-020-08668-6

Reichert, G., Schmidl, C., Haslinger, W., Schwabl, M., Moser, W., Aigenbauer, S., Wöhler, M., Hochenauer, C., 2016. Investigation of user behavior and assessment of typical operation mode for different types of firewood room heating appliances in Austria. Renew. Energy 93, 245–254. https://doi.org/10.1016/j.renene.2016.01.092

Salthammer, T., Schripp, T., Wientzek, S., Wensing, M., 2014. Impact of operating wood-burning fireplace ovens on indoor air quality. Chemosphere 103, 205–211. https://doi.org/10.1016/j.chemosphere.2013.11.067

Sánchez-Soberón, F., Mari, M., Kumar, V., Rovira, J., Nadal, M., Schuhmacher, M., 2015. An approach to assess the Particulate Matter exposure for the population living around a cement plant: Modelling indoor air and particle deposition in the respiratory tract. Environ. Res. 143, 10–18. https://doi.org/10.1016/j.envres.2015.09.008

Saraga, D.E., Makrogkika, A., Karavoltsos, S., Sakellari, A., Diapouli, E., Eleftheriadis, K., Vasilakos, C., Helmis, C., Maggos, T., 2015. A pilot investigation of PM indoor/outdoor mass concentration and chemical analysis during a period of extensive fireplace use in Athens. Aerosol Air Qual. Res. 15, 2485–2495. https://doi.org/10.4209/aaqr.2015.02.0100

Sarangapani, R., Robinan Gentry, P., Covington, T.R., Teeguarden, J.G., Clewell, H.J., 2003. Evaluation of the potential impact of age- and gender-specific lung morphology and ventilation rate on the dosimetry of vapors, Inhalation Toxicology. 15, 101-130. https://doi.org/10.1080/08958370390226350

Schlesinger, R.B., Kunzli, N., Hidy, G.M., Gotschi, T., Jerrett, M., 2006. The health relevance of ambient particulate matter characteristics: Coherence of toxicological and epidemiological inferences. Inhal. Toxicol. 18, 95–125. https://doi.org/10.1080/08958370500306016

Schmid, O., Cassee, F.R., 2017. On the pivotal role of dose for particle toxicology and risk assessment: exposure is a poor surrogate for delivered dose. Part. Fibre Toxicol. 14, 52. https://doi.org/10.1186/s12989-017-0233-1

Schwarze, P.E., Øvrevik, J., Lag, M., Refsnes, M., Nafstad, P., Hetland, R., Dybing, E., 2006. Particulate matter properties and health effects: consistency of epidemiological and toxicological studies. Hum. Exp. Toxicol. 25, 559–579.

Sheikh, M., Poustchi, H., Pourshams, A., Khoshnia, M., Gharavi, A., Zahedi, M., Roshandel, G., Sepanlou, S.G., Fazel, A., Hashemian, M., Abaei, B., Sotoudeh, M., Nikmanesh, A., Merat, S., Etemadi, A., Moghaddam, S.N., Islami, F., Kamangar, F., Pharoah, P.D., Dawsey, S.M., Abnet, C.C., Boffetta, P., Brennan, P., Malekzadeh, R., 2020. Household fuel use and the risk of gastrointestinal cancers: The golestan cohort study. Environ. Health Perspect. 128, 1–9. https://doi.org/10.1289/EHP5907

Sigsgaard, T., Forsberg, B., Annesi-Maesano, I., Blomberg, A., Bølling, A., Boman, C., Bønløkke, J., Brauer, M., Bruce, N., Héroux, M.E., Hirvonen, M.R., Kelly, F., Künzli, N., Lundbäck, B., Moshammer, H., Noonan, C., Pagels, J., Sallsten, G., Sculier, J.P., Brunekreef, B., 2015. Health impacts of anthropogenic biomass burning in the developed world. Eur. Respir. J. 46, 1577–1588. https://doi.org/10.1183/13993003.01865-2014

Sood, A., 2012. Indoor fuel exposure and the lung in both developing and developed countries: An update. Clin. Chest Med. 33, 649-665. https://doi.org/10.1016/j.ccm.2012.08.003

Stabile, L., Buonanno, G., Avino, P., Frattolillo, A., Guerriero, E., 2018. Indoor exposure to particles emitted by biomass-burning heating systems and evaluation of dose and lung cancer risk received by population. Environ. Pollut. 235, 65–73. https://doi.org/10.1016/j.envpol.2017.12.055

Vicente, E.D., Alves, C.A., 2018. An overview of particulate emissions from residential biomass combustion. Atmos. Res. 199, 159–185. https://doi.org/10.1016/J.ATMOSRES.2017.08.027

Vicente, E.D., Vicente, A.M., Evtyugina, M., Oduber, F.I., Amato, F., Querol, X., Alves, C., 2020. Impact of wood combustion on indoor air quality. Sci. Total Environ. 705, 135769. https://doi.org/10.1016/j.scitotenv.2019.135769

Wöhler, M., Andersen, J.S., Becker, G., Persson, H., Reichert, G., Schön, C., Schmidl, C., Jaeger, D., Pelz, S.K., 2016. Investigation of real life operation of biomass room heating appliances - Results of a European survey. Appl. Energy 169, 240–249. https://doi.org/10.1016/j.apenergy.2016.01.119

Wolff, F., Kothe, H., Mubiru, A., Gashirabake, J., Uwimana, I., Dalhoff, K., 2020. Positive impact of improved cookstove usage on respiratory health in Congolese refugees: a prospective cohort study. Environ. Sci. Pollut. Res. 27, 4509–4512. https://doi.org/10.1007/s11356-019-06816-1

Xi, J., Si, X.A., Kim, J.W., 2015. Chapter 5 - Characterizing Respiratory Airflow and Aerosol Condensational Growth in Children and Adults Using an Imaging-CFD Approach, in: Becker, id M., Kuznetsov, A. V. (Eds.), Heat Transfer and Fluid Flow in Biological Processes. Academic Press, pp. 125–155.

CHAPTER 8

Chapter 8. *In vitro* toxicity of indoor and outdoor PM_{10} from residential wood combustion

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Abstract

Particulate matter (PM_{10}) was collected, indoors and outdoors, when wood burning appliances (open fireplace and woodstove) were in operation. The PM_{10} ecotoxicity was assessed with the *Vibrio fischeri* bioluminescence inhibition assay, while the cytotoxicity was evaluated by the WST-8 and lactate dehydrogenase (LDH) release assays using A549 cells. Extracts of PM_{10}-bound polycyclic aromatic hydrocarbons (PAH) were tested for their mutagenicity through the TA98 and TA100 Ames test. The bioluminescent inhibition assay revealed that indoor particles released from the fireplace were the most toxic. Indoors, the reduction in A549 cell metabolic activity was over two times higher for the fireplace in comparison with the woodstove (32 ± 3.2% and 72 ± 7.6% at the highest dose, respectively). Indoor particles from the fireplace were found to induce greater cytotoxicity than the corresponding outdoor samples. Combined WST-8 and LDH results suggest that PM_{10} exposure induce apoptotic cell death pathway in which the cell membrane integrity is maintained. Indoor and outdoor samples lacked direct and indirect mutagenic activity in any of the tester strains. For indoor-generated PM_{10}, organic carbon and PAH were significantly correlated with cell viability and bioluminescence reduction, suggesting a role of organic compounds in toxicity.

Keywords: Bioluminescence inhibition, Cytotoxicity, Mutagenicity, Particulate matter, Residential wood combustion

8.1. Introduction

Over the years, a wealth of publications has focused on the quantification and characterisation of particulate matter (PM) emissions arising from residential biomass combustion (Vicente and Alves, 2018). PM has been a focus of special research attention because adverse health outcomes associated with exposure to this pollutant have been observed in epidemiological studies (Atkinson et al., 2015; Dockery, 2009; Pope, 2000). While epidemiological studies reveal associations between health outcomes and exposure to PM, *in vitro* and *in vivo* models are useful to study the mechanisms involved in the PM-related health effects (Cho et al., 2018; Nemmar et al., 2013; Schlesinger et al., 2006).

The toxicity assessment of biomass burning particles produced under controlled laboratory conditions (source characterisation studies) has been conducted *in vivo* with rodents (e.g. Danielsen et al., 2010; Uski et al., 2012) and *in vitro* using different cell lines, such as epithelial cells of the respiratory tract and alveolar macrophages (Danielsen et al., 2009; Dilger et al., 2016; Kocbach et al., 2008; Totlandsdal et al., 2014), as well as different bacterial strains (Canha et al., 2016; Turóczi et al., 2012; Vu et al., 2012). Many studies underlined that the type of combustion appliance has an important role on the toxicological effects of PM emissions (Canha et al., 2016; Corsini et al., 2017; Jalava et al., 2012; Tapanainen et al., 2011; Vu et al., 2012). Additionally, the fuel burned (Arif et al., 2017; Canha et al., 2016; Corsini et al., 2017; Kasurinen et al., 2017; Vu et al., 2012) and the combustion conditions (Canha et al., 2016; Jalava et al., 2010; Uski et al., 2014; Vu et al., 2012) were also investigated.

In addition to being a recognised major source of ambient PM (Vicente and Alves, 2018, and references therein), residential biomass burning has also a noticeable impact on indoor air quality (Castro et al., 2018; de Gennaro et al., 2015; Guo et al., 2008; McNamara et al., 2013; Salthammer et al., 2014; Vicente et al., 2020). Furthermore, people spend most of their time in indoor environments (e.g. Brasche and Bischof, 2005; Schweizer et al., 2007), meaning that it is where most of human exposure occurs (Morawska et al., 2013). Despite its importance, the *in vitro* toxicity of indoor particles arising from the use of biomass combustion appliances has been less studied. Regarding *in vitro* mammalian assays aiming at assessing the toxicity of indoor PM from biomass burning, the studies of Ke et al. (2018) and Marchetti et al. (2019) represent the bulk of research so far. Marchetti et al. (2019) investigated the toxicological properties of indoor PM_{10} from an open fireplace fuelled with different biomasses (pellets, charcoal and wood). The authors performed *in vitro* assays using human lung cells (A549) and reported that the effects on the biological endpoints were strongly related to the biomass fuel burned, which generated particles with distinct chemical composition. Ke et al. (2018) evaluated the cytotoxicity of soluble constituents emitted by biomass combustion on human skin keratinocytes using a multilayered dynamic cell culture platform. A decline in cell viability after cell exposure and an increase in apoptosis rates were reported.

Despite the knowledge provided by the mentioned studies, particulate matter from residential biomass combustion has distinct physicochemical properties as a result of fuel type, combustion appliance and household behavior (e.g. Lamberg et al., 2011; Vicente et al., 2015). These properties are key features triggering different biological effects, such as inflammatory responses, cytotoxicity, genotoxicity and oxidative stress (Corsini et al., 2019; Happo et al., 2013; Jalava et al., 2008, 2007). Thus, a toxicological profile of a relevant indoor pollution source is of utmost importance to better understand the potential health risk posed by wood burning emissions and to develop appropriate control strategies.

Taking into account the ethical issues related to *in vivo* testing, as well as its higher cost and time-consuming nature, *in vitro* assays were selected to carry out the present study. This work aimed to evaluate the toxicity of indoor PM generated from Portuguese combustion appliances, which are common in the Mediterranean region, using different *in vitro* tests. Furthermore, outdoor sampling was also carried out in order to compare the results with those from indoor generated particles. The PM overall ecotoxicity was assessed with the *Vibrio fischeri* bioluminescence inhibition bioassay. The PM_{10} cytotoxicity was determined by the WST-8 and lactate dehydrogenase (LDH) release assays using a human lung epithelial cell line (A549). The mutagenicity of PM-bound polycyclic aromatic hydrocarbons (PAHs) was evaluated through the *Salmonella* reverse mutation assay.

8.2. Materials and Methods

8.2.1. Particle collection and characterisation

A detailed description of the sampling strategy can be found in a previous study (Vicente et al., 2020). Briefly, the PM_{10} sampling was carried out in two unoccupied houses equipped with traditional wood burning appliances, one with an open fireplace and the other with a woodstove. Each combustion appliance was operated for about 8 hours per day for three and four days (woodstove and fireplace, respectively) under minimum ventilation conditions. No concurrent activities took place during the sampling period. Background concentrations were determined over four days in each room. Particulate matter (PM_{10}) was collected onto quartz filters (Pall Corporation, Ann Harbor, USA) with a high-volume air sampler (MCV, CAV-A/mb, Barcelona, Spain) working with a constant flow of 30 m^3 h^{-1}. During the wood burning period, concurrent samples were collected outdoors in order to evaluate the atmospheric PM_{10} in a rural area highly exposed to emissions from biomass burning for residential heating in the cold months of the year and also characterised by the inexistence of other major pollution sources (e.g. industry, traffic). After the PM_{10} gravimetric quantification, the samples were analysed for organic (OC) and elemental carbon (EC), water soluble ions, metals and detailed organic composition. The full description of the analytical techniques and the PM_{10} chemical composition can be found in a previous work (Vicente et al., 2020).

8.2.2. Sample preparation for toxicological assays

Ecotoxicity: Sample preparation followed the protocol developed by Kováts et al. (2012). Briefly, one filter punch of 1.9 cm from each PM_{10} sample was ground in an agate mortar and then transferred into pre-cleaned glass vials. Suspensions were prepared adding 2 ml of high-purity water.

Cytotoxicity: Two filter punches of 47 mm from each PM_{10} sample were firstly extracted by refluxing dichloromethane (125 ml) for 24 h and then two times with methanol in an ultrasonic bath (25 ml for 10 min, each extraction). After each extraction, the total organic extracts were filtered and then concentrated to a volume lower than 1 ml using a Turbo Vap® II concentrator (Biotage) and finally evaporated under nitrogen flow. The final extract was reconstituted in dimethyl sulfoxide (DMSO, Sigma Aldrich).

Mutagenicity: Samples were firstly extracted as described above for the cytotoxicity assay. After drying, the total organic extract was then transferred onto activated silica gel columns and fractionated using solvents of different polarity. After each elution, the different organic fractions were dried following the procedure described above. Target compounds (16 EPA priority PAHs and some other aromatics - benzo[e]pyrene, perylene, p-terphenyl and retene) in the concentrated extracts were analysed by gas chromatography - mass spectrometry (GC-MS). The results were reported elsewhere (Vicente et al., 2020). Afterwards, the dried extracts from each sample were resuspended into DMSO and then tested for mutagenicity.

8.2.3. Ecotoxicity testing

The *V. fischeri* bioluminescence inhibition assay has been widely used for ecotoxicological screening and assessment of diverse potentially toxic substances including atmospheric pollutants (Abbas et al., 2018). The ecotoxicity testing was carried out using the direct contact test system (referred to as Flash system), which is standardised (ISO 21338:2010: water quality – kinetic determination of the inhibitory effects of sediment, other solids and coloured samples on the light emission of *Vibrio fischeri*/kinetic luminescent bacteria test). Briefly, the lyophilised bacteria were rehydrated with the reconstitution solution and stabilised at 12 °C for 30 min before the measurement using a luminometer (Luminoskan Ascent, Thermo Scientific). Duplicated series of eleven two-fold serial dilution in 2% NaCl were prepared for each sample in 96 well plates. The dilutions were performed following the manufacturer protocol with the supplied diluent reagent (2% NaCl solution in water), to ensure optimal osmotic conditions for the bacteria. After the bacterial suspension was added to the sample, bioluminescence intensity was continuously recorded for the first 30 seconds. After the pre-set exposure time (30 minutes), luminescence intensity was read again. The peak value observed immediately after the addition of the bacteria into the sample was used as a reference for calculations in order to take into account the turbidity or colour of the sample (Lappalainen et al., 2001). The light inhibition (INH%) was calculated based on the following equations:

$$KF = \frac{IC_{30}}{IC_0} \qquad (1)$$

$$INH\ (\%) = 100 - \frac{IT_{30}}{KF \times IT_0} \times 100 \qquad (2)$$

where KF is the correction factor, IC_0 and IC_{30} are the luminescence intensities of the control at the beginning and after 30 min, IT_0 and IT_{30} are the luminescence intensities of the sample at the beginning and after the 30 min contact time. EC_{50} (concentration that causes 50% reduction in the bioluminescence output of the test organisms relative to the control under the given experimental conditions) values were calculated from the dose-response curves on serial dilutions of the extracts using the Ascent Software provided by Aboatox Co., Finland. The EC_{50} values were then used to calculate the Toxicity Units (TU, unitless), which are defined as follows (Aammi et al., 2017; Romano et al., 2020):

$$TU_{50} = \frac{100\ (\%)}{EC_{50}\ (\%)} \qquad (3)$$

Four toxicity levels were proposed on the basis of the TU values: $TU_{50} < 1$ non-toxic, $1 < TU_{50} < 10$ toxic, $10 < TU_{50} < 100$ very toxic and $TU_{50} > 100$ extremely toxic (Romano et al., 2020).

8.2.4. Cell culture and cytotoxicity assays

In the present study, the human adenocarcinoma alveolar epithelial cell line A549 was used to perform the cytotoxicity tests. This lung cell line is a useful model and widely used to assess the biological effects of PM samples (Cho et al., 2018; Jia et al., 2017; Peixoto et al., 2017).

A549 cells were cultured in 25 cm^2 flasks (Corning®) with 5 ml of Kaighn's Modification of Ham's F-12 Medium (F-12K), supplemented with 10% (v/v) Fetal Bovine Serum (FBS) (Gibco), 1% of penicillin-streptomycin (Gibco) and 1% Fungizone (Gibco) at 37 °C, 5% CO_2 in humidified atmosphere. Cell confluence and morphology were observed under an inverted microscope (Nikon® Eclipse TS100). Subculture was performed every 2-3 days, when culture reached approximately 90% confluence. After removal of the culture medium, cells were washed with 2 ml of phosphate buffered saline (PBS, Gibco) and incubated with 1.5 ml Trypsin-EDTA (0.25% trypsin, 1 mM EDTA) for 5 min, to cleave proteins that enable cell adherence to the flask and cell-cell adhesion. After cell detachment from the culture flask, trypsin was inactivated by adding 3 ml of supplemented medium to the culture. Cells were harvested and seeded in a new flask with complete culture medium.

The PM_{10} cytotoxicity was examined using two complementary methods: WST-8 assay to evaluate the cell metabolic activity and lactate dehydrogenase (LDH) activity assay to assess the integrity of the cell membrane.

The WST-8 assay (CCK-8 kit, Sigma-Aldrich®) was performed by following the manufacturer instructions. Briefly, cells were seeded in a 96 well plate at 4×10^3 cells/well and incubated 24 h for adhesion. The PM_{10} suspension was diluted in complete medium to obtain the final concentrations of 0.1, 0.5, 1, 5, 10, 50, 100 and 150 $\mu g\ ml^{-1}$ (corresponding to 0.03, 0.16, 0.31, 1.6, 3.1, 16, 31 and 47 $\mu g\ cm^{-2}$). The DMSO concentration in the culture medium was kept below 1.2% (v/v). The lowest range of doses at the alveolar epithelium (0.03 to 0.31 $\mu g\ cm^{-2}$) was determined based on modelling (particle dosimetry model ExDoM2) (Vicente et al., submitted for publication) using the PM_{10} measurements from the field campaign, while the highest range of doses exceeds environment concentrations. The highest doses were selected to generate differences in toxic responses between PM_{10} samples and control exposures in order to evaluate mechanisms of action. Additionally, higher doses allow comparison with results of previous studies. Cellular exposure was achieved by replacing the culture medium in each well with fresh PM-containing medium. The final volume for exposure was 0.1 ml per well. The outer peripheral wells of the 96-well plates were also filled in to reduce medium evaporation from the exposure wells. After 24 h exposure, the wells were emptied and filled with culture medium and 10 µl of WST–8 reagent. Then, the plate was incubated for 2 h at culture conditions and the absorbance was measured at 450 nm in a microplate reader

(Biotek® - Gen5™ software). Two independent assays were performed with five technical replicates each and the results compared with the control (no exposure). After the subtraction of the background absorbance (culture medium without cells), the cellular viability was calculated as the ratio between the absorbance from wells exposed to particle suspensions and the absorbance of the control group (unexposed).

The LDH assay was carried out using the cell free supernatants after cell exposure using the LDH assay kit (Cytotoxicity Detection Kit LDH, Roche Diagnostics, France). The A549 cells were seeded and treated with PM_{10} extracts as in the WST-8 assay. After 24 h exposure, the supernatants were collected from each well and added to a new 96-well plate. The LDH activity measurement was conducted according to the instructions in the assay kit. Briefly, the reagent mixture was added to each well and incubated for 30 min at room temperature and protected from light and finally the absorbance was measured at 490 nm (Biotek® - Gen5™ software). The positive control was obtained exposing the cells to Triton-X and the background was culture medium without cells. Two independent experiments with three technical replicates were performed to test each sample. The cellular viability in relation to the control group (unexposed) is calculated from equation 4 (the background absorbance was corrected as described for the WST-8 assay):

$$Cell\ viability\ (\%\ of\ control) = \frac{LDH_{lysed} - LDH_{exposed}}{LDH_{lysed} - LDH_{control}} \times 100\% \qquad (4)$$

where LDH lysed is the absorbance from wells treated with Triton-X (maximum LDH release), LDH exposed is the absorbance from wells exposed to particle suspensions, and LDH control is the absorbance from cells in the control group (spontaneous LDH release). Field blanks and solvent controls (DMSO) were also included in the assays. The viabilities of blank samples and solvents were not significantly different from the unexposed control.

8.2.5. Mutagenicity assay

Mutagenicity of the PM_{10} -bound PAHs was evaluated by the *Salmonella* reverse mutation assay (Ames test, pre-incubation method) (Mortelmans and Zeiger, 2000; OECD, 1997). Although the reverse mutation test relies on the use of prokaryotic cells, hampering the direct extrapolation of the results to human health effects, it is a useful initial screening tool for genotoxic activity and has been widely employed to assess atmospheric PM (Claxton et al., 2004, and references therein; OECD, 1997). Despite the differences between prokaryotic and mammalian cells (uptake, metabolism, chromosome structure and DNA repair processes), many compounds that are positive in this test are mammalian carcinogens (OECD, 1997).

In the present study, two *Salmonella typhimurium* strains, TA98 and TA100 (Trinova Biochem GmbH), were selected, which are used to determine frameshift mutations and base pair substitution mutations, respectively (Mortelmans and Zeiger, 2000; OECD, 1997). The direct and indirect mutagenic potential was determined in the absence and presence of an exogenous activating metabolising enzyme system (S9, Sigma Aldrich) to detected mutagens that require metabolic activation to form DNA-reactive intermediates (Ames et al., 1975; OECD, 1997). For assays performed without metabolic activation system, the positive controls were sodium azide (Acros Organics) and 2-nitrofluorene (Sigma Aldrich) for TA100 and TA98, respectively. For assays performed with metabolic activation system, the positive control was 2-aminoanthracene (Sigma Aldrich). The spontaneous mutant frequency was evaluated by negative controls exposing bacteria to DMSO and distilled sterile water. The *Salmonella typhimurium* strains were grown in nutrient broth for 15-18 h at 37 °C. After the incubation period, the tester strains were exposed to the chemical for 20 min in 0.5 ml of either buffer or S9 mix, prior to plating on glucose agar minimal medium. After 48 h incubation at 37 °C, the number of revertant colonies was determined. The solutions used for the assay were prepared according to Mortelmans and Zeiger (2000). Taking into consideration the limited volume of sample, each extract was tested at its maximum concentration (range from 10 to 150 ng per plate) in order to assess the mutagenicity. Three technical replicates were performed for each concentration.

8.2.6. Statistical analysis

Data analysis was carried out with SPSS software (IBM Statistics software v. 24). Shapiro-Wilk and Levene's tests were firstly applied to evaluate the normality of data and homogeneity of variances, respectively. The results from the cytotoxicity analysis were evaluated by the non-parametric Kruskal Wallis test followed by Dunn's post hoc tests and Bonferroni adjustment to the p-value. A correlation analysis was undertaken between the toxic responses (bioluminescent inhibition assay and WST-8) and chemical particulate composition using Spearman correlation coefficients. The results of the mutagenicity were analyzed through a one-way analysis of variance (ANOVA) followed by the Dunnett's post hoc test, to identify significant differences between the negative control and the PM_{10}-bound PAHs samples. Moreover, the mutagenicity ratio (MR: ratio between the average number of revertants in the sample and the average number of revertants in the solvent control plates) above 2 was used as criteria to identify mutagenic effects (Mortelmans and

Zeiger, 2000). All differences were regarded as statistically significant at $p < 0.05$. No significant differences were detected between the number of revertent colonies of the DMSO and sterilised water plate controls, whereby the DMSO control was used as negative control in the statistical analysis.

8.3. Results and Discussion

8.3.1. Bioluminescence inhibition assay

Several authors have supported the use of *V. fischeri* bioluminescence inhibition assay as a first screening to examine the particulate matter toxicity (Aammi et al., 2017; Kováts and Horváth, 2016; Roig et al., 2013). The assay is sensitive and performs well regarding the display of false toxicity results (Kováts et al., 2012).

The overall toxicity of PM_{10} samples was assessed using the aqueous extracts and expressed as percentage of bioluminescence inhibition after 30 min of exposure time. PM_{10} collected when the fireplace was lit showed the highest inhibition with EC_{50} values ranging from 6.6 to 17 $\mu g\ ml^{-1}$. The PM_{10} extracts resulting from the use of the woodstove caused a less pronounced effect on the bacterial suspensions with EC_{50} values ranging from 15 to 81 $\mu g\ ml^{-1}$. Outdoors, the concentrations causing 50% reduction in the *V. fischeri* bioluminescence relative to the control after 30 min of exposure were 26 to 72 $\mu g\ ml^{-1}$. Previous studies, using the *V. fischer*i bioluminescence inhibition bioassay, have assessed the toxicity of atmospheric PM and temporal patterns highlighting a higher toxicity for samples collected in the cold season than those obtained in moderate or warm temperatures (Aammi et al., 2017; Kováts et al., 2012; Roig et al., 2013; Turóczi et al., 2012). Aammi et al. (2017) collected coarse PM ($PM_{2.5\text{-}10}$) samples using a passive sampling method on a monthly basis, in twelve sampling sites from three districts in Istanbul, Turkey. The samples were extracted using DMSO and the toxicity was evaluated using the Microtox bioassay. The researchers suggested that seasonal activities, such as space heating, and meteorological factors (e.g. lower levels of atmospheric mixing and higher stability more likely during winter) were possibly responsible for the higher toxicity of samples collected in winter.

In this study, the indoor TU_{50} values varied from very toxic to extremely toxic (15 to 103) for samples obtained during the operation of the fireplace (Fig. 8.1A). For samples of the room equipped with woodstove, TU_{50} values varied within the range 1.4 (toxic) – 14 (very toxic) (Fig. 8.1B). Despite being equipped with a front door, an increase in PM_{10} concentrations and associated contaminants was still noticeable during the woodstove operation due to the opening of the door to start combustion and for refueling (Vicente et al., 2020).

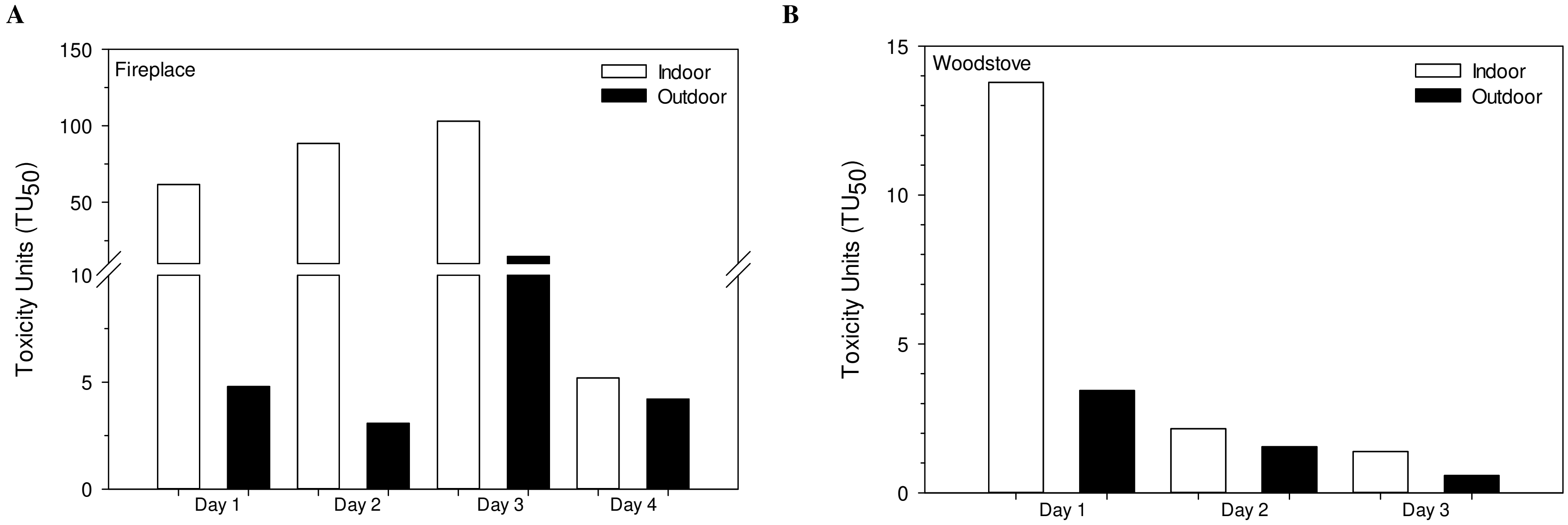

Figure 8.1. Toxicity Units (TU_{50}) calculated from EC_{50} values obtained from the *Vibrio fischeri* bioluminescent inhibition assay for the samples collected indoors during the operation of the fireplace (A) and the woodstove (B) and corresponding outdoor samples.

Indoor air background samples were collected in both rooms, one equipped with a fireplace and the other with a woodstove. For these background air samples, the TU_{50} values varied from 0.79 to 1.3. Outdoors, the TU_{50} values were lower than those recorded for samples collected in the rooms when wood burning appliances were being used and were in the range from 0.58 (non-toxic) to 5.2 (toxic).

Previous studies have underlined the capability of the assay to display a comprehensive range of toxicity values for PM samples collected at sites impacted by dissimilar sources and pollutant loads. Aammi et al. (2017) found remarkable differences in the TU_{50} recorded at different sites in Istanbul. In a heavily polluted site (local industry) TU_{50} values of 85.7 and 106 were reported, while lower values, in the range from 0.05 to 0.09, were registered in the "clean air" site. The authors pointed out that samples collected in central urban areas impacted by traffic and sites impacted by industry were significantly more toxic than the others. TU_{50} ranging from 1.5 to 3.1 (it was not possible to calculate the TU_{50} for all samples due to the low toxicity) were documented by Romano et al. (2020) for PM_{10} samples collected during moderate and warm seasons at a coastal site of the Central Mediterranean, away from large pollution sources. In the study of Roig et al. (2013), it was also possible to observe varying degrees of toxicity in PM_{10} samples collected in Catalonia (Spain) in contrasting seasons and monitoring sites (industrial, urban, and rural), which were impacted by different emission sources (cement plant, waste landfill, and municipal solid waste incinerator).

The comparison of the results of the present study with those published in the literature should be viewed with caution due to the array of sampling methods, sample extraction procedures and protocols for carrying out the bioluminescent inhibition assay. Regarding this latter, most of the studies have followed the Microtox bioassay, which differ in several aspects from the protocol used in the present study, for example in relation to the inhibition calculation method (Kováts et al., 2012).

8.3.2. Cellular metabolic activity and cellular membrane integrity

The effects of the PM_{10} samples (concentration range from 0.1 μg ml^{-1} to 150 μg ml^{-1}) on the metabolic activity of human epithelial cells were investigated with the WST-8 assay and displayed as a percentage of viability in comparison with that from unexposed cells (control). Fig. 8.2 documents a decrease in cell viability for all samples collected either inside or outside. For indoor samples collected when the fireplace was in use (Fig. 8.2A), a significant reduction of cell viability in comparison with control was reached at a concentration of 50 μg ml^{-1} for almost all samples (one sample displayed a significant reduction from 10 μg ml^{-1}). Particles from the operation of the woodstove (Fig. 8.2B) also caused a decrease in cellular metabolic activity, with significant differences compared to control starting from 100 μg ml^{-1}.

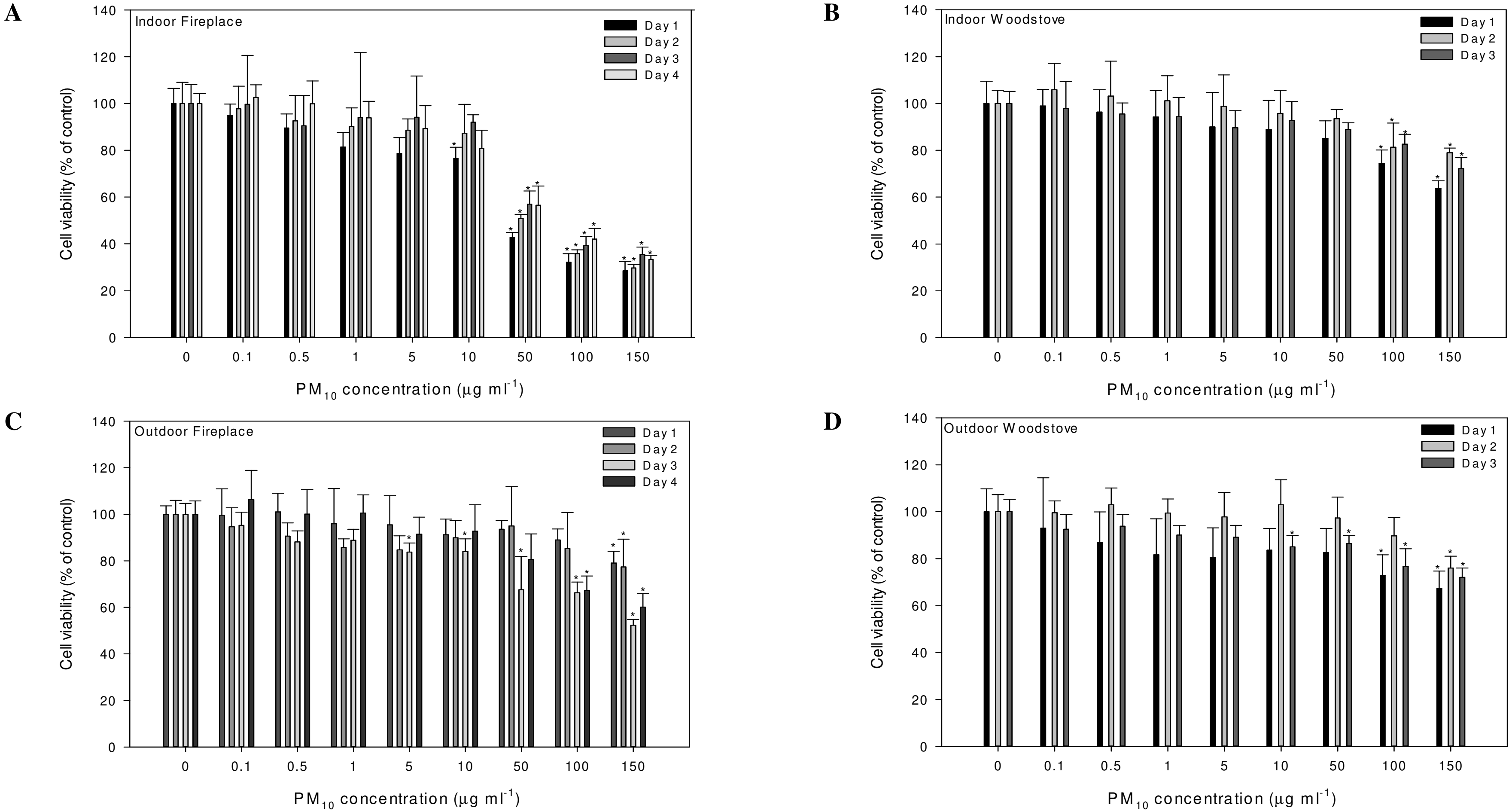

Figure 8.2. Cell viability assessed with WST-8 assay after 24 h exposure to increasing PM$_{10}$ concentrations of indoor samples during the operation of the fireplace (A) and the woodstove (B) and corresponding outdoor samples (C and D for fireplace and woodstove, respectively): 0 (control), 0.1, 0.5, 1, 5, 10, 50, 100 and 150 µg ml^{-1}. Bars represent the mean ± standard deviation of two independent experiments with five technical replicates each. Statistical analysis was performed by Kruskal-Wallis followed by Dunn's multiple comparison test. Asterisks indicate statistical significance compared to control (*n* = 10, $p<0.05$).

The metabolic activity of the cells declined down to 31.7 ± 3.19% at the highest dose (150 µg ml^{-1}) for particles generated when using the fireplace, whereas the same PM_{10} dose from the woodstove decreased the metabolic activity down to 71.6 ± 7.60%. Thus, the combustion technology had a remarkable effect on the cytotoxic potency of the particulate samples. A comparison between the cytotoxicity of indoor PM_{10} and the respective background (absence of source), was also carried out. The reduction in cell viability induced by PM_{10} samples collected indoors when the fireplace was in operation was significantly higher than that of samples obtained when the source was inactive (starting at 0.5, 50, 100 and 10 µg ml^{-1} for days 1, 2, 3 and 4, respectively). In turn, only one PM_{10} sample collected during the use of the woodstove presented significantly higher cytotoxicity than the background at the highest dose (150 µg ml^{-1}).

Previously, investigations focused on the characterisation of emissions at source have underlined the role of combustion appliances on the cytotoxicity of particles from small scale devices using the 3-[4,5-dimethylthiazole-2-yl]-2,5-diphenyltetrazolium bromide assay (MTT) (Jalava et al., 2012; Tapanainen et al., 2011). Studies assessing the cytotoxicity of atmospheric particulate matter during the cold and warm months of the year have reported higher cytotoxic potential of samples collected during winter (Gualtieri et al., 2010; Happo et al., 2013; Van Drooge et al., 2017). Seasonal pollution sources, such as biomass burning for residential heating, in association with meteorological factors, have been described as the main responsible factors.

In the present study, outdoor samples caused a decrease from 21 to 48% in A549 metabolic activity. A decrease in cell viability, with significant differences compared to control starting at doses ranging from 5 to 150 µg ml^{-1}, depending on the sampling day, were recorded. The daily variability in the cytotoxicity of outdoor particles was noticeable (Fig. 8.2C and D) and might be ascribed to distinct weather conditions in different monitoring days.

The comparison of indoor and outdoor PM_{10} cytotoxicity, for matched pair data, was also carried out. The reduction in cell viability induced by PM_{10} samples collected when the fireplace was in operation was significantly higher indoors than the parallel samples collected outdoors (starting at 5, 50, 100 and 10 µg ml^{-1} for day 1, 2, 3 and 4, respectively), whereas such effect was not seen with the woodstove samples. Fig. 8.3 displays the comparison of indoor/outdoor cytotoxicity at the highest dose tested (150 µg ml^{-1}).

The effects of the PM_{10} samples (concentration range from 0.1 µg ml^{-1} to 150 µg ml^{-1}) on the membrane integrity of A549 cells, investigated with the LDH assay, are displayed in Fig. 8.4 as a percentage of viability in comparison with that from unexposed cells (control). The results revealed no significant increase in the release of the cytoplasmic enzyme LDH into the culture supernatant after cell exposure, reflecting the maintenance of the cell membrane integrity.

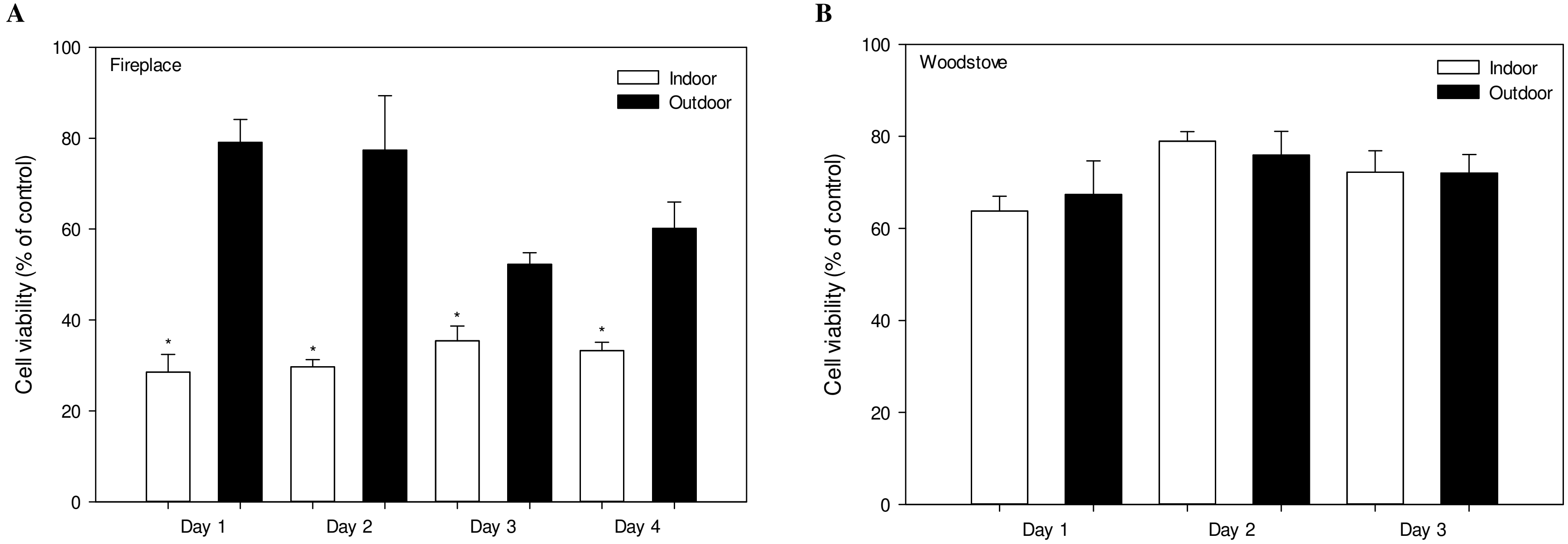

Figure 8.3. Cell viability assessed with WST-8 assay after 24 h exposure to the highest PM_{10} concentrations (150 μg ml^{-1}) from samples collected indoors during the operation of the fireplace (A) and the woodstove (B) and corresponding outdoor samples. Bars represent the mean ± standard deviation of two independent experiments. Statistical analysis was performed by Kruskal Wallis. Asterisks indicate statistical significance compared to outdoor PM_{10} samples (n = 10, $p<0.05$).

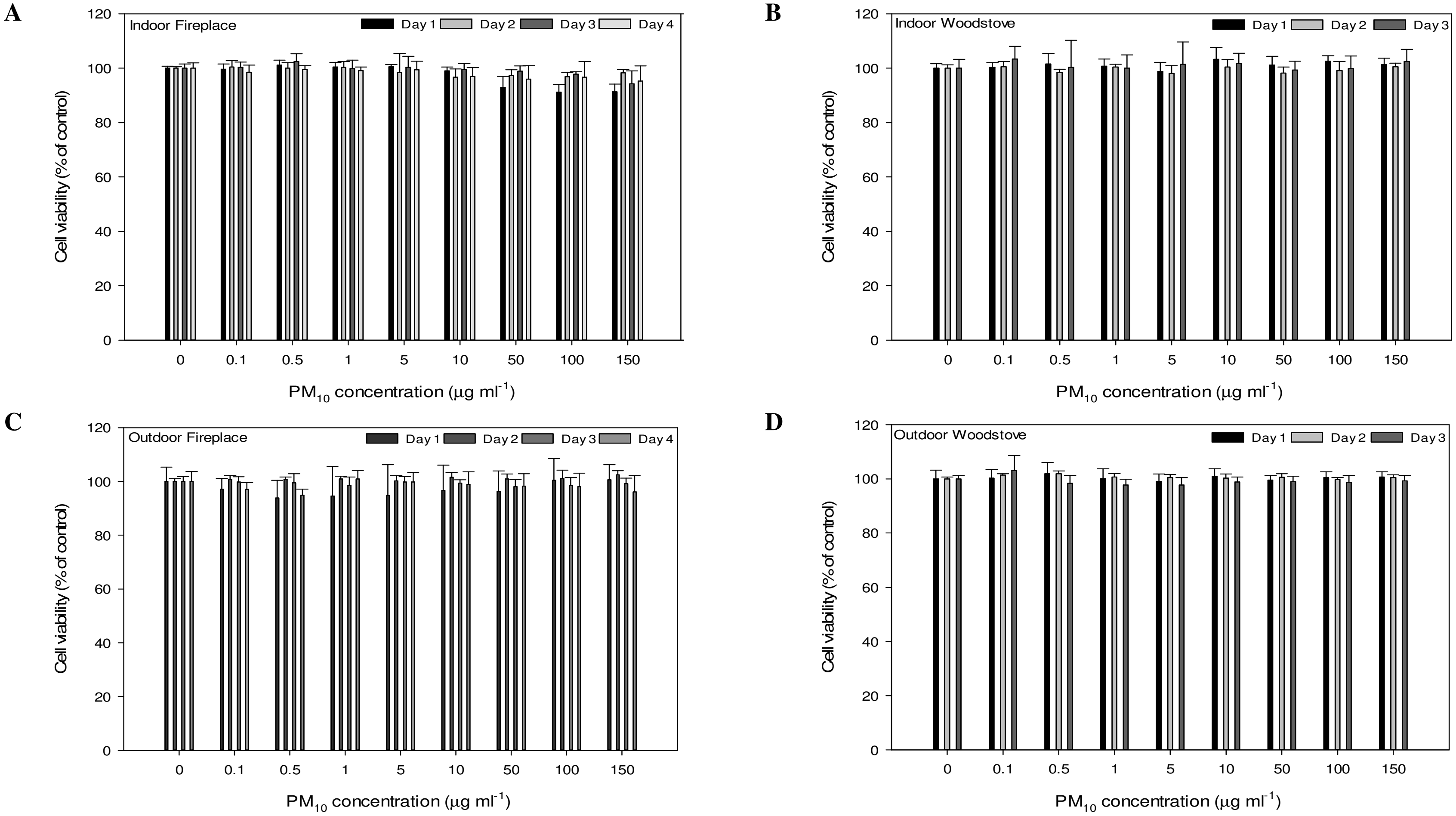

Figure 8.4. Cell viability assessed with LDH assay after 24 h exposure to increasing PM_{10} concentrations during the operation of the fireplace (A) and the woodstove (B) and respective outdoor samples (C and D for fireplace and woodstove, respectively): 0 (control), 0.1, 0.5, 1, 5, 10, 50, 100 and 150 µg ml^{-1}. Bars represent the mean ± standard deviation of two independent experiments with three technical replicates each. Statistical analysis was performed by Kruskal-Wallis. Asterisks indicate statistical significance compared to control ($n = 6$, $p<0.05$).

This is in agreement with the results obtained by Kocbach et al. (2008). The researchers observed no decrease in the monocyte cell line THP-1 viability (measured as LDH release) after exposure to the extracts of wood smoke particles collected from a conventional Norwegian stove. Similarly, Kasurinen et al. (2017) obtained size-segregated PM emissions from two wood-fired appliances and tested different cell viability endpoints (metabolic activity, membrane integrity, and lysosomal damage) in order to investigate the mechanisms behind the cytotoxicity of wood combustion-generated particles. The authors found no significant reduction of the membrane integrity nor in lysosomal integrity after PM exposure compared to unexposed cells. However, all samples caused a significant reduction in the A549 metabolic activity. The results obtained by the researchers suggested that the mechanism of cell death was apoptosis in which the integrity of the plasma membrane is maintained. The results obtained by Marchetti et al. (2019) also indicated apoptosis behind the cell (A549) viability impairment after cell exposure to indoor particles arising from wood combustion in an open fireplace.

8.3.3. Mutagenicity assay

The number of revertant colonies obtained from the mutagenicity tests with PAHs extracted from PM_{10} and MR are presented in Table 8.1.

PAH extracts from PM_{10} samples collected indoors and outdoors showed no direct- or indirect-acting mutagenic effect towards both strains under the test conditions. The significantly higher ($p < 0.05$) number of revertants in the positive control plates in comparison with the number in the solvent control and in sample containing plates, as well as the MR between positive and negative controls, demonstrate the effective performance of the assays.

Several researches have pointed out the importance of PAH metabolic activation into primary and secondary metabolites on the toxicological effects observed. On the other hand, the toxicity of the parent PAHs is, in general, considered negligible (Mesquita et al., 2014 and references therein). Despite the proved importance of metabolic activation during the organism detoxification process, studies focusing on PM-bound PAHs from biomass burning emissions have reported a mutagenic effect in the absence of a metabolic agent using specific *Salmonella* strains (Canha et al., 2016; Vu et al., 2012). Vu et al. (2012) tested $PM_{2.5}$-bound PAH extracts from the combustion of different biofuels (seven wood species and briquettes) in two appliances (fireplace and woodstove) under two operating conditions (cold and hot start) for mutagenic activities using the Ames test with *Salmonella typhimurium* TA98 and TA100. The authors reported a direct-acting mutagenicity for almost all biofuels and concluded that combustion in a fireplace seems to favour the emission of mutagenic compounds. When S9 was introduced to the test, the mutagenic effect disappeared, suggesting that the samples contained direct-acting base-pair and frameshift mutagens that lose their mutagenicity after being metabolised by enzymes from the S9 liver fraction. The same conclusion was drawn by Canha et al. (2016) who reported a decrease of mutagenicity of the extracts of PM_{10}-bound PAHs from small scale residential combustion of different biofuels in a woodstove and pellet stove when metabolic activation was added. Oanh et al. (2002) assessed the mutagenic potency (Ames test) of particles released from three different cookstoves burning different fuels. The results for the TA98 strain indicated the presence of both direct and indirect mutagenic activity in PM samples from sawdust and wood. On the other hand, the TA100 strain only detected direct mutagenic activity of PM samples.

Table 8.1. Mutagenicity of PAH extracts of particles collected indoors and outdoors to S. typhimurium TA98 and TA100 strains in the absence (-S9) and presence (+S9) of metabolic activation.

			TA100 -S9		TA100 +S9		TA98 -S9		TA98 +S9	
		ng PAHs/plate	Rev/plate	MR	Rev/plate	MR	Rev/plate	MR	Rev/plate	MR
Fireplace										
Indoor	Day 1	100	162 ± 30	1.2	179 ± 15	1.1	21 ± 2	1.3	17 ± 5	0.89
	Day 2	150	136 ± 8	1.0	191 ± 26	1.2	15 ± 3	0.94	16 ± 1	0.84
	Day 3	150	164 ± 8	1.2	181 ± 14	1.1	20 ± 3	1.3	16 ± 5	0.84
	Day 4	50	124 ± 20	0.94	143 ± 4	0.89	16 ± 4	1.0	16 ± 1	0.84
Outdoor	Day 1	30	146 ± 15	1.1	138 ± 23	0.86	21 ± 2	1.3	22 ± 11	1.2
	Day 2	30	111 ± 31	0.84	169 ± 7	1.0	22 ± 3	1.4	18 ± 6	0.95
	Day 3	30	137 ± 20	1.0	154 ± 14	1.0	21 ± 2	1.3	16 ± 4	0.84
	Day 4	30	104 ± 27	0.79	146 ± 25	0.91	23 ± 4	1.4	26 ± 5	1.4
Woodstove										
Indoor	Day 1	55	129 ± 7	0.98	169 ± 21	1.0	15 ± 8	0.94	28 ± 8	1.5
	Day 2	10	132 ± 14	1.0	180 ± 26	1.1	12 ± 1	0.75	28 ± 6	1.5
	Day 3	25	125 ± 8	0.95	140 ± 27	0.87	9 ± 2	0.56	21 ± 6	1.1
Outdoor	Day 1	30	124 ± 23	0.94	145 ± 12	0.90	11 ± 4	0.69	18 ± 3	0.95
	Day 2	20	124 ± 11	0.94	148 ± 7	0.92	8 ± 4	0.50	16 ± 2	0.84
	Day 3	15	151 ± 15	1.1	159 ± 22	0.99	12 ± 3	0.75	13 ± 2	0.68
	PC		3077 ± 681*	**24**	524 ± 83*	**3.3**	131 ± 24*	**8.2**	268 ± 78*	**14**
	DMSO		132 ± 23		161 ± 15		16 ± 6		19 ± 3	

Values are means ± standard deviation of 3 plates. MR = mutagenicity ratio; Rev/plate = revertants per plate; PC = positive control. Statistical analysis was performed by one-way ANOVA with Dunnett's multiple comparison test. Asterisks indicate statistical significance compared to negative control ($p<0.05$). Mutagenicity ratios above 2 are marked in bold.

Galvão et al. (2018) collected PM_{10} samples during intense and moderate biomass burning periods in the Brazilian Amazon region. The extractable organic matter was used to assess the mutagenic potential of the samples using two different bacterial strains (TA98 and YG1041). The researchers reported that the mutagenic potencies were higher in the absence of metabolic activation, regardless of the strain used, showing a large contribution of direct acting mutagens.

In addition to different protocols (e.g. standard plate incorporation assay, pre-incubation assay, microsuspension assay) and bacterial strains applied to assess the PM mutagenicity, distinct sample preparation procedures have been described in the literature. For example, the studies of Canha et al. (2016) and Vu et al. (2012) were performed with the PAH extracts, while Oanh et al. (2002) and Galvão et al. (2018) carried out the Ames test with the total extractable organic matter. Moreover, the test concentrations evaluated through the Ames assay are highly variable, which may have contributed to the discrepancies in the results.

8.3.4. Correlations between biological responses and PM_{10} chemical composition

Correlations between the PM_{10} chemical composition and the impairment of cellular metabolic activity and luminescence inhibition were studied (Table 8.2). Detailed information on the chemical composition of PM_{10} has been described in a previous study (Vicente et al., 2020).

Indoors, the increase in toxicity, i.e., decrease in cellular metabolic activity of A549 cells and reduction in *V. fischeri* bioluminescence, was correlated with organic carbon. Outdoors, no significant correlations were found.

Indoors, the sum of PM_{10}-bound PAHs was significantly associated with toxicity. Over the years, discordant conclusions have been drawn regarding the role of PAHs on the cytotoxicity of biomass burning particles. While some source characterisation studies, aiming at assessing the toxic potential of PM emissions, reported significant correlations between cytotoxicity and PM-bound PAHs (Kasurinen et al., 2016; Sun et al., 2018), others recorded no correlation (Arif et al., 2017; Jalava et al., 2012). The role of PAHs in the *V. fischeri* bioluminescence inhibition has also been previously highlighted (Alves et al., 2021; Evagelopoulos et al., 2009).

The correlations between the PM_{10} toxicity and individual PAH compounds also revealed statistically significant relationships. Among the studied compounds, retene, chrysene and benzo[a]antracene were significantly correlated with the reduction in A549 cell viability (Table 8.2).

Table 8.2. Spearman correlation coefficients between PM$_{10}$ chemical composition and responses in A549 cells and *V. fischeri*.

	Indoor		Outdoor	
	WST-8	*V. fischeri*	WST-8	*V. fischeri*
Carbonaceous compunds				
OC	**-0.786***	**-0.821***	-0.357	0.214
EC	-0.571	-0.250	0.000	0.214
Monosaccharide anhydrides				
Levoglucosan	-0.571	-0.643	0.071	-0.250
Mannosan	-0.536	-0.679	-0.179	-0.429
Galactosan	-0.643	-0.607	-0.429	**-0.786***
Σ Monosaccharide anhydrides	-0.571	-0.643	-0.143	-0.500
Resin acids and derivatives				
Abietic acid	**-0.821***	-0.714	-0.335	-0.512
Dehydroabietic acid	**-0.893****	**-0.893****	0.036	-0.143
Hydroxydehydroabietic acid	-0.185	0.482	-0.036	-0.536
Oxodehydrohabietic acid methyl ester	-0.643	-0.679	-0.214	-0.750
Pimaric acid	**-0.821***	-0.714	-0.143	-0.500
Isopimaric acid	-0.750	-0.536	-0.321	-0.714
Podocarpic acid	-0.321	-0.107	-0.143	-0.393
Σ Resin acids and derivatives	**-0.857***	**-0.786***	-0.036	-0.286
Sterols				
Cholesterol	-0.107	0.321	0.393	0.464
Dihydrocholesterol	-0.679	**-0.786***	0.321	0.286
Stigmasterol	-0.750	-0.107	-0.429	-0.393
β-Sitosterol	-0.714	-0.679	-0.214	-0.464
Σ Sterols	-0.714	-0.679	-0.464	-0.750
Substituted benzenes and phenolic compounds[a]				
Sinapic acid	**-0.786***	-0.643	-0.179	-0.536
Vanillin	**-0.778***	**-0.889****	0.071	-0.393
Acetovanilone	-0.630	**-0.778***	0.214	0.071
3-Vanilpropanol	-0.649	**-0.757***	-0.214	-0.571
Homovanillic alcohol	-0.630	**-0.778***	0.071	-0.571
Syringic acid	**-0.821***	-0.643	-0.107	-0.286
Syringaldehyde	**-0.927****	-0.519	0.667	0.259
Acetosyringone	-0.630	**-0.778***	0.036	-0.321
4-Hydroxycinnamic (p-coumaric) acid	**-0.857***	-0.750	-0.223	-0.045
3,4-Dihydroxy-cinnamic (caffeic) acid	-0.75	**-0.786***	-0.286	-0.643
3-Hydroxybenzoic acid	**-0.821***	**-0.929****	0.036	-0.607
Protocatechoic acid	**-0.955****	-0.595	0.018	-0.577
1-Methyl-3,5-dihydroxybenzene (orcinol)	**-0.815***	**-0.778***	-0.134	-0.267
Pyrogallol	-0.750	**-0.786***	-0.250	-0.679
Hydroquinone	-0.667	**-0.847***	-0.270	**-0.757***
PAHs				
Naphthalene	0.079	0.571	0.670	0.079
Acenaphthylene	-0.453	-0.256	0.223	-0.089
Acenaphthene	-0.741	-0.222	0.612	0.408
Fluorene	-0.612	-0.408	0.591	0.079
Phenanthrene	-0.571	-0.536	0.414	-0.180
Anthracene	-0.643	-0.357	-0.296	-0.371
Fluoranthene	-0.571	-0.750	0.107	-0.500
Pyrene	0.071	-0.286	-0.071	-0.464
Chrysene	**-0.821***	-0.464	0.286	-0.286
Benzo[a]anthracene	**-0.821***	-0.464	0.071	-0.464
p-Terphenyl	-0.750	**-0.786***	0.250	-0.321

Retene	**-0.786***	**-0.964****	0.500	-0.214
Perylene	-0.464	-0.036	-0.286	**-0.786***
Benzo[b]fluoranthene	-0.500	-0.107	-0.286	-0.500
Benzo[k]fluoranthene	-0.464	-0.036	-0.536	-0.643
Benzo[e]pyrene	-0.500	-0.107	-0.107	-0.571
Benzo[a]pyrene	-0.679	-0.286	-0.107	-0.679
Benzo[g,h,i]perylene	0.107	0.500	-0.357	-0.536
Dibenzo[a,h]anthracene	-0.250	0.429	-0.500	-0.393
Indeno[1,2,3-cd]pyrene	-0.107	0.286	-0.714	-0.607
Σ PAHs	**-0.929****	**-0.857***	-0.036	-0.536
Water soluble ions				
Chloride	0.750	**0.893****	-0.286	0.143
Nitrate	0.286	**0.786***	-0.036	-0.214
Sulfate	0.679	0.571	0.143	-0.143
Fluoride	-0.214	-0.643	-0.234	-0.685
Phosphate	**0.906****	**0.768***	-0.286	0.214
Sodium	0.607	0.750	-0.071	0.250
Potassium	0.500	0.321	-0.679	**-0.821***
Magnesium	0.750	0.500	-0.214	0.214
Calcium	0.286	0.036	-0.214	-0.714
Σ Water soluble ions	**0.857***	**0.929****	-0.071	0.464

Significant correlation coefficients at the p-level < 0.05 and 0.01, are marked with * and **, respectively. OC: organic carbon; EC: elemental carbon. [a]Only significant correlations are displayed.

Previous studies, aiming at assessing the cytotoxic potential of retene and other polyaromatic compounds in biomass burning emissions, reported the ability of this alkylated phenanthrene to significantly decrease cell viability (A549) at a dose of 30 ng ml^{-1} after 72 h of exposure (Alves et al., 2017; Peixoto et al., 2019). In the present study, the sum of polyaromatic compounds associated with outdoor PM_{10} showed no correlation with the toxicity assessed with the WST-8 assay and only perylene was significantly correlated with the *V. fischeri* bioluminescent inhibition.

In the present study, anhydrosugars were the dominant group of organic compounds in samples collected both indoors and outdoors (Vicente et al., 2020). Indoors, no significant correlations were recorded between increased PM_{10} toxicity towards A549 cells and monosaccharide anhydrides (both their sum and each isomer individually). Similarly, monosaccharide anhydrides showed no association with the decrease in cellular metabolic activity of epithelial lung cells for outdoor samples. Previous studies, assessing PM collected at sites impacted by biomass burning, have found associations between these compounds and increased toxicity using different cell lines (Van Den Heuvel et al., 2018; Van Drooge et al., 2017). Van Den Heuvel et al. (2018) evaluated the biological effects of PM_{10} sampled in ambient air at an urban traffic site and a rural background location in Belgium. The researchers exposed BEAS-2B cells to PM_{10} to study the cell damage and death, reporting that reduced cell viability was associated with biomass burning markers (levoglucosan, mannosan and galactosan). Van Drooge et al. (2017) evaluated the toxicity of organic extracts from outdoor PM_1 samples from rural and urban locations in JEG-3 human placental cells.

The researchers correlated the cytotoxicity of the samples collected in winter at the rural site with biomass burning tracer compounds (levoglucosan, mannosan, galactosan and dehydroabietic acid), and with other combustion products (benzo[b+j+k]fluoranthene, benzo[e]pyrene, benzo[a]pyrene and indeno[1,2,3-cd]pyrene). Outdoors, the *V. fischeri* bioluminescent inhibition was significantly correlated with galactosan.

Indoors, several other biomass burning markers, such as resin acids, phenolic compounds and sterols, displayed significant correlations with toxicity. The resin acids abietic and pimaric, as well as the oxidised derivative dehydroabietic acid, were significantly correlated with PM cytotoxicity (WST-8). Additionally, dehydroabietic acid was also found to correlate with the *V. fischeri* bioluminescence inhibition. Several guaiacol and syringol type methoxyphenols (e.g. vanillin, acetovanilone, 3-vanilpropanol, syringaldehyde, sinapic acid and syringic acid) linked to PM_{10} from the indoor air were significantly correlated with cytotoxic effects (WST-8) and/or with bioluminescence inhibition.

Although a number of studies have suggested that ionic species (e.g. NO_3^-, Cl^-, SO_4^{2-}) may participate in cytotoxicity induced by ambient particles (Chen et al., 2006; Happo et al., 2014; Perrone et al., 2010; Velali et al., 2016), in the present research only phosphate presented a positive significant correlation with the WST-8 assay for indoor samples, implying a decreasing effect for increasing ionic PM_{10} mass fractions. Outdoors, water soluble potassium was correlated with the *V. fisheri* bioluminescence inhibition.

It must be mentioned that correlations with the elemental composition of the particles was not undertaken since pooled samples were used for the analyses by inductively coupled plasma (Vicente et al., 2020) due to sample shortage. Despite the relatively low contribution of major and trace elements to the PM_{10} mass (2.20 and 14.1 wt% of the PM_{10}) (Vicente et al., 2020), it is possible that some of these elements may have contributed to the toxicity of the samples. In fact, previous *in vitro* studies involving particles from biomass burning have underlined the importance of PM-bound metals in particle-mediated cytotoxicity (Arif et al., 2017; Kasurinen et al., 2017, 2016; Uski et al., 2015). Studies assessing the cytotoxicity of atmospheric PM also highlighted the role of metals on the results, pointing out significant correlations between decreased cell viability and PM-bound elements, such as cadmium, zinc, copper, chromium, lead, vanadium, tin and arsenic (Happo et al., 2014; Perrone et al., 2010; Roig et al., 2013; Van Den Heuvel et al., 2016; Velali et al., 2016). Roig et al. (2013) also found that several of these PM-bound elements correlated with the decrease in bioluminescence of bacterial suspensions (*V. fischeri*).

The apparent inconsistency between the results of the current work and literature data may be associated with several factors, which might have a pronounced effect on results: i) different cell lines (Arif et al., 2017; Corsini et al., 2017; Danielsen et al., 2009; Gualtieri et al., 2010); ii) sample preparation procedures (e.g. extraction solvent and method, resuspension solvent) (Danielsen et al., 2009; Landkocz et al., 2017); iii) PM size fraction under analysis; iv) cytotoxicity test selected (e.g. Alamar Blue, MTT, WST-1,8, LDH); v) test conditions (e.g. incubation time, exposure doses, among others) (Cavanagh et al., 2009; Danielsen et al., 2009; Gualtieri et al., 2010; Happo et al., 2013; Hiebl et al., 2017; Landkocz et al., 2017; Peixoto et al., 2017).

8.4. Conclusions

Residential settings are of utmost importance in relation to human exposure to environmental pollutants since it is where people spend most of their time. Despite being one of the major health determinants, most regulations that set air quality requirements only apply to outdoor and workplace environments. In the coldest months of the year, biomass burning is a major source of atmospheric pollutants and it was also proven to be a major indoor source of hazardous compounds, including particulate matter. The present study aimed at investigating the toxicity induced by wood burning particles, in indoor and outdoor environments, using various bioassays (*V. fischeri* inhibition assay, WST-8, LDH and Ames test). The overall toxicity was assessed using aqueous extracts of PM_{10} samples by the *V. fischeri* inhibition assay. The results allowed to discriminate between different levels of toxicity, highlighting that samples from the operation of the open fireplace were more toxic than those collected when the woodstove was in use. It was also concluded that the particulate material in rooms with wood combustion equipment is more toxic than that observed outdoors. The PM_{10} cytotoxicity was determined by measuring the mitochondrial activity with the WST-8 assay in human A549 lung epithelial cells. After exposure, a reduction in the cellular metabolic activity for all indoor and outdoor samples was recorded. At the highest concentration, the cell viability impairment was about two-fold higher for the samples collected with the fireplace in operation compared to those of the woodstove. PM_{10} samples significantly decreased the metabolic activity of the mitochondria and showed clear daily variability. The outdoor samples were significantly less cytotoxic than their corresponding indoor air counterparts during the operation of the fireplace, whereas no such effect was observed with the woodstove samples. After the exposure period, no significant elevation in LDH secretion was observed at all tested concentrations for both indoor and outdoor samples.

The correlation analysis suggests that particle bound constituents can induce changes in biological responses. Organic carbon of indoor particles was found to play a significant role in the *V. fischeri* bioluminescent activity and A549 metabolic activity. Several combustion-related organic compounds, such as PAHs, displayed significant correlations with the increase in toxicity using both assays. In outdoor samples, a lower number of compounds were found to correlate with the impairment of the targeted cells. Taking into account the results of the present study, homeowners should be encouraged to upgrade the wood burning technology in order to reduce the products of incomplete combustion bound to PM.

The bioassays used in the present study are useful for a first screening of the potential toxicity of particulate matter and associated compounds and can be indicated as efficient methods to routinely complement chemical analysis. Despite the valuable insight given by these tests, other complementary bioassays are needed to make inferences about impacts on human health. *In vitro* studies involving lung cells can be improved by the use of cell co-cultures in which the *in vivo* cell interactions, which can exacerbate or inhibit the toxicological response, can be simulated. Additionally, to overcome the limitations of submerged cell culturing, future work should focus on air-liquid interface systems, in which the exposure is performed through aerosolised particles mimicking more closely physiologic conditions in the lung and therefore creating more realistic conditions of exposure via inhalation. Moreover, it should be borne in mind that *in vivo* exposure is affected not only by the exposure concentrations but also by the deposition rate of particles, clearance mechanisms and retention of particles within the respiratory system, which are not represented in these bioassays.

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References

Aammi, S., Karaca, F., Petek, M., 2017. A toxicological and genotoxicological indexing study of ambient aerosols ($PM_{2.5-10}$) using *in vitro* bioassays. Chemosphere 174, 490–498. https://doi.org/10.1016/j.chemosphere.2017.01.141

Abbas, M., Adil, M., Ehtisham-ul-Haque, S., Munir, B., Yameen, M., Ghaffar, A., Shar, G.A., Asif Tahir, M., Iqbal, M., 2018. *Vibrio fischeri* bioluminescence inhibition assay for ecotoxicity assessment: A review. Sci. Total Environ. 626, 1295–1309. https://doi.org/10.1016/j.scitotenv.2018.01.066

Alves, C.A., Vicente, E.D., Evtyugina, M., Vicente, A.M.P., Sainnokhoi, T.A., Kováts, N., 2021. Cooking activities in a domestic kitchen: chemical and toxicological profiling of emissions. Sci. Total Environ. 772, 145412. https://doi.org/10.1016/j.scitotenv.2021.145412

Alves, N.D.O., Vessoni, A.T., Quinet, A., Fortunato, R.S., Kajitani, G.S., Peixoto, M.S., De Souza Hacon, S., Artaxo, P., Saldiva, P., Menck, C.F.M., De Medeiros, S.R.B., 2017. Biomass burning in the Amazon region causes DNA damage and cell death in human lung cells. Sci. Rep. 7, 1–13. https://doi.org/10.1038/s41598-017-11024-3

Ames, B.N., Joyce, M., Yamasaki, E., 1975. Methods for detecting carcinogens and mutagens with the salmonella/mammalian-microsome mutagenicity test. Mutat. Res. 31, 347–363.

Arif, A.T., Maschowski, C., Garra, P., Garcia-Kaufer, M., Petithory, T., Trouve, G., Dieterlen, A., Mersch-Sundermann, V., Khanaqa, P., Nazarenko, I., Gminski, R., Gier, R., 2017. Cytotoxic and genotoxic responses of human lung cells to combustion smoke particles of Miscanthus straw, softwood and beech wood chips. Atmos. Environ. 163, 138–154. https://doi.org/10.1016/j.atmosenv.2017.05.019

Atkinson, R.W., Mills, I.C., Walton, H.A., Anderson, H.R., 2015. Fine particle components and health - A systematic review and meta-analysis of epidemiological time series studies of daily mortality and hospital admissions. J. Expo. Sci. Environ. Epidemiol. 25, 208–214. https://doi.org/10.1038/jes.2014.63

Brasche, S., Bischof, W., 2005. Daily time spent indoors in German homes – Baseline data for the assessment of indoor exposure of German occupants. Int. J. Hyg. Environ. Health 208, 247–253. https://doi.org/10.1016/J.IJHEH.2005.03.003

Canha, N., Lopes, I., Vicente, E.D., Vicente, A.M., Musa Bandowe, B.A., Almeida, S.M., Alves, C.A., 2016. Mutagenicity assessment of aerosols in emissions from domestic combustion processes. Environ. Sci. Pollut. Res. 24. https://doi.org/10.1007/s11356–016–6292-2

Castro, A., Calvo, A.I., Blanco-Alegre, C., Oduber, F., Alves, C., Coz, E., Amato, F., Querol, X., Fraile, R., 2018. Impact of the wood combustion in an open fireplace on the air quality of a living room: Estimation of the respirable fraction. Sci. Total Environ. 628–629, 169–176. https://doi.org/10.1016/j.scitotenv.2018.02.001

Cavanagh, J.E., Trought, K., Brown, L., Duggan, S., 2009. Exploratory investigation of the chemical characteristics and relative toxicity of ambient air particulates from two New Zealand cities. Sci. Total Environ. 407, 5007–5018. https://doi.org/10.1016/j.scitotenv.2009.05.020

Chen, S.J., Cheng, S.Y., Shue, M.F., Huang, K.L., Tsai, P.J., Lin, C.C., 2006. The cytotoxicities induced by PM_{10} and particle-bound water-soluble species. Sci. Total Environ. 354, 20–27. https://doi.org/10.1016/j.scitotenv.2004.11.012

Cho, C., Hsieh, W., Tsai, C., Chen, C., Chang, H., Lin, C., 2018. *In Vitro* and *in vivo* experimental studies of $PM_{2.5}$ on disease progression. Int. J. Environ. Res. Public Health 15, 1–26. https://doi.org/10.3390/ijerph15071380

Claxton, L.D., Matthews, P.P., Warren, S.H., 2004. The genotoxicity of ambient outdoor air, a review: Salmonella mutagenicity. Mutat. Res. - Rev. Mutat. Res. 567, 347–399. https://doi.org/10.1016/j.mrrev.2004.08.002

Corsini, E., Marinovich, M., Vecchi, R., 2019. Ultrafine particles from residential biomass combustion: A review on experimental data and toxicological response. Int. J. Mol. Sci. 20. https://doi.org/10.3390/ijms20204992

Corsini, E., Ozgen, S., Papale, A., Galbiati, V., Lonati, G., Fermo, P., Corbella, L., Valli, G., Bernardoni, V., Dell'Acqua, M., Becagli, S., Caruso, D., Vecchi, R., Galli, C.L., Marinovich, M., 2017. Insights on wood combustion generated proinflammatory ultrafine particles (UFP). Toxicol. Lett. 266, 74–84. https://doi.org/10.1016/j.toxlet.2016.12.005

Danielsen, P.H., Loft, S., Jacobsen, N.R., Jensen, K.A., Autrup, H., Ravanat, J.L., Wallin, H., Møller, P., 2010. Oxidative stress, inflammation, and DNA damage in rats after intratracheal instillation or oral exposure to ambient air and wood smoke particulate matter. Toxicol. Sci. 118, 574–585. https://doi.org/10.1093/toxsci/kfq290

Danielsen, P.H., Loft, S., Kocbach, A., Schwarze, P.E., Møller, P., 2009. Oxidative damage to DNA and repair induced by Norwegian wood smoke particles in human A549 and THP-1 cell lines. Mutat. Res. Toxicol. Environ. Mutagen. 674, 116–122. https://doi.org/10.1016/j.mrgentox.2008.10.014

de Gennaro, G., Dambruoso, P.R., Di Gilio, A., di Palma, V., Marzocca, A., Tutino, M., 2015. Discontinuous and continuous indoor air quality monitoring in homes with fireplaces or wood stoves as heating system. Int. J. Environ. Res. Public Health 13, 1–9. https://doi.org/10.3390/ijerph13010078

Dilger, M., Orasche, J., Zimmermann, · Ralf, Paur, H.-R., Silvia Diabaté, ·, Weiss, · Carsten, 2016. Toxicity of wood smoke particles in human A549 lung epithelial cells: the role of PAHs, soot and zinc. Arch. Toxicol. 90, 3029–3044. https://doi.org/10.1007/s00204-016-1659-1

Dockery, D.W., 2009. Health effects of particulate air pollution. Ann. Epidemiol. 19, 257–63. https://doi.org/10.1016/j.annepidem.2009.01.018

Evagelopoulos, V., Zoras, S., Samaras, P., Triantafyllou, A., Albanis, T., Kassomenos, P., 2009. Toxicity of fine and coarse atmospheric particles using *Vibrio fischeri*, in: Kungolos, A., Aravossis, K., Karagiannidis, A., Samaras, P. (Eds.), 2nd International Conference on Environmental Management, Engineering, Planning and Economics (CEMEPE 2009) & SECOTOX Conference. Greece.

Galvão, M.F. de O., Alves, N. de O., Ferreira, P.A., Caumo, S., Vasconcellos, P. de C., Artaxo, P., Hacon, S. de S., Roubicek, D.A., de Medeiros, S.R.B., 2018. Biomass burning particles in the Brazilian Amazon region: Mutagenic effects of nitro and oxy-PAHs and assessment of health risks. Environ. Pollut. 233, 960–970. https://doi.org/10.1016/j.envpol.2017.09.068

Gualtieri, M., Øvrevik, J., Holme, J.A., Perrone, M.G., Bolzacchini, E., Schwarze, P.E., Camatini, M., 2010. Differences in cytotoxicity versus pro-inflammatory potency of different PM fractions in human epithelial lung cells. Toxicol. Vitr. 24, 29–39. https://doi.org/10.1016/j.tiv.2009.09.013

Guo, L., Lewis, J.O., McLaughlin, J.P., 2008. Emissions from Irish domestic fireplaces and their impact on indoor air quality when used as supplementary heating source. Glob. Nest J. 10, 209–216.

Happo, M., Markkanen, A., Markkanen, P., Jalava, P., Kuuspalo, K., Leskinen, A., Sippula, O., Lehtinen, K., Jokiniemi, J., Hirvonen, M.R., 2013. Seasonal variation in the toxicological properties of size-segregated indoor and outdoor air particulate matter. Toxicol. Vitr. 27, 1550–1561. https://doi.org/10.1016/j.tiv.2013.04.001

Happo, M.S., Sippula, O., Jalava, P.I., Rintala, H., Leskinen, A., Komppula, M., Kuuspalo, K., Mikkonen, S., Lehtinen, K., Jokiniemi, J., Hirvonen, M.R., 2014. Role of microbial and chemical composition in toxicological properties of indoor and outdoor air particulate matter. Part. Fibre Toxicol. 11, 60. https://doi.org/10.1186/s12989-014-0060-6

Hiebl, B., Peters, S., Gemeinhardt, O., Niehues, S.M., Jung, F., 2017. Impact of serum in cell culture media on *in vitro* lactate dehydrogenase (LDH) release determination. J. Cell. Biotechnol. 3, 9–13. https://doi.org/10.3233/jcb-179002

Jalava, P.I., Happo, M.S., Kelz, J., Brunner, T., Hakulinen, P., Mäki-Paakkanen, J., Hukkanen, A., Jokiniemi, J., Obernberger, I., Hirvonen, M.-R., 2012. *In vitro* toxicological characterization of particulate emissions from residential biomass heating systems based on old and new technologies. Atmos. Environ. 50, 24–35. https://doi.org/10.1016/j.atmosenv.2012.01.009

Jalava, P.I., Salonen, R.O., Nuutinen, K., Pennanen, A.S., Happo, M.S., Tissari, J., Frey, A., Hillamo, R., Jokiniemi, J., Hirvonen, M., 2010. Effect of combustion condition on cytotoxic and inflammatory activity of residential wood combustion particles. Atmos. Environ. 44, 1691–1698. https://doi.org/10.1016/j.atmosenv.2009.12.034

Jalava, P.I., Salonen, R.O., Pennanen, A.S., Happo, M.S., Penttinen, P., Hälinen, A.I., Sillanpää, M., Hillamo, R., Hirvonen, M.R., 2008. Effects of solubility of urban air fine and coarse particles on cytotoxic and inflammatory responses in RAW 264.7 macrophage cell line. Toxicol. Appl. Pharmacol. 229, 146–160. https://doi.org/10.1016/j.taap.2008.01.006

Jalava, P.I., Salonen, R.O., Pennanen, A.S., Sillanpää, M., Hälinen, A.I., Happo, M.S., Hillamo, R., Brunekreef, B., Katsouyanni, K., Sunyer, J., Hirvonen, M.R., 2007. Heterogeneities in inflammatory and cytotoxic responses of RAW 264.7 macrophage cell line to urban air coarse, fine, and ultrafine particles from six European sampling campaigns. Inhal. Toxicol. 19, 213–225. https://doi.org/10.1080/08958370601067863

Jia, Y., Wang, Q., Liu, T., 2017. Toxicity research of $PM_{2.5}$ compositions *in vitro*. Int. J. Environ. Res. Public Health 14, 232. https://doi.org/10.3390/ijerph14030232

Kasurinen, S., Jalava, P.I., Happo, M.S., Sippula, O., Uski, O., Zimmermann, R., Jokiniemi, J., Koponen, H., Hirvonen, M., 2017. Particulate emissions from the combustion of birch, beech, and spruce logs cause different cytotoxic responses in A549 Cells. Environ. Toxicol. 32, 1487–1499. https://doi.org/10.1002/tox

Kasurinen, S., Jalava, P.I., Uski, O., Happo, M.S., Mäki-paakkanen, J., Jokiniemi, J., Obernberger, I., Hirvonen, M., 2016. Toxicological characterization of particulate emissions from straw, Miscanthus, and poplar pellet combustion in residential boilers. Aerosol Sci. Technol. 50, 41–51. https://doi.org/10.1080/02786826.2015.1121198

Ke, S., Liu, Q., Deng, M., Zhang, X., Yao, Y., Shan, M., 2018. Cytotoxicity analysis of indoor air pollution from biomass combustion in human keratinocytes on a multilayered dynamic cell culture platform. Chemosphere 208, 1008–1017. https://doi.org/10.1016/j.chemosphere.2018.06.058

Kim Oanh, N.T., Nghiem, L.H., Phyu, Y.L., 2002. Emission of polycyclic aromatic hydrocarbons, toxicity, and mutagenicity from domestic cooking using sawdust briquettes, wood, and kerosene. Environ. Sci. Technol. 36, 833–839. https://doi.org/10.1021/es011060n

Kocbach, A., Namork, E., Schwarze, P.E., 2008. Pro-inflammatory potential of wood smoke and traffic-derived particles in a monocytic cell line. Toxicology 247, 123–132. https://doi.org/10.1016/j.tox.2008.02.014

Kováts, N., Ács, A., Kovács, A., Ferincz, Á., Turóczi, B., Gelencsér, A., 2012. Direct contact test for estimating the ecotoxicity of aerosol samples. Environ. Toxicol. Pharmacol. 33, 284–287. https://doi.org/10.1016/j.etap.2011.12.021

Kováts, N., Horváth, E., 2016. Bioluminescence-based assays for assessing eco- and genotoxicity of airborne emissions. Luminescence 31, 918–923. https://doi.org/10.1002/bio.3102

Lamberg, H., Nuutinen, K., Tissari, J., Ruusunen, J., Yli-Pirilä, P., Sippula, O., Tapanainen, M., Jalava, P., Makkonen, U., Teinilä, K., Saarnio, K., Hillamo, R., Hirvonen, M.R., Jokiniemi, J., 2011. Physicochemical characterization of fine particles from small-scale wood combustion. Atmos. Environ. 45, 7635–7643. https://doi.org/10.1016/j.atmosenv.2011.02.072

Landkocz, Y., Ledoux, F., André, V., Cazier, F., Genevray, P., Dewaele, D., Martin, P.J., Lepers, C., Verdin, A., Courcot, L., Boushina, S., Sichel, F., Gualtieri, M., Shirali, P., Courcot, D., Billet, S., 2017. Fine and ultrafine atmospheric particulate matter at a multi-influenced urban site: Physicochemical characterization, mutagenicity and cytotoxicity. Environ. Pollut. 221, 130–140. https://doi.org/10.1016/j.envpol.2016.11.054

Lappalainen, J., Juvonen, R., Nurmi, J., Karp, M., 2001. Automated color correction method for *Vibrio fischeri* toxicity test. Comparison of standard and kinetic assays. Chemosphere 45, 635–641.

Marchetti, S., Longhin, E., Bengalli, R., Avino, P., Stabile, L., Buonanno, G., Colombo, A., Camatini, M., Mantecca, P., 2019. *In vitro* lung toxicity of indoor PM_{10} from a stove fueled with different biomasses. Sci. Total Environ. 649, 1422–1433. https://doi.org/10.1016/j.scitotenv.2018.08.249

McNamara, M., Thornburg, J., Semmens, E., Ward, T., Noonan, C., 2013. Coarse particulate matter and airborne endotoxin within wood stove homes. Indoor Air 23, 498–505. https://doi.org/10.1111/ina.12043

Mesquita, S.R., van Drooge, B., Barata, C., Vieira, N., Guimarães, L., Piña, B., 2014. Toxicity of atmospheric particle-bound PAHs: An environmental perspective. Environ. Sci. Pollut. Res. 21, 11623–11633. https://doi.org/10.1007/s11356-014-2628-y

Morawska, L., Afshari, A., Bae, G.N., Buonanno, G., Chao, C.Y.H., Hänninen, O., Hofmann, W., Isaxon, C., Jayaratne, E.R., Pasanen, P., Salthammer, T., Waring, M., Wierzbicka, A., 2013. Indoor aerosols: From personal exposure to risk assessment. Indoor Air 23, 462–487. https://doi.org/10.1111/ina.12044

Mortelmans, K., Zeiger, E., 2000. The Ames Salmonella / microsome mutagenicity assay. Mutat. Res. - Fundam. Mol. Mech. Mutagen. 455, 29–60.

Nemmar, A., Holme, J.A., Rosas, I., Schwarze, P.E., Alfaro-Moreno, E., 2013. Recent advances in particulate matter and nanoparticle toxicology: A review of the *in vivo* and *in vitro* studies. Biomed Res. Int. 2013, 279371. https://doi.org/10.1155/2013/279371

OECD, 1997. Test Guideline 471. Bacteria reverse mutation. In: OCED Guidelines for the Testing of Chemicals. Organisation for Economic Co-operation and Development, Paris, France.

Peixoto, M.S., da Silva Junior, F.C., de Oliveira Galvão, M.F., Roubicek, D.A., de Oliveira Alves, N., Batistuzzo de Medeiros, S.R., 2019. Oxidative stress, mutagenic effects, and cell death induced by retene. Chemosphere 231, 518–527. https://doi.org/10.1016/j.chemosphere.2019.05.123

Peixoto, M.S., de Oliveira Galvão, M.F., Batistuzzo de Medeiros, S.R., 2017. Cell death pathways of particulate matter toxicity. Chemosphere 188, 32–48. https://doi.org/10.1016/j.chemosphere.2017.08.076

Perrone, M.G., Gualtieri, M., Ferrero, L., Porto, C. Lo, Udisti, R., Bolzacchini, E., Camatini, M., 2010. Seasonal variations in chemical composition and *in vitro* biological effects of fine PM from Milan. Chemosphere 78, 1368–1377. https://doi.org/10.1016/j.chemosphere.2009.12.071

Pope, C.A., 2000. Epidemiology of fine particulate air pollution and human health: Biologic mechanisms and who's at risk? Environ. Health Perspect. 108, 713–723. https://doi.org/10.2307/3454408

Roig, N., Sierra, J., Rovira, J., Schuhmacher, M., Domingo, J.L., Nadal, M., 2013. *In vitro* tests to assess toxic effects of airborne PM_{10} samples. Correlation with metals and chlorinated dioxins and furans. Sci. Total Environ. 443, 791–797. https://doi.org/10.1016/j.scitotenv.2012.11.022

Romano, S., Perrone, M.R., Becagli, S., Pietrogrande, M.C., Russo, M., Caricato, R., Lionetto, M.G., 2020. Ecotoxicity, genotoxicity, and oxidative potential tests of atmospheric PM_{10} particles. Atmos. Environ. 221, 117085. https://doi.org/10.1016/j.atmosenv.2019.117085

Salthammer, T., Schripp, T., Wientzek, S., Wensing, M., 2014. Impact of operating wood-burning fireplace ovens on indoor air quality. Chemosphere 103, 205–211. https://doi.org/10.1016/j.chemosphere.2013.11.067

Schlesinger, R.B., Kunzli, N., Hidy, G.M., Gotschi, T., Jerrett, M., 2006. The health relevance of ambient particulate matter characteristics: Coherence of toxicological and epidemiological inferences. Inhal. Toxicol. 18, 95–125. https://doi.org/10.1080/08958370500306016

Schweizer, C., Edwards, R.D., Bayer-Oglesby, L., Gauderman, W.J., Ilacqua, V., Juhani Jantunen, M., Lai, H.K., Nieuwenhuijsen, M., Künzli, N., 2007. Indoor time–microenvironment–activity patterns in seven regions of Europe. J. Expo. Sci. Environ. Epidemiol. 17, 170–181. https://doi.org/10.1038/sj.jes.7500490

Sun, J., Shen, Z., Zeng, Y., Niu, X., Wang, J., Cao, J., Gong, X., Xu, H., Wang, T., Liu, H., Yang, L., 2018. Characterization and cytotoxicity of PAHs in $PM_{2.5}$ emitted from residential solid fuel burning in the Guanzhong Plain, China. Environ. Pollut. 241, 359–368. https://doi.org/10.1016/j.envpol.2018.05.076

Tapanainen, M., Jalava, P.I., Mäki-paakkanen, J., Hakulinen, P., Happo, M.S., Lamberg, H., Ruusunen, J., Tissari, J., Nuutinen, K., Yli-pirilä, P., Hillamo, R., Salonen, R.O., Jokiniemi, J., Hirvonen, M., 2011. *In vitro* immunotoxic and genotoxic activities of particles emitted from two different small-scale wood combustion appliances. Atmos. Environ. 45, 7546–7554. https://doi.org/10.1016/j.atmosenv.2011.03.065

Totlandsdal, A.I., Øvrevik, J., Cochran, R.E., Herseth, J., Bølling, A.K., Låg, M., Schwarze, P., Lilleaas, E., Jørn, A., Kubátová, A., Totlandsdal, A.I., Øvrevik, J., Cochran, R.E., Totlandsdal, A.I., Øvrevik, J., Cochran, R.E., Herseth, J., 2014. The occurrence of polycyclic aromatic hydrocarbons and their derivatives and the proinflammatory potential of fractionated extracts of diesel exhaust and wood smoke particles J. Environ. Sci. Heal. Part A 49, 383–396. https://doi.org/10.1080/10934529.2014.854586

Turóczi, B., Hoffer, A., Tóth, Á., Kováts, N., Ács, A., Ferincz, Kovács, A., Gelencsér, A., 2012. Comparative assessment of ecotoxicity of urban aerosol. Atmos. Chem. Phys. 12, 7365–7370. https://doi.org/10.5194/acp-12-7365-2012

Uski, O., Jalava, P.I., Happo, M.S., Leskinen, J., Sippula, O., Tissari, J., Mäki-paakkanen, J., Jokiniemi, J., Hirvonen, M., 2014. Different toxic mechanisms are activated by emission PM depending on combustion efficiency. Atmos. Environ. 89, 623–632. https://doi.org/10.1016/j.atmosenv.2014.02.036

Uski, O., Jalava, P.I., Happo, M.S., Torvela, T., Leskinen, J., Mäki-Paakkanen, J., Tissari, J., Sippula, O., Lamberg, H., Jokiniemi, J., Hirvonen, M.R., 2015. Effect of fuel zinc content on toxicological responses of particulate matter from pellet combustion *in vitro*. Sci. Total Environ. 511, 331–340. https://doi.org/10.1016/j.scitotenv.2014.12.061

Uski, O.J., Happo, M.S., Jalava, P.I., Brunner, T., Kelz, J., Obernberger, I., Jokiniemi, J., Hirvonen, M.R., 2012. Acute systemic and lung inflammation in C57Bl/6J mice after intratracheal aspiration of particulate matter from small-scale biomass combustion appliances based on old and modern technologies. Inhal. Toxicol. 24, 952–965. https://doi.org/10.3109/08958378.2012.742172

Van Den Heuvel, R., Den Hond, E., Govarts, E., Colles, A., Koppen, G., Staelens, J., Mampaey, M., Janssen, N., Schoeters, G., 2016. Identification of PM_{10} characteristics involved in cellular responses in human bronchial epithelial cells (Beas-2B). Environ. Res. 149, 48–56. https://doi.org/10.1016/j.envres.2016.04.029

Van Den Heuvel, R., Staelens, J., Koppen, G., Schoeters, G., 2018. Toxicity of urban PM_{10} and relation with tracers of biomass burning. Int. J. Environ. Res. Public Health 15, 1–19. https://doi.org/10.3390/ijerph15020320

Van Drooge, B.L., Marqueño, A., Grimalt, J.O., Fernández, P., Porte, C., 2017. Comparative toxicity and endocrine disruption potential of urban and rural atmospheric organic PM_1 in JEG-3 human placental cells. Environ. Pollut. 230, 378–386. https://doi.org/10.1016/j.envpol.2017.06.025

Velali, E., Papachristou, E., Pantazaki, A., Choli-Papadopoulou, T., Planou, S., Kouras, A., Manoli, E., Besis, A., Voutsa, D., Samara, C., 2016. Redox activity and *in vitro* bioactivity of the water-soluble fraction of urban particulate matter in relation to particle size and chemical composition. Environ. Pollut. 208, 774–786. https://doi.org/10.1016/j.envpol.2015.10.058

Vicente, E.D., Duarte, M.A., Calvo, A.I., Nunes, T.F., Tarelho, L.A.C., Custódio, D., Colombi, C., Gianelle, V., Sanchez de la Campa, A., Alves, C.A., 2015. Influence of operating conditions on chemical composition of particulate matter emissions from residential combustion. Atmos. Res. 166, 92–100. https://doi.org/10.1016/j.atmosres.2015.06.016

Vicente, E.D., Alves, C.A., 2018. An overview of particulate emissions from residential biomass combustion. Atmos. Res. 199, 159–185. https://doi.org/10.1016/j.atmosres.2017.08.027

Vicente, E.D., Vicente, A.M., Evtyugina, M., Oduber, F.I., Amato, F., Querol, X., Alves, C., 2020. Impact of wood combustion on indoor air quality. Sci. Total Environ. 705. https://doi.org/10.1016/j.scitotenv.2019.135769

Vicente, E.D., Alves, C.A., Martins, V., Almeida, S.M., Lazaridis, M., submitted for publication. Lung-deposited dose of particulate matter from residential exposure to smoke from wood burning. Environ. Sci. Pollut. Res.

Vu, B., Alves, C.A., Gonçalves, C., Pio, C., Gonçalves, F., Pereira, R., 2012. Mutagenicity assessment of aerosols in emissions from wood combustion in Portugal. Environ. Pollut. 166, 172–181. https://doi.org/10.1016/j.envpol.2012.03.005.

CHAPTER 9

Chapter 9. Conclusions and future research perspectives

9.1. Conclusions

The research described in this work is a step towards a better chemical and toxicological characterisation in residential microenvironments of particles emitted by wood-fired heating equipment and of particulate emissions derived from the residential combustion of pellets.

Generally, the development of new technologies, such as pellet fuelled appliances, for residential combustion allowed the reduction of particulate and gaseous emissions. However, the selection of the pellet fuel for residential heating has proven to be crucial regarding the environmental performance of small-scale pellet stoves. The PM_{10} emissions derived from the combustion of different types of pellets in a residential pellet stove, as well as their chemical and toxic properties, were the focus of three studies included in this thesis (Papers II, III and IV). Additionally, the effect of the operating conditions of the pellet stove (nominal and partial loads) on emissions was also a topic of research. Sampling was conducted under controlled laboratory conditions in an experimental setup. New and comprehensive information was obtained on the effect of pellet certification and the use of alternative raw materials on particle emissions and specific chemical and toxicological properties. The main conclusions that can be drawn from the laboratory measurements are listed below:

1. The combustion of two types of pellets with identical quality class (ENplus A1), and one brand of non-certified pellets, showed that even certified material does not always meet emission requirements set by the Ecodesign directive.

2. Given the variability of emissions from different commercial pellets during combustion in a stove at partial and nominal loads, no operating condition could be indicated as optimal.

3. PM_{10} emissions from combustion of commercial pellets in a residential stove operated at nominal load were generally low, ranging from 23.2 to 46.2 mg MJ^{-1} (below the limit imposed by the Ecodesign directive of ~ 65.0 mg MJ^{-1}). Nevertheless, differences were recorded between particulate emissions from distinct brands of certified pellets. The combustion of laboratory made pellets from alternative raw material (*Acacia longifolia*, an invasive species in Portugal) generated PM_{10} emissions, on average, 3 to 4 times higher than those of commercial pellets. These higher emissions can be ascribed to the higher ash content of the fuel.

4. In accordance with previous studies on emissions from the combustion of wood pellets, the particulate emissions were mainly composed of inorganic material. The dominant water soluble

species in PM_{10} varied depending on the type of pellet burned: sulphate was dominant in particles resulting from the combustion of certified pellets, while chloride was the most abundant in PM_{10} generated from the combustion of acacia and non-certified pellets. The second major contributing species to the PM_{10} mass was potassium, regardless of the pellet type burned. The sodium content in particles from acacia pellets was, on average, 3 to 7 times higher than in samples from commercial pellets. This is probably related to the saline ecosystem where the acacia trees grew.

5. The carbonaceous fraction in particles from the combustion of commercial pellets was generally dominated by EC, while OC was the most abundant in particulate emissions from acacia pellets. Carbonaceous particulate mass fractions were noticeably lower compared to those from batch fired combustion appliances and are in the range of those reported for the combustion of pellets in automatically fed appliances. Automatically fed systems allow to reduce the particulate organic carbon, however, insufficient mixing of combustion gases and air, result in fuel-rich areas in the flame zone, providing conditions for the formation of soot particles.

6. Levoglucosan, mainly formed by pyrolysis of cellulose, was detected in all samples. The highest mass fraction was recorded in particles from the combustion of acacia pellets. Phenolic compounds were dominated by coniferyl-type lignin pyrolysis products in samples collected during the combustion of commercial pellets, in accordance with the composition of softwood lignin. On the other hand, guaiacol and syringol type methoxyphenols were present in particulate samples from acacia pellets, reflecting the lignin structure of angiosperm plants. PM_{10}-bound PAHs displayed substantially lower mass fractions in the emissions from acacia pellets. Several other constituents were quantified in PM_{10} samples, including various types of acids, sterols, and polyols. The contribution of these compounds to the PM_{10} mass varied with the pellet type burned.

7. Regarding the toxicity, the main difference was observed between particles from the combustion of acacia pellets and those emitted by commercial pellets. The results showed that the PM_{10} of acacia pellets was the most ecotoxic and cytotoxic, while mutagenicity was not detected for any biofuel. Further research is needed to establish the causative chemical components in particles emitted from residential pellet combustion.

8. From the results obtained, it can be concluded that, despite the lower emissions achievable in automatically fired pellet appliances, the woody raw material selected for pelletisation can dramatically increase emissions, affecting not only the chemical properties of the released particles, but also their toxicological potency.

9. The database obtained in this study from laboratory measurements conducted to characterise country specific fuels can contribute to improving existing emission inventories. Given that local or regional source profiles are essential for PM source apportionment studies carried out with receptor models, the new emission datasets are also useful as they append to the emergent

speciation profiles for major sources in Europe (SPECIEUROPE). Moreover, this work also highlights the need for further improvement of fuels and combustion technologies for the residential heating sector. The pellet certification process should be tightened up. The testing of biofuels should be regularly performed by qualified and recognised laboratories.

Given that traditional appliances still dominate and the hitherto scarcity of work on the characterisation of indoor-generated emissions, a field campaign was carried out to investigate the impact of wood combustion on particulate matter levels in residential microenvironments and the associated chemical and toxicological properties. In addition, for comparison purposes, outdoor and background air (in the absence of indoor sources) samples were also collected and analysed. Novel information on human exposure, lung dose and toxicity of particles in residential settings impacted by biomass combustion was obtained (Papers V, VI and VI). Major findings from the field campaign are listed below:

1. The increase in PM_{10} concentrations due to the use of traditional wood burning appliances (fireplace and woodstove), compared to the indoor background air, was noticeable. During open fireplace operation, PM_{10} levels increased over 12 times compared to background concentrations, while the woodstove resulted in a 2-fold enhancement. The PM_{10} temporal profiles allowed to identify ignition and refuelling of both appliances as critical steps in generating indoor peak concentrations.

2. The PM_{10} sampled in the room equipped with fireplace was mainly composed of carbonaceous material (43.9 ± 5.04 wt% of PM_{10}) as a result of the incomplete combustion conditions typical of traditional appliances operating at low temperatures. The total carbon in indoor particles almost halved when the woodstove was in use (24.0 ± 7.37 wt% of PM_{10}). Water soluble ions and trace elements showed variable contributions to the indoor PM_{10} mass and were generally higher during the operation of the woodstove.

3. The fireplace operation increased indoor PAH concentrations 59 times in comparison with the levels recorded in the absence of the source, while the use of the woodstove contributed to a 3-fold enhancement over background measurements. Concentrations of total particulate bound PAHs collected during the operation of the fireplace largely exceeded those obtained in the experiments with woodstove (10 times, on average).

4. Anhydrosugars were the dominant group of organic compounds in PM_{10} generated by the fireplace, accounting for 10 to 13 wt% of the OC mass, while lower mass fractions (1.2 to 3.1 wt%) were recorded during the operation of the woodstove. Levoglucosan was found to be one of the most abundant species among the individually identified compounds. Consistent with the combustion of mixtures of hard and softwood, guaiacol and syringol type methoxyphenols were detected in indoor particles.

5. The cancer risks associated with inhalation exposure to particulate-bound PAHs in the room equipped with woodstove were found to be negligible, while in the microenvironment heated with fireplace the health-based guideline levels were exceeded. The excess lifetime cancer risk resulting from exposure to Cr(VI) when using the fireplace and woodstove was higher than 1.0×10^{-6} and 1.0×10^{-5}, respectively.

6. From the dosimetry study, the effect of combustion appliance was clearly illustrated. The total dose received while operating the fireplace was two-fold the one received in the room with a woodstove and more than 10 times higher than in the absence of the source. Although the highest amount of the deposited particles was recorded in the extrathoracic region (68-79%), more than 90% of the particles deposited in the alveolar–interstitial region remained deposited after 24-h of exposure.

7. The effects of combustion appliance on biological outcomes were explored. The results evidenced different toxic potentials for particles emitted when using the fireplace or the woodstove. Indoor-generated particles by the fireplace were the most ecotoxic and cytotoxic, whereas mutagenicity was not detected in any of the tested samples. PM_{10} samples collected during the operation of the fireplace induced greater metabolic activity impairment in human lung epithelial cells than the samples obtained when the source was inactive, while only one PM_{10} sample collected during the use of the woodstove presented significantly higher cytotoxicity than the background at the highest dose. Similarly, when comparing indoor/outdoor parallel samples, a significantly higher cytotoxicity was observed in samples collected in the room equipped with fireplace than in the corresponding outdoor samples, whereas such effect was not seen with the woodstove samples.

8. Indoor organic carbon was found to play a significant role in the *V. fischeri* bioluminescent activity and A549 cell metabolic activity. Several combustion-related organic compounds, such as PAHs and biomass burning tracers, displayed significant correlations with the increase in toxicity using both assays. These findings add to the growing body of evidence that toxicological responses are related to the particle chemical characteristics.

The results from exposure, dose and bioreactivity of indoor particles gathered in this work suggest that homeowners should be encouraged to upgrade the wood burning technology to reduce the products of incomplete combustion bound to PM inside the residences. Fireplace and woodstove changeout programmes supported by financial incentives should be created and advertised. A plan for the engagement of homeowners is crucial to create awareness about the health threat posed by this source and promote a change in behaviour.

9.2. Future research perspectives

Despite the large dataset presented in this work from measurements both in laboratory and residential settings, there is still need for future work in this research field to shed light on topics still not explored.

Over the past years, research efforts have been devoted to quantifying the emissions from residential combustion appliances. Nevertheless, combustion technologies are expected to continue to evolve, which means that emission factors will need to be updated. Technical improvements in residential combustion appliances, as well as the development of economically viable particulate emission control devices (e.g. baghouse filters or electrostatic precipitators), will give rise to particles with specific characteristics whose physicochemical and toxicological properties will need to be scrutinised. Future research focused on the relationships between the toxicological features and the chemical composition of the particles is recommended to find out which constituents induce adverse effects and advise which biofuels and combustion technologies are safer from an environmental and health point of view. The elemental composition of the biomass combustion particles and their effects were not included in this work, but should not be ruled out in future research, given the mounting evidence pointing to their importance in toxicological responses. The detailed chemical characterisation of the fuel should also be addressed in future work aiming at investigating new raw materials for pelletisation, since molar ratios among certain elements might serve as indicators for particulate emissions.

Regarding the influence of biomass combustion appliances on indoor air quality, this work was based on a limited number of samples and further research is needed to elucidate the effects of stove design, stove operation, household characteristics, ventilation patterns and weather conditions on the indoor PM levels and associated properties. The influence of meteorological conditions on indoor pollutant levels could be a research topic to be covered in the future since the operation of combustion appliances under natural draft conditions may lead to increased concentrations under unfavourable weather conditions. Strategies to improve air quality in homes equipped with biomass combustion equipment should also be addressed in future works.

In the present study, the dose received by subjects exposed to particulate matter was derived based on particulate mass concentrations. In future research, particulate number concentrations should also be included in the analysis. Moreover, the exposure scenario considered in this work only encompassed the indoor source under analysis for an 8-h period. It would be interesting to evaluate the daily dose received including all microenvironments to which a subject is exposed. This evaluation would allow to determine the contribution of residential heating to the total daily dose.

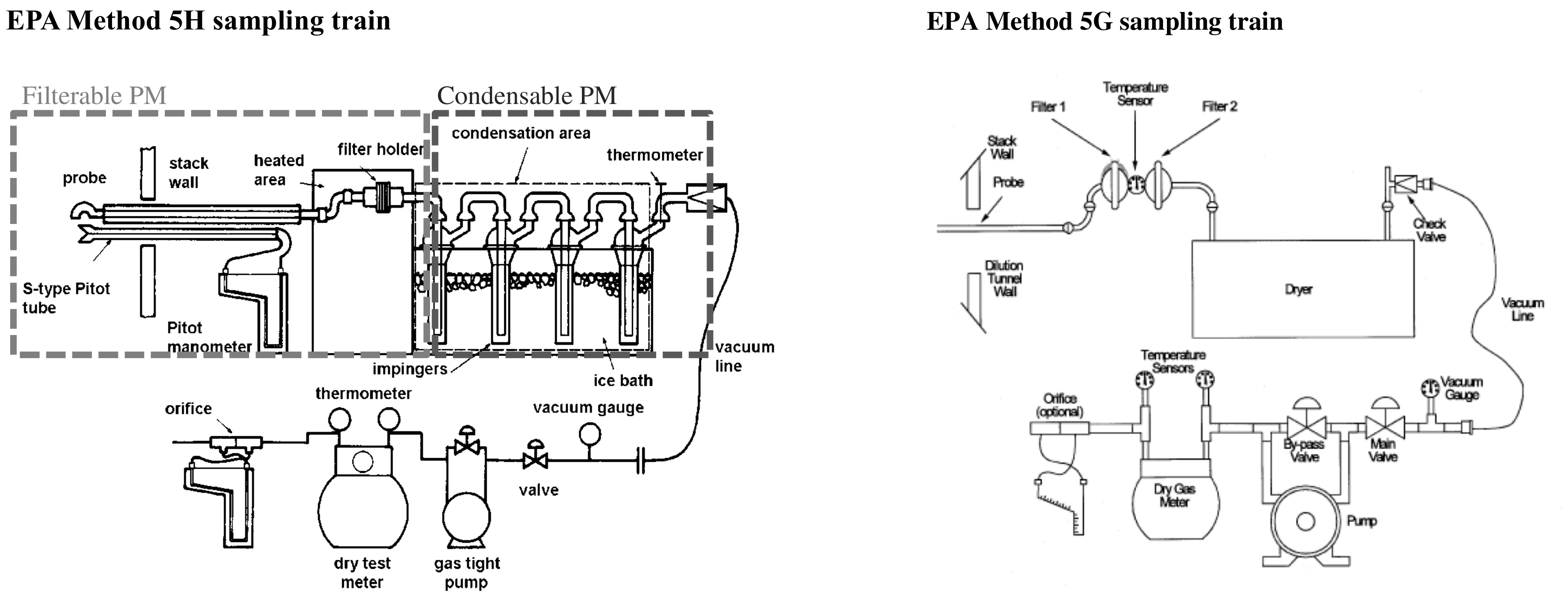
The results obtained in the present study with the *Vibrio fischeri* bioluminescence assay suggest that the bacteria-based method may be an easy-to-apply and inexpensive assay for a first screening of toxicity. However, the more complex is the model used the more meaningful are the conclusions derived. Although air-liquid interface exposures are more complex and costlier, which constitute a drawback for large screening studies, they allow creating more realistic exposure conditions and should be used in future research after a preliminary assessment of toxicity with more cost-effective assays.

Supplementary Material

Supplementary Material A1 – from chapter 2

Table A1. Summary of standard methods for emission determination from wood burning appliances.

Country	Standard reference	Title	Year
Germany	DIN-plus 13240	Roomheaters fired by solid fuel - Requirements and test methods.	2005
	VDI 2066 (Blatt 1)	Particulate matter measurement. Dust measurement in flowing gases. Gravimetric determination of dust load.	1975
	VDI 2066 (Blatt 5)	Particulate matter measurement - Dust measurement in flowing gases; particle size selective measurement by impaction method - Cascade impactor.	1994
Norway	NS 3058-1	Enclosed wood heaters - Smoke emission - Part 1: Test facility and heating pattern.	1994
	NS 3058-2	Enclosed wood heaters - Smoke emission - Part 2: Determination of particulate emission.	1994
	NS 3059	Enclosed wood heaters - Smoke emission - Requirements.	1994
USA	EPA Method 5H	Determination of particulate matter emissions from wood heaters from a stack location.	1988
	EPA Method 5G	Determination of particulate matter emissions from wood heaters - Dilution tunnel sampling location.	1988
	Method 28	Certification and auditing of wood heaters.	1988
Australian/New Zealand	AS/NZS 4012	Domestic solid fuel burning appliances - Method for determination of power output and efficiency.	1999
	AS/NZS 4013	Domestic solid fuel burning appliances - Method for determination of flue gas emission.	1999



EPA Method 5H sampling train

EPA Method 5G sampling train

Figure A1. Schematic diagram of the EPA sampling system used for EPA Method 5H and 5G (source: EPA, 1988).

Supplementary Material A2 – from chapter 6

Table A2.1. PM_{10} concentrations (µg m^{-3}) and mass fractions (%wt. PM_{10}) of major and trace elements.

	Indoor Fireplace	Indoor Background	Outdoor	Indoor Woodstove	Indoor Background	Outdoor
PM_{10} (µg m^{-3})	319 ± 173	25.9 ± 2.45	80.1 ± 19.8	78.5 ± 24.0	28.6 ± 5.83	32.2 ± 16.7
%wt. PM_{10}						
Al	0.259	0.495	1.08	0.880	0.219	0.653
Ca	0.654	-	1.01	5.16	-	2.84
Fe	0.074	0.0385	0.276	0.536	0.0129	0.479
K	0.617	0.0557	1.02	2.20	0.1740	2.20
Mg	0.227	0.1541	0.1661	1.83	0.1413	1.12
Na	0.280	0.8406	0.9372	1.59	1.18	6.74
Li	0.0002	0.0004	-	0.0007	-	-
Sc	-	0.0001	0.0003	-	-	-
Ti	0.0060	0.0102	0.0223	0.0435	0.0033	0.0242
V	0.0005	0.0011	0.0019	0.0028	0.0006	0.0084
Cr	0.0007	0.0032	0.0029	0.0116	-	0.0175
Mn	0.0586	-	0.0091	0.3779	-	0.0112
Co	0.0002	0.0002	-	0.0013	0.0000	-
Ni	0.0017	0.0036	0.0071	0.0004	0.0004	-
Cu	0.0048	0.0039	0.0095	0.0147	-	0.0176
Ga	0.0001	0.0002	0.0002	0.0003	0.0001	-
Ge	-	0.0003	-	-	-	-
As	0.0004	0.0010	0.0016	0.0014	0.0004	0.0009
Se	0.0000	0.0000	-	-	-	-
Rb	0.0024	0.0007	0.0021	0.0056	0.0010	0.0028
Sr	0.0046	0.0013	0.0058	0.0295	-	0.0055

Y	0.0002	0.0048	0.0007	-	0.0026	-
Zr	0.0033	0.0405	0.0282	-	-	-
Nb	-	0.0004	-	-	0.0001	-
Cd	0.0002	-	0.0007	0.0006	-	0.0010
Sn	0.0004	0.0017	0.0032	0.0022	0.0006	0.0040
Sb	0.0008	0.0003	0.0057	0.0003	0.0000	-
La	0.0006	0.0017	0.0006	0.0026	0.0006	-
Ce	0.0010	0.0032	0.0010	0.0054	0.0011	-
Pr	0.0000	0.0003	0.0001	0.0004	0.0001	-
Nd	0.0001	0.0014	0.0005	0.0010	0.0006	-
Sm	0.0000	0.0006	0.0001	-	0.0003	-
Eu	-	0.0004	-	-	0.0003	-
Gd	0.0000	0.0008	0.0001	-	0.0004	-
Tb	-	0.0002	-	-	0.0001	-
Dy	0.0001	0.0011	0.0001	-	0.0005	-
Ho	-	0.0002	-	-	0.0001	-
Er	0.0000	0.0003	0.0001	-	0.0002	-
Tm	-	0.0004	-	-	0.0003	-
Yb	0.0000	0.0003	0.0000	-	0.0002	-
Hf	0.0001	0.0016	0.0012	-	-	-
W	-	0.0004	0.0008	0.0004	-	0.0017
Pb	0.0026	0.0021	0.0062	0.0043	0.0054	0.0050
Th	0.0000	0.0010	0.0003	-	0.0002	-
U	0.0001	0.0011	0.0000	-	0.0005	-
Σ elements	2.20	1.67	4.61	12.7	1.74	14.1
Σ element oxides	3.13	2.56	6.74	18.2	2.49	19.6

- below the detection limit or not detected. The measured element concentrations were converted into the respective mass concentrations of the most common oxides (Al_2O_3, MgO, MnO, Fe_2O_3, TiO_2, K_2O, etc.).

Table A2.2. Concentrations (ng m^{-3}) of homologous compound series and diagnostic parameters.

	Indoor Fireplace	Indoor Background	Outdoor	Indoor Woodstove	Indoor Background	Outdoor
n-Alkanes						
Undecane	-	-	0.716±0.650	0.419±0.366	-	0.378±0.420
Dodecane	-	-	1.25±1.11	0.905±0.337	-	0.518±0.559
Tridecane	-	-	0.867±0.885	0.816±0.128	-	0.364±0.501
Tetradecane	-	0.0395	0.616±0.829	0.759±0.121	-	-
Pentadecane	-	-	-	0.320±0.323	-	-
Hexadecane	-	0.078	-	-	-	0.0808±0.114
Heptadecane	-	1.62	-	-	-	-
Octadecane	0.124±0.0881	0.158	0.186±0.169	0.119±0.167	-	-
Nonadecane	0.111±0.175	0.281	-	0.332±0.192	-	0.0266±0.0345
Eicosane	0.510±0.562	0.324	0.0490±0.0865	0.670±0.0665	-	0.0292±0.0425
Heneicosane	1.04±1.08	0.396	0.307±0.347	1.40±0.301	-	0.141±0.109
Docosane	1.12±1.16	0.0604	0.585±0.776	2.24±0.487	-	0.435±0.163
Tricosane	1.13±1.26	-	1.32±1.36	3.40±0.912	-	0.847±0.932
Tetracosane	0.901±1.32	-	1.66±2.22	6.30±3.15	-	1.68±1.84
Pentacosane	0.984±1.41	0.0356	4.02±3.74	11.7±9.41	-	2.71±2.99

Hexacosane	0.677±1.03	0.0576	4.88±5.17	15.7±13.7	-	3.52±4.19
Heptacosane	1.24±1.74	0.149	7.03±6.37	21.1±20.5	-	3.59±4.19
Octacosane	0.463±0.925	0.212	6.55±6.82	23.6±25.2	-	3.39±4.13
Nonacosane	1.93±2.84	0.0248	8.41±6.64	27.6±30.5	-	3.02±3.43
Triacontane	0.481±0.945	-	4.46±4.60	24.7±28.9	-	1.88±2.36
Hentriacontane	3.66±4.41	0.161	4.60±4.60	29.7±35.6	-	1.24±1.77
Dotriacontane	0.189±0.344	0.0582	1.48±2.07	24.6±31.5	-	0.636±0.946
Tritriacontane	-	-	0.180±0.264	14.6±19.8	-	-
Tetratriacontane	-	-	0.145±0.290	12.4±18.1	-	-
Pentatriacontane	-	-	-	8.74±13.8	-	-
Hexatriacontane	-	-	-	-	-	-
Heptatriacontane	-	-	-	-	-	-
CPI	1.81±1.23	2.7	2.02±1.32	0.987±0.116	-	1.06±0.172
C_{max}	C_{30}	C_{16}	C_{28}	C_{30}	-	C_{26}
n-Alkenes						
1-Tetradecene	-	0.205	0.713±1.07	1.30±0.292	-	0.548±0.770
1-Hexadecene	-	0.102	-	0.207±0.251	-	0.138±0.154
1-Octadecene	-	0.0257	-	0.127±0.117	-	0.114±0.105
1-Eicosene	-	-	-	0.317±0.197	-	0.0665±0.0404
9-Tricosene	0.405±0.497	-	0.129±0.206	0.387±0.177	-	0.0661±0.0623

Squalene	-	-	-	-	-	-
n-Alkanols						
Decanol	0.412±0.140	0.0077	0.148±0.0609	0.101±0.110	0.0011	0.0794±0.0259
Undecanol	-	-	-	-	-	-
Dodecanol	-	1.25	-	5.13±1.92	-	1.97±1.15
Tridecanol	-	-	-	-	-	-
Tetradecanol	-	3.57	-	22.1±14.9	1.04	4.74±1.25
Pentadecanol	16.3±5.25	1.41	5.39±1.10	7.63±4.95	0.421	2.19±0.410
Hexadecanol	59.2±14.6	1.25	14.4±8.99	52.6±25.7	0.777	6.17±2.47
Heptadecanol	-	-	-	2.64±1.52	-	-
Octadecanol	42.5±16.0	0.165	5.44±1.04	22.4±12.4	-	-
Nonadecanol	-	-	-	-	-	-
Eicosanol	-	-	-	-	-	-
Heneicosanol	-	-	-	-	-	-
Docosanol	598±270	1.2	113±47.2	72.7±52.4	2.13	37.7±26.5
Tricosanol	5.31±2.36	0.0078	0.667±0.173	0.488±0.457	0.0162	0.259±0.234
Tetracosanol	85.6±44.8	-	9.86±5.49	-	-	2.94±2.10
Pentacosanol	3.36±1.75	0.0209	0.494±0.144	0.601±0.740	0.0136	0.167±0.128
Hexacosanol	186±243	-	10.4±5.47	-	0.233	2.15±2.76
Heptacosanol	2.00±1.06	0.0034	0.419±0.195	0.323±0.345	0.0054	0.146±0.197

Octacosanol	22.1±11.2	0.0984	7.93±5.39	3.11±3.75	0.123	2.74±3.27
Nonacosanol	-	-	2.02±0.849	-	-	-
Tricontanol	3.80±2.03	0.0096	2.70±1.44	0.407±0.374	0.0351	0.803±1.09
CPI	38.1±16.3	5.24	18.6±4.49	16.5±7.09	9.5	18.5±4.17
C_{max}	C_{22}	C_{14}	C_{22}	C_{22}	C_{22}	C_{22}
n-Alkanoic acids						
Hexanoic	3.88±4.50	-	1.05±0.874	0.489±0.437	-	0.586±0.383
Octanoic	6.31±1.98	-	2.25±1.36	0.889±0.832	-	0.526±0.281
Nonanoic	15.5±4.52	-	4.98±3.13	3.65±3.71	-	2.02±1.17
Decanoic	4.13±3.01	-	5.18±2.29	4.44±3.83	-	0.327±0.322
Undecanoic	0.604±0.555	0.0465	1.05±0.838	1.17±0.732	-	0.361±0.353
Dodecanoic	40.0±8.88	0.840	11.6±3.13	26.5±12.6	-	3.85±2.34
Tetradecanoic	90.0±27.3	1.20	12.1±11.2	66.7±23.7	-	6.39±1.63
Pentadecanoic	17.2±11.0	0.377	8.20±7.53	26.5±10.8	-	3.18±1.33
Hexadecanoic	516±519	2.73	50.8±32.6	65.4±43.5	-	11.6±8.56
Heptadecanoic	59.2±66.3	0.190	6.66±4.72	8.89±8.29	-	1.92±1.23
Octadecanoic	235±209	1.30	10.6±8.57	82.0±80.2	-	17.8±7.53
Nonadecanoic	2.85±2.93	0.0017	1.44±2.02	1.82±1.48	0.0079	0.710±0.382
Eicosanoic	89.2±69.3	-	14.4±6.35	7.19±5.67	-	4.33±4.16
Heneicosanoic	-	-	3.76±1.68	-	-	-

Docosanoic	65.1±68.6	-	101±126	41.8±32.3	-	34.7±31.1
Tricosanoic	-	-	6.31±6.12	-	-	1.52±0.991
Tetracosanoic	165±96.2	0.390	43.1±11.5	4.29±5.66	1.20	9.98±8.97
Pentacosanoic	40.2±46.2	-	5.13±1.44	-	-	0.512±0.678
Hexacosanoic	85.1±54.4	0.0801	37.5±24.7	-	0.202	4.82±3.58
Heptacosanoic	-	-	1.43±0.836	-	-	-
Octacosanoic	24.7±3.84	-	5.90±2.59	-	-	1.62±2.32
Nonacosanoic	-	-	0.405±0.362	-	-	-
Triacontanoic acid	-	-	3.05±1.35	-	-	1.07±1.63
CPI	9.52±2.84	-	6.78±0.58	6.23±0.945	-	7.62±1.37
C_{max}	C_{16}	C_{16}	C_{22}	C_{18}	C_{24}	C_{22}
n-Alkenoic acids						
9-Hexadecenoic (palmitoleic)	1.10±1.19	-	1.55±2.03	14.6±11.1	0.0041	0.902±0.359
9-cis-Hexadecenoic (linoleic)	152±110	0.0031	6.22±2.37	8.14±9.87	0.0181	2.78±1.63
9-Octadecenoic (oleic)	426±269	0.0114	7.86±2.33	19.7±19.4	0.0718	3.84±2.98
n-Alkanedioic acids						
Ethanedioic (oxalic)	1341±1211	-	35.3±42.0	534±239	-	36.8±43.0
Butanedioic (succinic)	655±285	-	93.5±49.1	36.4±11.8	-	23.6±34.1
Heptanedioic (pimelic)	10.7±7.17	-	4.87±2.42	2.29±1.41	-	1.50±1.45
Octanedioic (suberic)	26.3±30.5	0.0362	11.3±9.37	6.22±2.82	-	5.25±1.08

Nonanedioic (azelaic)	92.3±52.5	0.146	44.5±25.9	19.3±12.6	0.0587	13.7±12.7
Decanedioic (sebacic)	10.8±4.45	-	7.79±5.66	2.40±1.56	-	1.97±2.12
Hexadecanedioic	44.8±22.5	-	2.65±0.894	0.264±0.306	0.0066	0.838±0.712

CPI for n-alkanes: CPI = ΣC_{13}-$C_{35}/\Sigma C_{12}$- C_{34}; CPI for n-alkanoic acids: CPI = ΣC_8-$C_{30}/\Sigma C_7$- C_{29}; CPI for n-alkanols: CPI = ΣC_8-$C_{30}/\Sigma C_7$- C_{29}

Table A2.3. Concentrations (ng m^{-3}) of saccharides and polyols.

	Indoor Fireplace	**Indoor Background**	**Outdoor**	**Indoor Woodstove**	**Indoor Background**	**Outdoor**
Levoglucosan	7924±5827	17.7	983±212	208±88.2	25.7	362±161
Mannosan	4945±3765	4.54	385±144	75.6±14.6	7.25	126±45.0
Galactosan	2437±1715	0.94	238±76.0	20.8±9.10	2.29	69.8±45.6
Sucrose	6.65±8.03	-	12.6±6.47	11.9±15.2	-	33.7±37.5
Inositol	70.0±91.5	-	5.09±5.96	-	-	4.24±5.26
Glucopyranose	296±136	0.217	44.1±20.1	14.5±15.0	0.379	36.5±9.09
Glucitol	62.9±43.2	0.362	68.3±25.0	14.8±15.4	0.714	19.5±12.1
D-glucuronic acid lactone	39.5±25.1	0.0901	7.35±4.78	2.34±2.44	0.132	6.03±1.66
Ribitol	-	0.970	17.5±11.9	14.4±11.3	25.8	9.41±3.73
Meso-Erythritol	302±160	-	34.6±10.1	8.82±8.98	-	5.36±6.31

Table A2.4. Concentrations (ng m^{-3}) of substituted benzenes and phenolic compounds.

	Indoor Fireplace	**Indoor Background**	**Outdoor**	**Indoor Woodstove**	**Indoor Background**	**Outdoor**
Benzyl alcohol	19.7±3.52	0.191	9.60±4.51	3.12±3.04	0.101	6.57±0.861
4-Hydroxybenzaldehyde	4.67±6.23	-	2.49±0.916	-	0.0171	0.905±0.764
Benzoic acid	4.14±2.92	-	3.54±2.19	18.3±22.8	-	1.25±0.599
Sinapic acid	3.70±3.01	0.0011	0.312±0.243	0.0432±0.0370	0.0034	0.0571±0.0622
Coniferyl alcohol	93.8±129	-	0.261±0.206	0.0033±0.0030	-	0.0122±0.0095
Vanillin	103±60.7	-	5.48±3.84	-	-	2.86±3.66
Acetovanillone	52.4±44.2	-	4.55±2.38	-	-	0.786±0.747
3-Vanillyl propanol	1422±1143	-	23.6±11.9	-	0.251	0.627±0.639
Vanillic acid	154±82.2	0.114	30.8±16.7	3.42±1.77	0.307	10.5±6.06
Homovanillic alcohol	362±386	-	10.0±0.394	-	-	1.13±0.983
Phthalic acid	197±52.1	0.0434	38.8±22.1	2.74±3.24	0.211	12.0±9.86
Isophthalic acid	-	-	3.64±5.46	38.2±44.8	-	-
Terephthalic acid	-	-	40.3±15.3	203±188	-	9.35±11.1
Syringic acid	175±62.5	0.160	36.6±22.8	2.78±2.36	0.597	8.14±5.92
Syringic acid methyl ester	104±99.6	-	23.6±3.15	-	-	4.11±2.44
Syringaldehyde	204±42.9	0.249	4.15±5.30	-	0.740	-
Sinapaldehyde	278±233	-	0.976±1.95	-	-	-

Acetosyringone	500±451	-	30.2±4.66	-	-	5.08±6.45
Sinapyl alcohol	94.2±127	-	0.0206±0.0093	-	-	0.0092±0.0116
4-Methylsyringol	16.2±18.4	-	2.18±1.18	-	-	-
4-Ethylsyringol	31.9±58.6	-	3.44±0.909	-	-	-
Coniferyl aldehyde	833±821	-	36.0±20.3	-	-	2.11±2.85
4-Hydroxycinnamic (p-coumaric) acid	33.9±17.0	0.0049	-	0.102±0.0630	0.0028	1.16±1.35
3,4-Dihydroxy-cinnamic (caffeic) acid	1.49±1.19	0.0002	0.112±0.0849	0.0079±0.0062	0.0020	0.0163±0.0136
4-Hydroxy-3-methoxycinnamic (ferulic) acid	15.1±13.3	0.0027	0.840±0.593	0.0792±0.0413	0.0077	0.190±0.159
3-Hydroxybenzoic acid	70.4±35.8	0.0164	11.8±2.44	3.16±3.08	0.0751	2.13±1.34
4-Hydroxybenzoic acid	76.9±103	0.0504	12.5±6.99	15.6±18.2	0.162	3.01±2.35
2,3,4-Trimethoxybenzoic (gallic) acid	3.40±5.39	0.0058	1.32±0.689	0.0692±0.0134	-	0.464±0.222
Trans-cinnamic acid	7.49±10.9	-	5.48±2.85	1.00±0.687	0.00251	1.92±3.05
Protocatechoic acid	168±73.4	0.0759	61.4±11.9	-	0.184	-
Eugenol	0.511±0.501	-	0.0175±0.0053	0.0063±0.0049	-	0.0066±0.0017
Isoeugenol	8.94±7.08	-	0.655±0.492	0.235±0.230	-	0.191±0.0148
4-Allyl-2,6-dimethoxyphenol (methoxy eugenol)	0.536±0.777	0.0049	0.150±0.108	0.324±0.486	0.0027	0.0928±0.0349
Hydroxyacetophenone	18.2±15.5	-	5.82±2.69	3.56±5.20	0.0450	2.54±0.676

2,6-Dimethoxyphenol	7.51±9.59	0.0004	0.254±0.155	0.0058±0.0029	0.0004	0.0162±0.0062
5-Isopropyl-3-Methylphenol	0.463±0.162	-	0.148±0.0682	0.0704±0.106	-	0.122±0.0558
2,4-Di-tert-butylphenol	4.43±1.31	2.31	8.34±7.62	3.90±1.54	0.432	-
2-Methoxy-4-propylphenol	18.1±28.7	0.0003	0.803±0.550	0.0090±0.0070	0.0004	0.0246±0.0109
4-Tert-butylphenol	9.70±1.80	0.486	9.18±3.03	2.14±1.75	0.231	1.84±1.61
4-Phenylphenol	6.89±6.08	0.0023	0.781±0.214	0.750±1.14	0.0028	0.182±0.0605
4-Octyphenol	76.2±45.8	0.0007	2.46±1.18	0.0897±0.109	0.0007	0.0843±0.0631
3-Methyl catechol	17.6±27.1	-	-	-	-	-
4-Methyl catechol	79.7±80.0	0.0005	0.0721±0.0354	0.0046±0.0041	0.0003	0.0230±0.0204
Pyrocatechol	54.6±74.2	0.0005	0.0607±0.0214	0.0144±0.0149	0.0002	0.0221±0.0181
Resorcinol	79.1±86.5	0.0027	4.24±2.57	1.56±1.35	0.0040	0.142±0.0275
1-Methyl-3,5-dihydroxybenzene (orcinol)	32.9±26.7	-	0.243±0.282	-	-	-
4-Hydroxyphenylethanol (tyrosol)	-	-	18.5±16.1	-	-	-
Pyrogallol	517±784	0.0011	0.480±0.311	0.0074±0.0051	0.0002	0.0154±0.0100
Hydroquinone	504±494	-	8.22±3.36	-	-	-
Methylhydroquinone	113±92.3	-	-	-	-	-
Bisphenol A	-	-	4.00±6.54	357±342	0.114	-
Matairesinol	10.4±5.82	-	0.374±0.446	-	-	-

Table A2.5. Concentrations (ng m^{-3}) of other organic compounds.

	Indoor Fireplace	**Indoor Background**	**Outdoor**	**Indoor Woodstove**	**Indoor Background**	**Outdoor**
Resin acids and derivatives						
Abietic acid	1060±747	0.0518	17.4±34.6	3.30±4.27	0.185	-
Dehydroabietic acid	6193±2845	25.4	577±351	190±88.6	53.9	199±90.3
15-Hydroxydehydroabietic acid	34.7±42.1	-	11.8±8.74	12.8±18.3	-	3.32±3.08
7-oxodehydroabietic acid methyl ester	788±504	0.120	109±38.8	46.4±22.6	0.408	34.0±27.0
Pimaric acid	864±506	-	69.5±45.0	20.7±12.0	-	20.8±11.2
Isopimaric acid	274±174	0.174	25.3±10.8	10.4±7.66	0.364	6.65±4.11
Podocarpic acid	1.78±1.08	0.0035	1.02±0.715	0.439±0.432	0.0128	0.379±0.243
Other acids						
Glyceric acid	25.2±20.9	-	10.6±7.16	2.10±2.25	-	5.70±7.23
Glycolic acid	255±305	-	25.8±29.8	24.8±13.9	-	19.0±9.47
3-Hydroxybutanoic acid	25.6±37.1	-	2.42±2.08	2.96±2.57	-	2.55±2.03
3,4-Dihydroxybutanoic acid	78.8±44.5	-	15.2±4.97	4.71±2.07	0.0149	1.73±2.99
Levulinic acid	118±27.4	-	53.3±18.3	27.1±27.1	-	15.9±3.92
Citric acid	18.6±17.6	-	5.87±5.08	6.59±7.27	0.133	3.86±4.54
Cis-Pinonic acid	2.67±3.17	0.170	5.52±2.62	2.32±1.27	0.397	2.92±2.00

Pinic acid	456±254	0.0160	27.5±17.7	12.3±6.31	0.0533	21.1±9.03
Sterols and triterpenoids						
Tocopherol	12.6±14.3	-	0.0238±0.0184	0.0029±0.0051	0.0004	0.0076±0.0083
Cholesterol	3.30±0.871	0.0018	0.426±0.140	1.40±1.46	0.0138	0.126±0.0790
5-Cholesten-3-ol	15.2±14.8	-	0.138±0.220	0.145±0.153	-	0.0224±0.0075
Stigmasterol	5.54±1.77	0.0092	0.385±0.145	0.457±0.523	0.0062	0.193±0.213
β-Sitosterol	456±317	0.0851	20.2±4.42	11.5±12.2	0.315	10.0±12.1
Stigmasta-3,5-dien-7-one	10.9±12.6	-	-	-	-	-
Lupeol	8.30±2.79	0.767	5.58±6.33	1.15±0.797	0.504	2.47±3.18

Table A2.6. CO and $PM_{2.5}$ concentrations reported in biomass burning households.

Country	Stove	CO (ppm)	$PM_{2.5}$ ($\mu g\ m^{-3}$)	Reference
Nepal	Traditional cooking stove	16.5 ± 7.6^{a}	418 ± 686^{b}	Bartington et al. (2017)
Nepal	Traditional cook stoves	29.0 ± 5.62^{c}	1336 ± 953^{d}	Parajuli et al. (2016)
	Improved cook stoves	24.6 ± 4.91^{c}	825 ± 731^{d}	
Honduras	Traditional stoves	14.3 ± 13.1^{a}	1002 ± 1089^{e}	Clark et al. (2010)
	Improved stoves	1.8 ± 3.2^{a}	266 ± 240^{e}	
Lijiang	Traditional Fireplace	5.1 ± 3.8^{d}	430 ± 280^{d}	Chowdhury et al. (2013)
	Traditional Stove with no Chimney	3 ± 2.3^{d}	270 ± 150^{d}	
	Improved Fireplace	2.4 ± 1.4^{d}	220 ± 120^{d}	
	Improved Stove	0.7 ± 0.3^{d}	150 ± 120^{d}	
Deqin	Traditional Fireplace	5.8 ± 2.6^{d}	710 ± 380^{d}	
	Traditional Stove with no chimney	11 ± 2.7^{d}	450 ± 130^{d}	
	Traditional Stove	4.4 ± 2.9^{d}	150 ± 80^{d}	
	Improved Stove	2.4 ± 2.1^{d}	100 ± 60^{d}	

[a] 1-h maximum

[b] 48-h average

[c] 12-h average

[d] 24-h average

[e] 8-h average

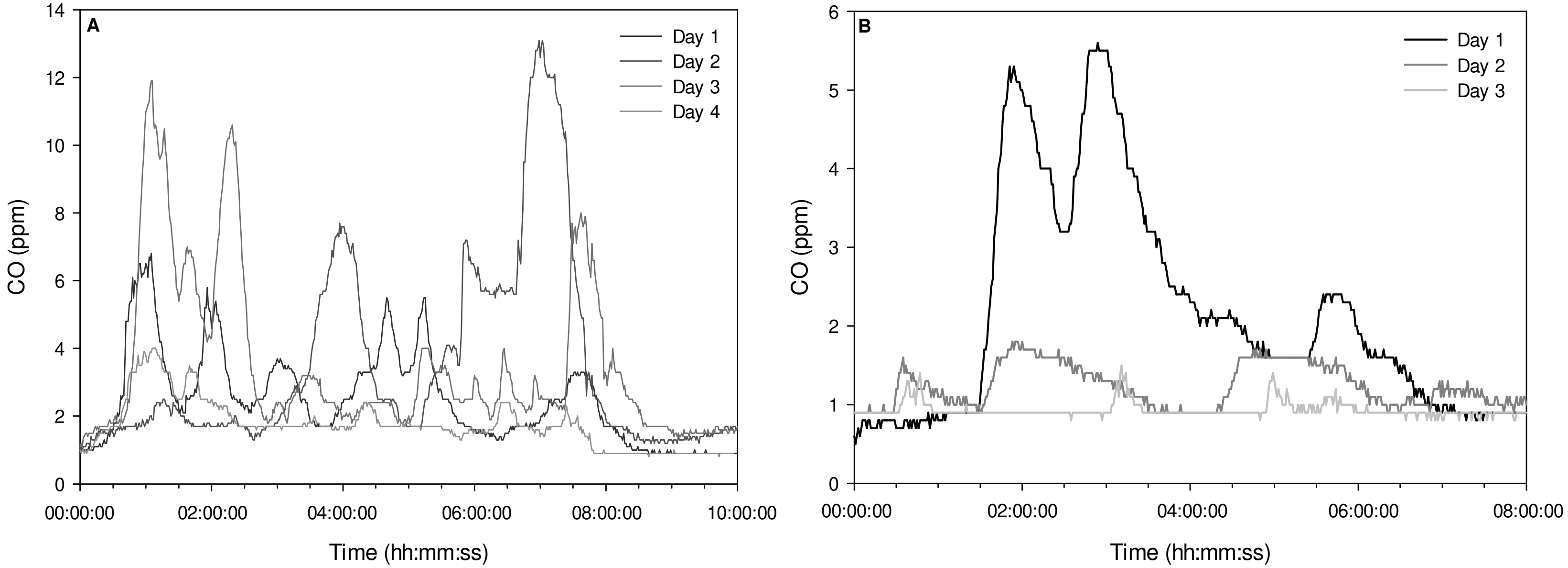


Figure A2.1. Indoor CO concentration profiles during the fireplace (A) and woodstove (B) operation.

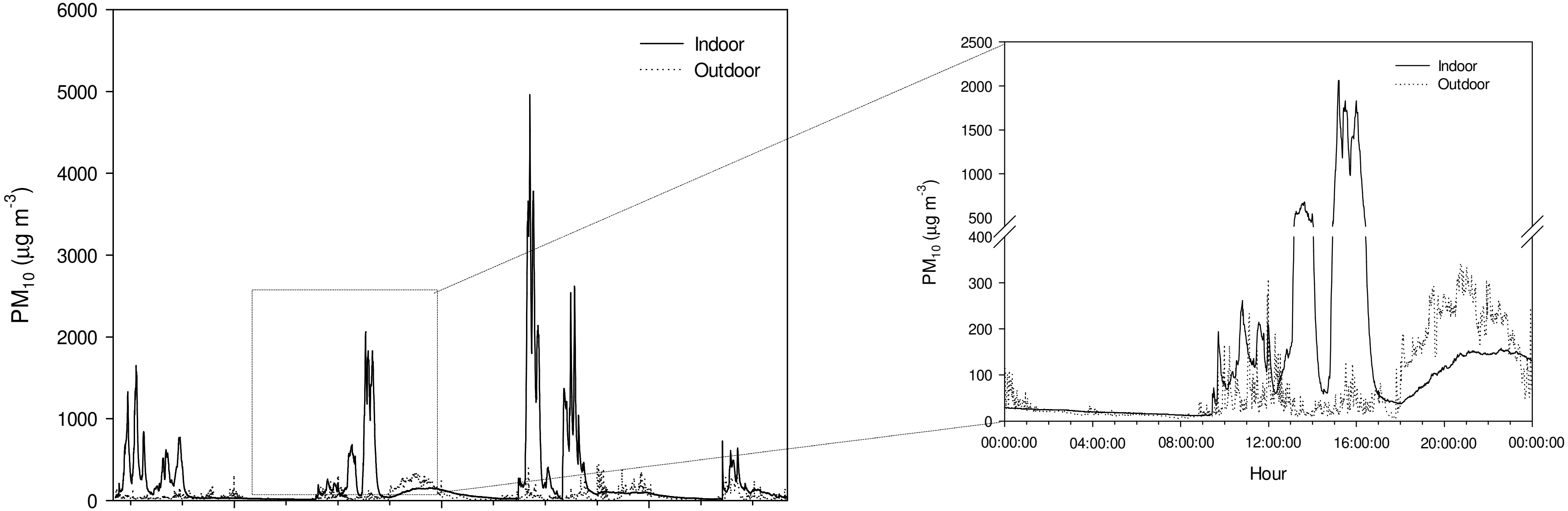


Figure A2.2. Indoor and outdoor PM$_{10}$ concentration profiles during the sampling campaign in a room equipped with a fireplace.

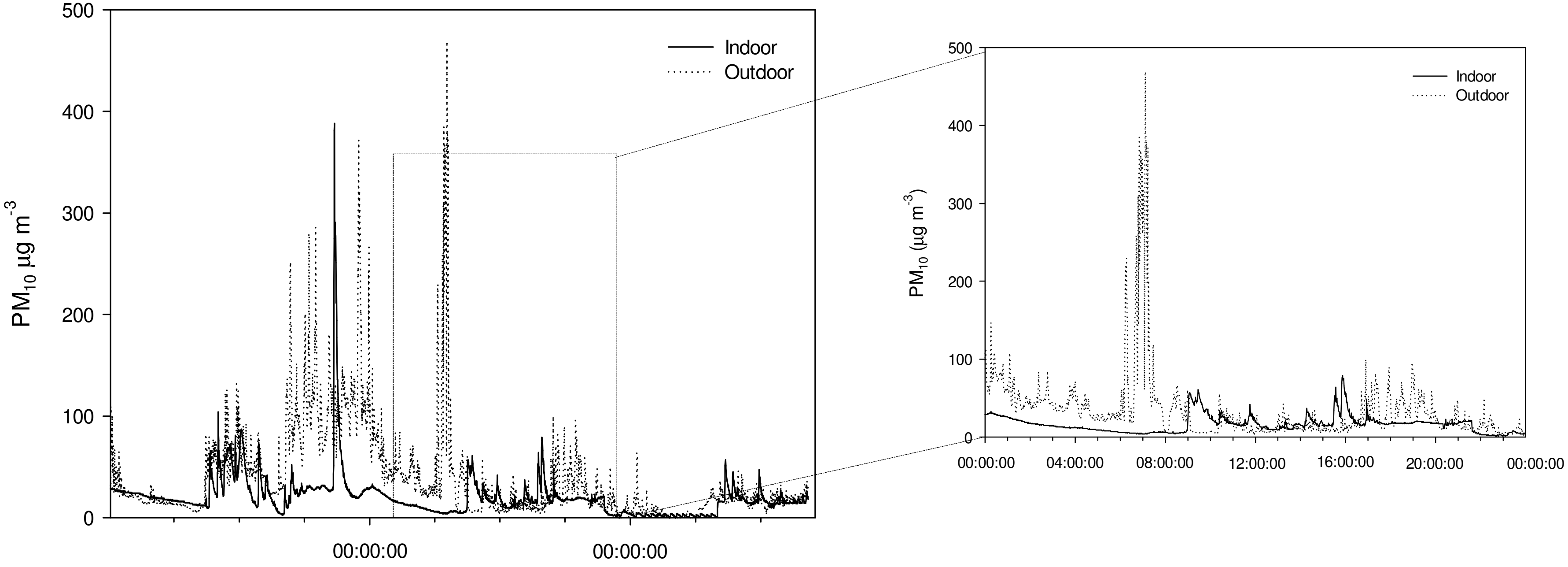


Figure A2.3. Indoor and outdoor PM$_{10}$ concentration profiles during the sampling campaign in a room equipped with a woodstove.

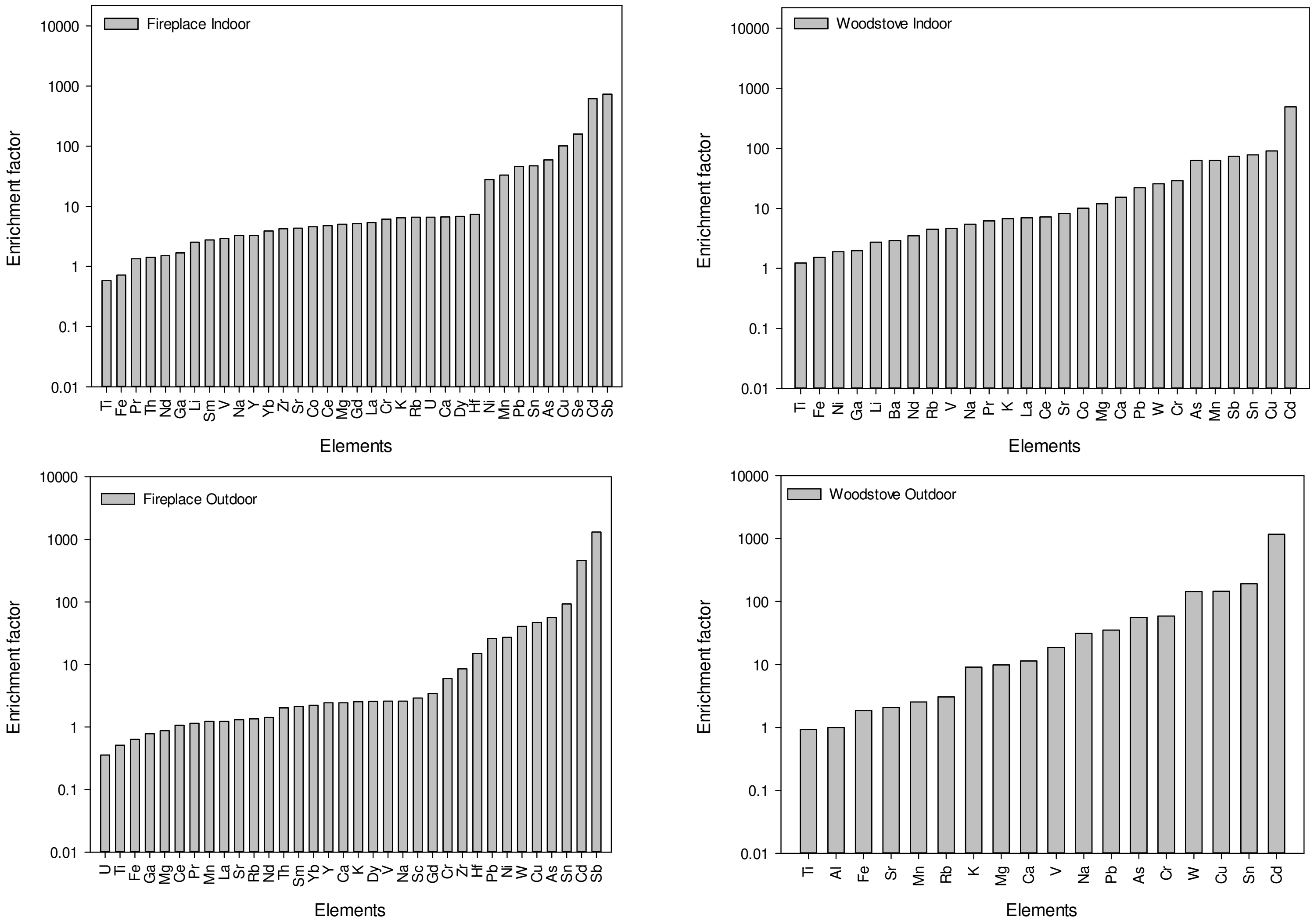


Figure A2.4. Enrichment factors for the different elements in PM_{10} samples.

References

Bartington, S.E., Bakolis, I., Devakumar, D., Kurmi, O.P., Gulliver, J., Chaube, G., Manandhar, D.S., Saville, N.M., Costello, A., Osrin, D., Hansell, \A.L., Ayres, J.G., 2017. Patterns of domestic exposure to carbon monoxide and particulate matter in households using biomass fuel in Janakpur, Nepal. Environ. Pollut. 220, 38–45. doi:10.1016/j.envpol.2016.08.074

Chowdhury, Z., Campanella, L., Gray, C., Al Masud, A., Marter-Kenyon, J., Pennise, D., Charron, D., Zuzhang, X., 2013. Measurement and modeling of indoor air pollution in rural households with multiple stove interventions in Yunnan, China. Atmos. Environ. 67, 161–169. doi:10.1016/j.atmosenv.2012.10.041

Clark, M.L., Reynolds, S.J., Burch, J.B., Conway, S., Bachand, A.M., Peel, J.L., 2010. Indoor air pollution, cookstove quality, and housing characteristics in two Honduran communities. Environ. Res. 110, 12–18. doi:10.1016/j.envres.2009.10.008

Parajuli, I., Lee, H., Shrestha, K.R., 2016. Indoor air quality and ventilation assessment of rural mountainous households of Nepal. Int. J. Sustain. Built Environ. 5, 301–311. doi:10.1016/j.ijsbe.2016.08.003.