



**Ana Margarida  
Proença Vicente**

**Caraterização de emissões gasosas e de partículas  
de fogos florestais**

**Characterisation of gas and particle emissions from  
wildfires**





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Dissertação 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 Auxiliar do Centro de Estudos do Ambiente e do Mar da Universidade de Aveiro e co-orientação do Doutor Casimiro Adrião Pio, Professor Catedrático do Departamento de Ambiente e Ordenamento da Universidade de Aveiro.

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## palavras-chave

Fogos florestais, Partículas atmosféricas, Gases de combustão, Caracterização química, Traçadores orgânicos, Fases de combustão

## resumo

Os incêndios florestais são uma importante fonte de emissão de compostos gasosos e de aerossóis. Em Portugal, onde a maioria dos incêndios ocorre no norte e centro do país, os incêndios destroem todos os anos milhares de hectares, com importantes perdas em termos económicos, de vidas humanas e qualidade ambiental. As emissões podem alterar consideravelmente a química da atmosfera, degradar a qualidade do ar e alterar o clima. Contudo, a informação sobre as características das emissões dos incêndios florestais nos países do Mediterrâneo é limitada. Tanto a nível nacional como internacional, existe um interesse crescente na elaboração de inventários de emissões e de regulamentos sobre as emissões de carbono para a atmosfera. Do ponto de vista atmosférico da monitorização atmosférica, os incêndios são considerados um desafio, dada a sua variabilidade temporal e espacial, sendo de esperar um aumento da sua frequência, dimensão e severidade, e também porque as estimativas de emissões dependem das características dos biocombustíveis e da fase de combustão. O objetivo deste estudo foi quantificar e caracterizar as emissões de gases e aerossóis de alguns dos mais representativos incêndios florestais que ocorreram no centro de Portugal nos verões de 2009 e de 2010. Efetuou-se a colheita de amostras de gases e de duas frações de partículas ( $PM_{2.5}$  e  $PM_{2.5-10}$ ) nas plumas de fumo em sacos Tedlar e em filtros de quartzo acoplados a um amostrador de elevado volume, respetivamente. Os hidrocarbonetos totais (THC) e óxidos de carbono (CO e  $CO_2$ ) nas amostras gasosas foram analisados em instrumentos automáticos de ionização de chama e detetores não dispersivos de infravermelhos, respetivamente. Para algumas amostras, foram também quantificados alguns compostos de carbonilo após reamostragem do gás dos sacos Tedlar em cartuchos de sílica gel revestidos com 2,4-dinitrofenilhidrazina (DNPH), seguida de análise por cromatografia líquida de alta resolução. Nas partículas, analisou-se o carbono orgânico e elementar (técnica termo-óptica), iões solúveis em água (cromatografia iónica) e elementos (espectrometria de massa com plasma acoplado por indução ou análise instrumental por ativação com neutrões). A especificação orgânica foi obtida por cromatografia gasosa acoplada a espectrometria de massa após extração com recurso a vários solventes e separação dos extratos orgânicos em diversas classes de diferentes polaridades através do fracionamento com sílica gel.



Os fatores de emissão do CO e do CO<sub>2</sub> situaram-se nas gamas 52-482 e 822-1690 g kg<sup>-1</sup> (base seca), mostrando, respetivamente, correlação negativa e positiva com a eficiência de combustão. Os fatores de emissão dos THC apresentaram valores mais elevados durante a fase de combustão latente sem chama, oscilando entre 0.33 e 334 g kg<sup>-1</sup> (base seca). O composto orgânico volátil oxigenado mais abundante foi o acetaldeído com fatores de emissão que variaram desde 1.0 até 3.2 g kg<sup>-1</sup> (base seca), seguido pelo formaldeído e o propionaldeído. Observou-se que as emissões destes compostos são promovidas durante a fase de combustão latente sem chama. Os fatores de emissão de PM<sub>2.5</sub> e PM<sub>10</sub> registaram valores entre 0.50-68 e 0.86-72 g kg<sup>-1</sup> (base seca), respetivamente. A emissão de partículas finas e grosseiras é também promovida em condições de combustão lenta. As PM<sub>2.5</sub> representaram cerca de 90% da massa de partículas PM<sub>10</sub>. A fração carbonosa das partículas amostradas em qualquer dos incêndios foi claramente dominada pelo carbono orgânico. Foi obtida uma ampla gama de rácios entre o carbono orgânico e o carbono elementar, dependendo das condições de combustão. Contudo, todos os rácios refletiram uma maior proporção de carbono orgânico em relação ao carbono elementar, típica das emissões de queima de biomassa. Os iões solúveis em água obtidos nas partículas da pluma de fumo contribuíram com valores até 3.9% da massa de partículas PM<sub>2.5</sub> e 2.8% da massa de partículas de PM<sub>2.5-10</sub>. O potássio contribuiu com valores até 15 µg mg<sup>-1</sup> PM<sub>2.5</sub> e 22 µg mg<sup>-1</sup> PM<sub>2.5-10</sub>, embora em massa absoluta estivesse maioritariamente presente nas partículas finas. Os rácios entre potássio e carbono elementar e entre potássio e carbono orgânico obtidos nas partículas da pluma de fumo enquadram-se na gama de valores relatados na literatura para emissões de queima de biomassa. Os elementos detetados nas amostras representaram, em média, valores até 1.2% e 12% da massa de PM<sub>2.5</sub> e PM<sub>2.5-10</sub>, respetivamente. Partículas resultantes de uma combustão mais completa (valores elevados de CO<sub>2</sub> e baixos de CO) foram caracterizadas por um elevado teor de constituintes inorgânicos e um menor conteúdo de matéria orgânica. Observou-se que a matéria orgânica particulada é composta principalmente por componentes fenólicos e produtos derivados, séries de compostos homólogos (alcanos, alcenos, ácidos alcanóicos e alcanóis), açúcares, biomarcadores esteróides e terpenóides, e hidrocarbonetos aromáticos policíclicos. O reteno, um biomarcador das emissões da queima de coníferas, foi o hidrocarboneto aromático dominante nas amostras das plumas de fumo amostradas durante a campanha que decorreu em 2009, devido ao predomínio de amostras colhidas em incêndios em florestas de pinheiros. O principal açúcar anidro, e sempre um dos compostos mais abundantes, foi o levoglucosano. O rácio levoglucosano/OC obtido nas partículas das plumas de fumo, em média, registaram valores desde 5.8 a 23 mg g<sup>-1</sup> OC. Os rácios levoglucosano/manosano e levoglucosano/(manosano+galactosano) revelaram o predomínio de amostras provenientes da queima de coníferas. Tendo em conta que a estimativa das emissões dos incêndios florestais requer um conhecimento de fatores de emissão apropriados para cada biocombustível, a base de dados abrangente obtida neste estudo é potencialmente útil para atualizar os inventários de emissões. Tem vindo a ser observado que a fase de combustão latente sem chama, a qual pode ocorrer simultaneamente com a fase de chama e durar várias horas ou dias, pode contribuir para uma quantidade considerável de poluentes atmosféricos, pelo que os fatores de emissão correspondentes devem ser considerados no cálculo das emissões globais de incêndios florestais. Devido à falta de informação detalhada sobre perfis químicos de emissão, a base de dados obtida neste estudo pode também ser útil para a aplicação de modelos no receptor no sul da Europa.



**keywords**

Wildfires, Atmospheric particles, Gaseous compounds, Chemical Characterisation, Organic Tracers, Combustion Regime, Emission factors

**abstract**

Wildfires are an important emission source of gaseous compounds and aerosol particles. In Portugal, where most fire events occur in northern and central areas of the country, wildfires destroy every year thousands of hectares, with important losses in terms of economic disruptions, human lives and environmental quality. Emissions can substantially perturb atmospheric chemistry, degrade air quality and alter weather and climate. However, limited data exist on the emission characteristics from this source in Mediterranean countries. At both national and international levels, there is an increasing focus on the establishment of emission inventories and regulations of regional carbon emissions to the atmosphere. From the standpoint of atmospherically-based carbon monitoring programs, fires are challenging because they tend to be extremely variable in intensity, space and time, they are expected to increase in number and severity in the future, and because emission estimates depend on biofuel characteristics and combustion phase. The aim of this study was to quantify and characterise the emissions of trace gases and aerosol particles from some of the most representative wildfires that occurred in central Portugal during the summers of 2009 and 2010. Gases and particles of two size fractions ( $PM_{2.5}$  and  $PM_{2.5-10}$ ) were collected from the smoke plumes in Tedlar bags and on quartz filters mounted on a high volume sampler, respectively. The gaseous compounds were subsequently analysed for total hydrocarbons (THC) and carbon oxides (CO and  $CO_2$ ) in automatic instruments with flame ionisation and non-dispersive infrared detectors, respectively. For some smoke samples, carbonyls were also quantified after drawing air from the Tedlar bags through cartridges containing silica gel coated with 2,4-dinitrophenylhydrazine (DNPH) reagent and followed by analysis by high performance liquid chromatography. Particles were analysed for organic and elemental carbon (thermal-optical technique), water-soluble ions (ion chromatography) and trace elements (inductively coupled plasma mass spectrometry or instrumental neutron activation analysis). The organic speciation was obtained by gas chromatography coupled to mass spectrometry after multi-solvent extraction and separation of the organic extracts into several classes of different polarities by flash chromatography on silica gel.



The CO and CO<sub>2</sub> emission factors were in the ranges 52-482 and 822-1690 g kg<sup>-1</sup> (dry basis), showing, respectively, negative and positive correlations with the combustion efficiency. The THC emission factors were higher during smouldering conditions with values ranging between 0.33 and 334 g kg<sup>-1</sup> (dry basis). The most abundant oxygenated volatile organic compound measured was acetaldehyde with emission factors ranging from 1.0 to 3.2 g kg<sup>-1</sup> (dry basis), followed by formaldehyde and propionaldehyde. The emission of these compounds were enhanced during the smouldering phase. PM<sub>2.5</sub> and PM<sub>10</sub> emission factors were in the ranges 0.50-68 and 0.86-72 g kg<sup>-1</sup> (dry basis), respectively. The emission of fine and coarse particles was promoted by smouldering combustion conditions.

PM<sub>2.5</sub> particles contributed to around 90% of the PM<sub>10</sub> mass. The carbonaceous fraction of smoke particulate samples from any of the fires was clearly dominated by organic carbon. A wide range of organic carbon-to-elemental carbon concentration ratios was obtained, depending on the combustion conditions. However, all the ratios reflected a much higher proportion of organic carbon in relation to elemental carbon, typical of biomass burning emissions. The water-soluble ions obtained in smoke particles contributed with values up to 3.9% of the PM<sub>2.5</sub> and 2.8% of the PM<sub>2.5-10</sub> particles. Potassium contributed up to 15 µg mg<sup>-1</sup> PM<sub>2.5</sub> and 22 µg mg<sup>-1</sup> PM<sub>2.5-10</sub>, although in absolute mass it was overwhelmingly present in fine particles. The potassium-to-elemental carbon and potassium-to-organic carbon ratios obtained in smoke particles were in accordance with those reported in the literature for biomass burning sources. Trace elements detected in smoke samples represented, on average, up to 1.2% and 12% of the PM<sub>2.5</sub> and PM<sub>2.5-10</sub> mass, respectively. Particles from a more complete combustion (higher CO<sub>2</sub> and lower CO values) were characterised by a higher content of inorganic constituents and a lower organic content. The particulate organic matter was mainly composed of phenolic compounds and their alteration products, homologous series (*n*-alkanes, *n*-alkenes, *n*-alkanoic acids and *n*-alkanols), sugar constituents, steroid and terpenoid biomarkers, and polycyclic aromatic hydrocarbons. Retene, a biomarker of softwood smoke, was the dominant aromatic hydrocarbon in smoke samples collected during the 2009 campaign, due to a predominance of samples from wildfires in pine forests. The major anhydrosugar, and always one of the most abundant compounds, was levoglucosan. The levoglucosan/OC ratio obtained in the smoke particles, on average, ranged from 5.8 to 23 mg g<sup>-1</sup> OC. The levoglucosan-to-mannosan and the levoglucosan-to-mannosan plus galactosan ratios determined reveal a predominance of samples from softwood combustion.

Since estimation of wildfire emissions requires knowledge of fuel-appropriate emissions factors, the comprehensive database obtained in this study is potentially useful to update the current emission inventories. It has been observed that the smouldering phase, which can occur simultaneously with the flaming front and continue for several hours to days, may contribute to significant amounts of atmospheric pollutants and the corresponding emission factors should be considered when calculating the global wildfire emissions. Due to the lack of detailed emission profiles, the databases obtained in this study can also be very helpful for receptor modelling in southern Europe.



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# List of publications

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

- I. Célia Alves, Ana Vicente, Teresa Nunes, Cátia Gonçalves, Ana Patrícia Fernandes, Fátima Mirante, Luís Tarelho, Ana Sanchez de la Campa, Xavier Querol, Alexandre Caseiro, Cristina Monteiro, Margarita Evtyugina and Casimiro Pio, 2011. Summer 2009 wildfires in Portugal: emission of trace gases and aerosol composition. *Atmospheric Environment* 45, 641-649.
- II. Célia Alves, Ana Vicente, Cristina Monteiro, Cátia Gonçalves, Margarita Evtyugina and Casimiro Pio, 2011. Emission of trace gases and organic components in smoke particles from a wildfire in a mixed-evergreen forest in Portugal. *Science of the Total Environment* 409, 8, 1466-1475.
- III. Ana Vicente, Célia Alves, Cristina Monteiro, Teresa Nunes, Fátima Mirante, Margarita Evtyugina, Mário Cerqueira and Casimiro Pio, 2011. Measurement of trace gases and organic compounds in the smoke plume from a wildfire in Penedono (central Portugal). *Atmospheric Environment* 45, 5172-5182.
- IV. Ana Vicente, Célia Alves, Cristina Monteiro, Teresa Nunes, Fátima Mirante, Mário Cerqueira, Ana Calvo and Casimiro Pio, 2012. Organic speciation of aerosols from wildfires in central Portugal during summer 2009. *Atmospheric Environment* 57, 186-196.
- V. Ana Vicente, Célia Alves, Ana Calvo, Ana Patrícia Fernandes, Teresa Nunes, Cristina Monteiro, Susana Marta Almeida and Casimiro Pio. Emission factors and detailed chemical composition of smoke particles from the 2010 wildfire season in central Portugal. Submitted to *Atmospheric Environment*.

# Abbreviations

BC	Black Carbon
BSTFA	<i>N,O</i> -bis(trimethylsilyl)-trifluoroacetamide
C	Carbon
CCN	Cloud Condensation Nuclei
CMB	Chemical Mass Balance
CO	Carbon Monoxide
CO <sub>2</sub>	Carbon Dioxide
CH <sub>4</sub>	Methane
CH <sub>3</sub> Cl	Methyl Chloride
CH <sub>3</sub> Br	Methyl Bromine
CPI	Carbon Preference Indices
DCM	Dichloromethane
EC	Elemental Carbon
EF	Emission Factor
EI	Electron Impact
EPA	Environmental Protection Agency
FCT	Portuguese Science Foundation
G	Galactosan
GC-MS	Gas Chromatography Mass Spectrometry
HPLC	High Performance Liquid Chromatography
ICP-MS	Inductive Coupled Plasma with Mass Spectrometry
INAA	Instrumental Neutron Activation Analysis
L	Levogluosan
M	Mannosan
MCE	Modified Combustion Efficiency
MeOH	Methanol
ND	Not Detected
NMHC	Non Methane Hydrocarbons
NO <sub>x</sub>	Nitrogen Oxides
N <sub>2</sub>	Nitrogen

N <sub>2</sub> O	Nitrous Oxide
O <sub>2</sub>	Oxygen
OC	Organic Carbon
OM	Organic Matter
PAH	Polycyclic Aromatic Hydrocarbons
PC	Pyrolysed Carbon
PM	Particulate Matter
PM <sub>1</sub>	Particulate Matter with Equivalent Aerodynamic Diameter < 1 μm
PM <sub>10</sub>	Particulate Matter with Equivalent Aerodynamic Diameter < 10 μm
PM <sub>2.5</sub>	Particulate Matter with Equivalent Aerodynamic Diameter < 2.5 μm
PM <sub>2.5-10</sub>	Particulate Matter with Equivalent Aerodynamic Diameter Between 2.5 and 10 μm
RRF	Relative Response Factors
SO <sub>2</sub>	Sulphur Dioxide
T	Temperature
TC	Total Carbon
THC	Total Hydrocarbons
TMCS	Trimethylchlorosilane
TMS	Trimethylsilyl
UV	Ultra Violet
USA	United States of America
VOC	Volatile Organic Compounds



# **CHAPTER 1**



# Chapter 1. General Information

## 1.1 Introduction

### 1.1.1 Concepts

The process of burning biomass has been used through the times with different purposes. Biomass burning results from either: 1) natural processes, such as ignition by lightning strikes; or 2) anthropogenic activity, such as burning vegetation for agricultural land clearing and preparing existing fields for planting. (Ortiz de Zárate et al., 2005; Simoneit, 2002).

“Wildfire” is the term applied to any unwanted, unplanned, damaging fire burning in forest, shrub or grass. While sometimes caused by lightning, nine out of ten wildfires are human-caused. There are three different classes of wildfires:

- a) Ground fires - Burn the organic materials beneath the surface litter;
- b) Surface fires - Burn surface litter;
- c) Crown fires - Burn from top to top of trees or shrubs.

The fire triangle or combustion triangle is a simple way of understanding the necessary ingredients of most fires. Each side of the triangle (Figure 1.1) represents one of the three ingredients needed to have a fire – oxygen, heat, and fuel – demonstrating the interdependence of these ingredients in creating and sustaining fire. When there is not enough heat generated to sustain the process, when the fuel is exhausted, removed, or isolated, or when oxygen supply is limited, then a side of the triangle is broken and the fire will die.

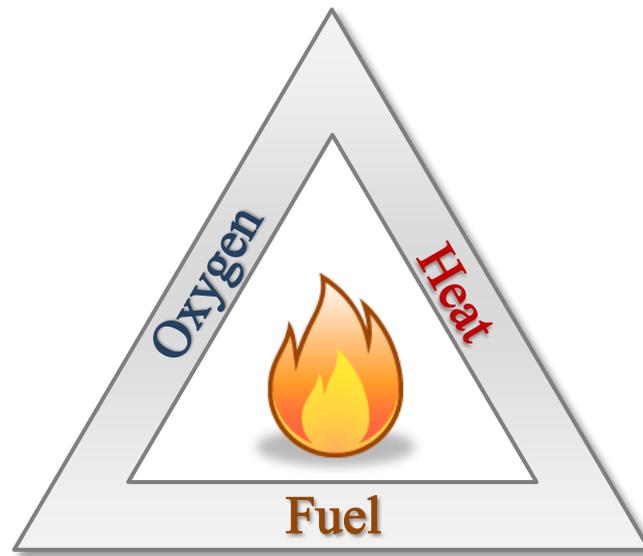


Figure 1.1 Fire triangle.

A **heat** source is responsible for the initial ignition of fire, and heat is also needed to maintain the fire and permit it to spread. Heat allows fire to spread by removing the moisture from nearby fuel, warming surrounding air, and preheating the fuel in its path, enabling it to travel more easily.

**Fuel** is any kind of combustible material, and is characterised by its moisture content (how wet the fuel is), size and shape, quantity, and the arrangement in which it is spread over the landscape. The moisture content determines how easily that fuel will burn.

Air contains about 21% **oxygen**, and most fires require at least 16% oxygen content to burn. Oxygen supports the chemical processes that occur during a wildland fire. When fuel burns, it reacts with oxygen from the surrounding air releasing heat and generating combustion products (i.e. gases, smoke and embers). This process is known as oxidation.

The complete combustion of wildland fuels (forests, grasslands, wetlands) requires a heat flux (temperature gradient), adequate oxygen supply, and sufficient burning time. The size and quantity of wildland fuels, meteorological conditions, and topographic features interact to modify the burning behaviour as the fire spreads, and the wildfire will attain different degrees of combustion efficiency during its lifetime (Hardy, et al., 2001; Mobley, 1976; Sandberg and Dost, 1990; Stanturf, 2008).

Wildfires are ignited by a variety of sources including lightning, untended campfires, off road vehicles, cigarettes, and arsonists. Regardless of the ignition source, the physics of combustion is the same. Combustion involves several phases (pre-combustion,

flaming, smouldering, and glowing) (Figure 1.2) as a fire advances through fuel, generating heat that produces a convection column that vertically lifts by-product gases, vapours, and particulates (smoke). In the pre-combustion (or pre-heating) phase, fuel elements ahead of the fire are heated, causing fuel drying. Heat induces thermal decomposition (pyrolysis) of some components of woody fuels, leading to combustible organic gases and vapours release. Biomass predominantly burned in the wildfires consists typically of lignin (18-35 %, dry matter), carbohydrates (65-70 %, dry matter), proteins, amino acids, and other metabolites, including volatile substances (such as alcohols, aldehydes and terpenes). It also contains minerals (up to 10%) and water (up to 60%). The carbohydrates are divided into cellulose (40-50%, dry matter) and hemicellulose (25-35 %, dry matter) (Andreae and Merlet, 2001; Pettersen, 1984).

During the pre-combustion stage of burning, heat energy is absorbed by the fuel which, in turn, gives off water vapour and flammable tars, pitches, and gases. They ignite when mixed with oxygen to initiate the flaming combustion phase. The flaming combustion phase is the luminous oxidation of gases evolved from the rapid decomposition of fuel. This phase follows the pre-combustion phase and precedes the smouldering combustion phase, which has a much slower combustion rate. Water vapour, soot, and tar comprise the visible smoke. Relatively efficient combustion produces minimal soot and tar, resulting in white smoke; high fuel moisture content also produces white smoke.

Smouldering combustion is the combined processes of dehydration, pyrolysis, solid oxidation, and scattered flaming combustion and glowing combustion, which occurs in the aftermath of flaming combustion. Smouldering combustion often is characterised by large amounts of smoke consisting mainly of tars. In some fuels, such as large woody debris or deep organic soils, smouldering combustion may last for days or even months.

The glowing combustion phase is the final phase of combustion following flaming and smouldering phases. Glowing combustion is the process whereby solid fuels are oxidised, accompanied by incandescence. All volatiles have already been driven off, oxygen reaches the combustion surfaces, and there is no visible smoke. This phase follows the smouldering combustion phase and continues until the temperature drops below the combustion threshold value, or until only non-combustible ash remains.

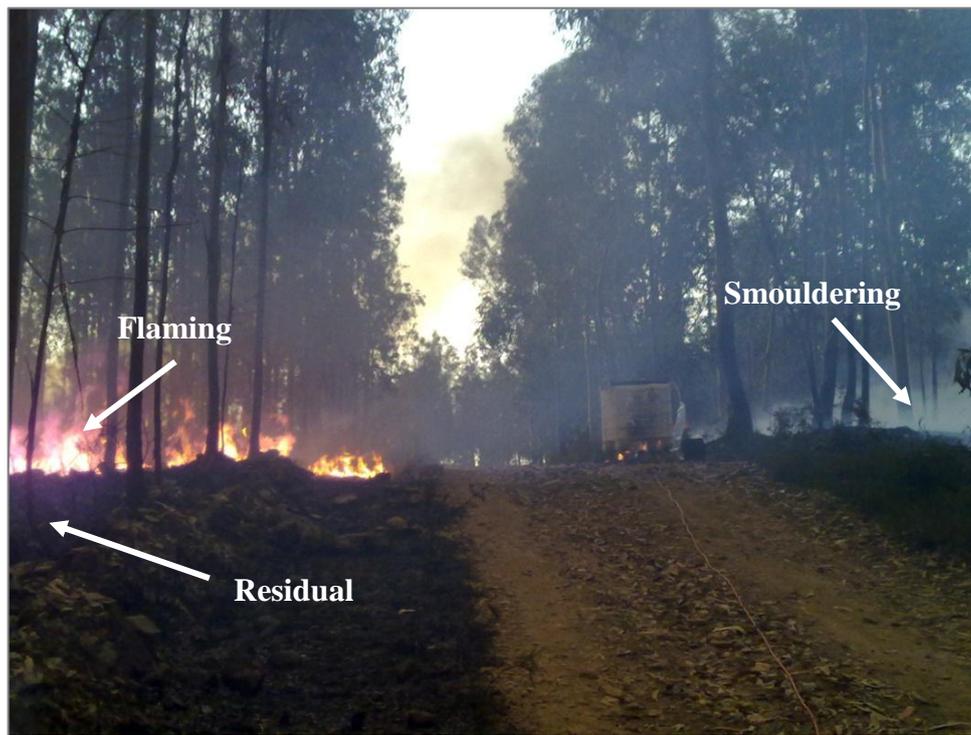


Figure 1.2 Different phases of the combustion process during a wildfire event.

## 1.2 Environmental impacts of wildfires

Biomass burning processes, and especially wildfires, represent a distinct biogeochemical process that plays a major role in the global carbon cycle (Ito, 2005; Turetsky et al., 2011) and on atmospheric chemistry (Anttila et al., 2008; Junquera et al., 2005; Koppmann et al., 2005; Pfister et al., 2008b; Yokelson et al., 2007b), with a strong effect at the regional scale (Alves et al., 2010a; Alves et al., 2010b; Alves et al., 2011a; Alves et al., 2011b; Balasubramanian and See, 2006; Jaffe et al., 2008; Liu et al., 2009; McMeeking et al., 2006; Pio et al., 2008) and also at sites thousands of kilometres from the source (Duck et al., 2007; Jaffe et al., 2004; Lewis et al., 2007; Petzold et al., 2007; Witham and Manning, 2007).

It has been estimated that from 1850 to 1980 between 90 Pg ( $90 \times 10^{15}$  g) and 120 Pg ( $120 \times 10^{15}$  g) of carbon dioxide ( $\text{CO}_2$ ) were emitted to the atmosphere from forest fires in the tropics. During the same period, the combustion of coal, oil, and gas in industrialised countries accounted for the emission of 165 Pg ( $165 \times 10^{15}$  g) of this greenhouse gas. Currently, an estimated  $5.6 \text{ Pg yr}^{-1}$  of carbon are emitted into the atmosphere due to fossil

fuel burning, whereas fires in tropical forests contribute another 2.4 Pg of carbon, i.e. about 40% of the total (NASA, 2009). In addition to CO<sub>2</sub>, biomass burning also releases into the atmosphere considerable amounts of other chemically active trace gases and aerosols. Emissions of carbon monoxide (CO) and methane (CH<sub>4</sub>) perturb atmospheric oxidation efficiency by reacting with hydroxyl radicals (Crutzen and Andreae, 1990). Just as in urban areas, emissions of nitric oxides (NO<sub>x</sub>) and hydrocarbons react to form ozone, leading to higher ozone levels in the tropics than in other regions due to the stronger impact of biomass burning in tropical regions (Thompson et al., 2001). Researchers also concluded that some biomass burning emissions are connected to edaphic biological processes. Bacteria in soil can boost production of nitrous oxide (N<sub>2</sub>O), a greenhouse gas. Nitrification is the biological process believed responsible for the production of this gas, together with nitric oxide (NO), using ammonium found naturally in soil and also in fire ash as the substrate. It has been observed that the enhanced concentrations of ammonium in the ash lead to more nitrification after a fire, thereby releasing additional NO and N<sub>2</sub>O. The emissions of these gases produced by bacteria after a fire may surpass the amounts emitted during biomass burning (Anderson et al., 1988; Weitz et al., 1998; Winstead et al., 1991). Methyl chloride (CH<sub>3</sub>Cl) and methyl bromine (CH<sub>3</sub>Br) released by biomass burning are sources of halogenated radicals, which lead to the chemical destruction of stratospheric ozone (Mead et al., 2008; Prasad et al., 2001; Yvon-Lewis et al., 2009). Global estimates of gas and particulate emissions from biomass burning are largely variable (Ito and Penner, 2004; Jain et al., 2006; Lobert et al., 1999; NASA, 2009; Randerson et al., 2006; Schultz et al., 2008; van der Werf et al., 2004; Warwick et al., 2006; Yoshida et al., 2006): 220-13500 Tg CO<sub>2</sub> yr<sup>-1</sup>, 120-680 Tg CO yr<sup>-1</sup>, 11-53 Tg CH<sub>4</sub> yr<sup>-1</sup>, 2-21 Tg NO<sub>x</sub> yr<sup>-1</sup>, 650-1120 Gg CH<sub>3</sub>Cl yr<sup>-1</sup> and 10-40 Gg CH<sub>3</sub>Br yr<sup>-1</sup>. Estimates of particulate matter smaller than 2.5 μm in aerodynamic diameter (PM<sub>2.5</sub>) from biomass burning are roughly 38 Tg yr<sup>-1</sup> (NASA, 2009; Randerson et al., 2006). A critical evaluation of the available data on emission factors (gram species per kilogram dry matter burned) for a long list of pyrogenic species from various types of biomass burning can be found in Andreae and Merlet (2001).

The radioactively active carbon-containing particles (Langmann et al., 2009; Ramanathan et al., 2001; Reid et al., 2005) emitted by biomass burning have strong climate-forcing impacts, either contributing to or counterbalancing the effects of greenhouse gases (Pfister et al., 2008a). In particular, elemental carbon particulate matter

(EC) has recently been identified as an important contributor to radiative heating of the atmosphere (Jacobson, 2001). Organic carbon particulate matter (OC), which is emitted along with EC, has a cooling effect on climate and may act to offset some of the global warming impact of EC emissions (Chen and Bond, 2010; Chung and Seinfeld, 2005; Penner et al., 1998). In the case of aerosols from biomass burning, OC is thought to totally balance the warming potential of EC, because these emissions are characterised by high OC/EC ratios (Alves et al., 2010b, 2011b; Schaap and Denier van der Gon, 2007). The large emissions from biomass burning strongly affect the atmospheric radiation balance, with a net loss up to 70% of photosynthetic active radiation at the surface of the forests (Artaxo et al., 2005).

Organic matter represents the major fraction of smoke aerosols, sometimes accounting for over 90% of the total mass (Graham et al., 2002, 2003; Yamasoe et al., 2000), whereas inorganic constituents account for a small fraction of the smoke aerosol mass (Alves et al., 2010b, 2011b). However, the combustion-related trace elements and water-soluble ions are biogeochemically active species, participating in nutrient cycling (Baker, 2006; Furutani et al., 2010).

Biomass burning particles degrade visibility, are efficient cloud condensation nuclei (CCN) and can influence the formation of precipitation (Petters et al., 2009; Reid et al., 2005; Reutter et al., 2009; Rose et al., 2010; Rosenfeld et al., 2008; Spracklen et al., 2007). The effect of biomass burning aerosols on the hydrological cycle remains one of the largest uncertainties in the climate system, since they have competing effects on clouds. Depending on the level of aerosol loading and the background cloud characteristics, biomass burning aerosols have been shown in observational studies to strengthen or inhibit cloud formation and/or growth through microphysical and absorptive pathways, respectively (Ramanathan and Carmichael, 2008; Randles and Ramaswamy, 2010).

In addition to being able to perturb climate and atmospheric chemistry, smoke aerosols possess a toxicity level greater than that of an equivalent dose of particulate matter in ambient air (Wegesser et al., 2009) and can have profound adverse health effects (Fowler, 2003; Jayachandran, 2008; Potera, 2009).

Future climate changes are expected to result in more frequent and intense wildfires (Carvalho et al., 2010; Flannigan et al., 2001) with far reaching consequences for the global carbon cycle, atmospheric chemistry, climate, ecosystems and human health.

### 1.3 Wildfires in Portugal

According to the Portuguese Forest Services nowadays the Portuguese forest area cover 3.3 million hectares, which correspond to 35.8% of the territory. The forest distribution in Portugal is presented in Figure 1.3. The north and centre regions are characterised by the presence of maritime pine, eucalypt, Portuguese oak and Portuguese chestnut, while the south is mainly covered by stone pine, cork oak and holm oak. The most abundant species are maritime pine, eucalypt, cork oak and holm oak, covering 86% of the Portuguese forest area.

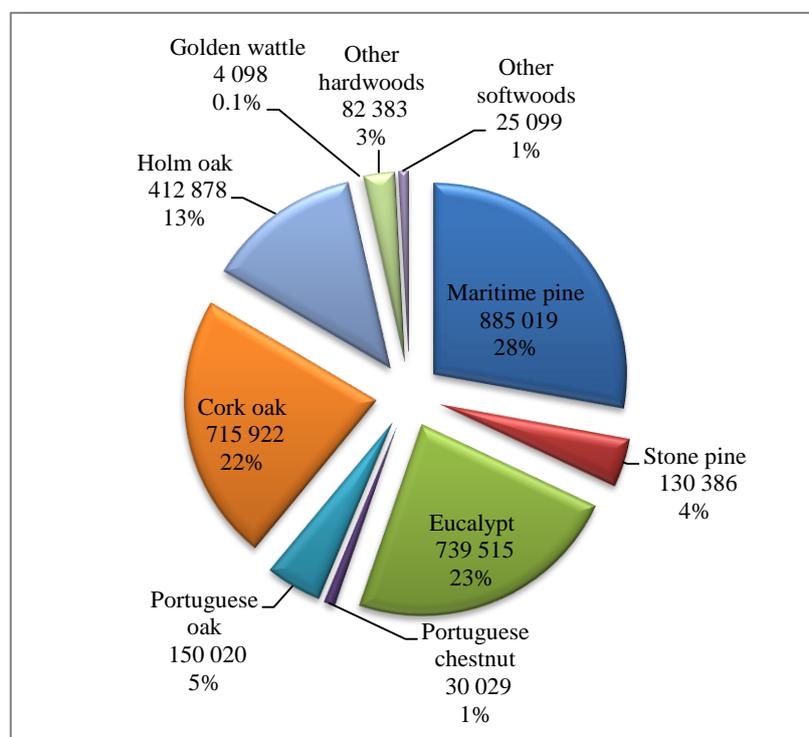


Figure 1.3 Distribution of forest in the Portuguese territory (ha and %) (Direcção Nacional de Gestão Florestal, 2010).

From January 1980 to August 2012 the annual burnt area ranged from 17 564 (in 2008) to 425 839 ha (in 2003), averaging 107 844 ha yr<sup>-1</sup> (Figure 1.4). In 2009, about 86 674 ha were burned (24 107 ha corresponding do plantations and 62 567 ha to forests and shrublands). In this year most wildfires occurred in central and northern Portugal. The largest wildfire occurring in 2009 broke out at Sabugal, in Guarda district. This fire began on August 30<sup>th</sup> and lasted for three days, with a total burnt area of 9 976 ha (DGRF, 2010).

In 2010, approximately 130 000 ha of burnt areas in Portugal resulted from wildfires of large dimension ( $\geq 100$  ha). The districts most affected by wildfires in 2010 were Guarda, Vila Real, Viana do Castelo and Viseu; the largest event was registered in the Viseu district, in São Pedro do Sul, with an area consumed by the fire of 5 066 ha (DGRF, 2011). There is an increasing likelihood that ignitions resulting in large fires will be more prevalent in the near future due to: (i) the decline in population density in inland regions and (ii) the current expected climatic trends of less rainfall and hotter weather (Moreira et al., 2010). The increase in the frequency and intensity of wildfires will result in far more intense emissions of trace gases and particles into the atmosphere.

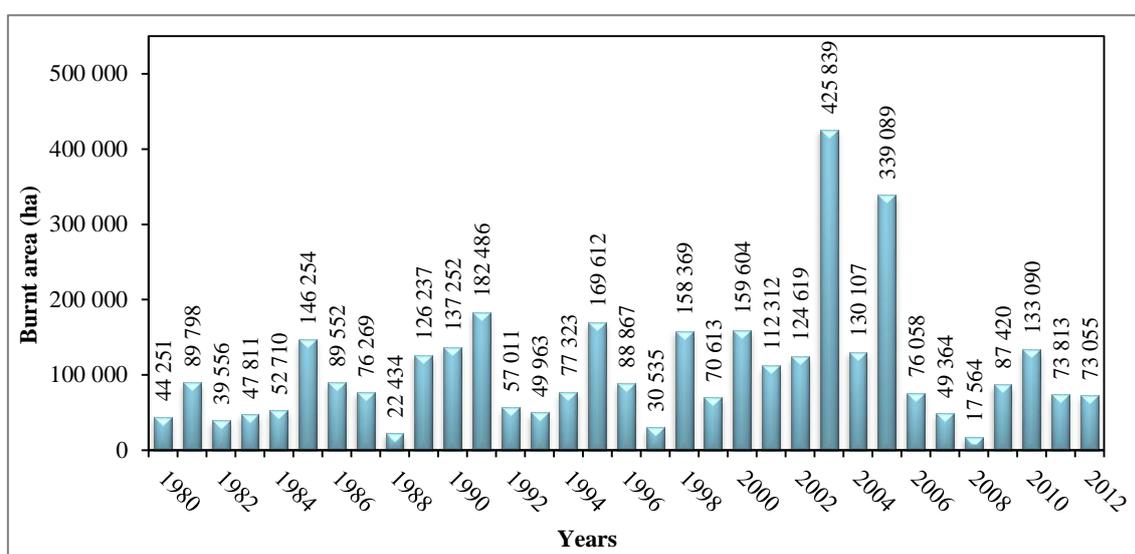


Figure 1.4 Distribution of burnt area since 1980.

## 1.4 Objectives

The detailed characterisation of the chemical composition and quantification of the amounts of trace gases and aerosols emitted from wildfires are critical to the establishment of sustainable environmental strategies. The knowledge about fire smoke composition is predominately focused on the emissions of CO, CO<sub>2</sub>, trace gases and particles and mostly available for the African savannah fires (Korontzi et al., 2003), Mexican forest, savannah and agricultural residues (Yokelson et al., 2011). The composition and amount of aerosols emitted by this process depend on various factors, such as combustion conditions, fuel type or meteorology. The studies related to fire emissions are very scarce and most of them have been carried out under controlled field conditions (Alves et al., 2010a,b; Lee et al.,

2005; Yan et al., 2008), especially making use of aircrafts to collect the smoke plumes (Hobbs et al., 2003; Yokelson et al., 2007a; Yokelson et al., 2007b). The importance of plume collection from real fires must be highlighted since laboratory experiments, and even prescribed field burnings, do not represent either the severity of wildfire events, or their emissions. Prescribed fires are only allowed under specific conditions, and depend on available resources, time of the year, weather and desired results. Unlike other sources, wildfire emissions are difficult to measure due to the unpredictability in space and time, dangerousness and, many times, inaccessibility of these events. Prompt availability and fast response are required to collect smoke samples from unexpected fire events, which frequently are located in areas of difficult access. Truly representative sampling is extremely hard to accomplish. The experimental approach most suitable for sampling emissions from wildfire smoke plumes, which during strong flaming combustions and especially under calm wind conditions are injected at high altitudes, is the use of very expensive aircraft means. In Portugal, where aerial means are used for fire fighting, other concurrent aeronautical activities near the sources are prohibited. Consequently, the sample collection is only possible at ground level. The Mediterranean regions are characterised by hot and dry summers, high diversity of plant species and unusual geographical/topographical variability related to the presence of a jagged coastline and frequent mountain ranges, often rather steep. These features give rise to a situation of high fire risk. In the Mediterranean regions, the duration, severity and coincidence of heat waves and wildfires have significantly increased in the last decade (Hoinka et al., 2009; and references therein; Piñol et al., 1998). However, detailed information on wildfire emissions is inexistent for these regions.

To evaluate the atmospheric impact of biomass burning, and particularly to represent it quantitatively in models of atmospheric transport and chemical transformations, accurate data on the emission of trace gases and aerosols from biomass fires are required. On the other hand, to correctly estimate wildfire emissions, spatiotemporally resolved information is required. Emission estimates are obtained by multiplying the amount of biomass burned within a grid cell during a time interval, with an emission factor, that is, the amount of the chemical species released per mass of biomass burned.

To accurately determine the impact of biomass burning it is essential to obtain the chemical characterisation and screening of emission profiles for this specific source. One goal of detailed analysis of biomass burning emissions is the potential use in receptor models, such as the molecular marker-based chemical mass balance (CMB). The SPECIATE database is an important product of the U.S. Environmental Protection Agency (EPA) that serves as the repository for source category-specific emission speciation profiles. The profiles contain weight fractions of chemical species of both volatile organic compounds (VOCs) and particulate matter (PM). However, “source profiles” for wildfires in this database are very limited and refer to prescribed burning in the USA. Thus, when SPECIATE profiles are used as input data to run the CMB model in order to estimate the source contributions to the PM mass monitored at a receptor site in the Mediterranean region, a great level of uncertainty is obtained.

Aiming to help fulfilling the gap that exists in the Mediterranean region, a detailed chemical characterisation of smoke emissions from several wildfires in Portugal (Figure 1.5) is presented in this thesis. The main objective was to obtain emission factors for both gases and particulate matter with aerodynamic diameter below  $2.5\ \mu\text{m}$  ( $\text{PM}_{2.5}$ ) and between  $2.5$  and  $10\ \mu\text{m}$  ( $\text{PM}_{2.5-10}$ ) (Figure 1.6) from summer wildfires occurring in central Portugal, as well to achieve a detailed chemical characterisation (Figure 1.7) of these two particle size fractions. Thus, it is expected to contribute with new data to model atmospheric processes, improve inventories and apply source apportionment methodologies. These goals fit into the subject of the project “Contribution of biomass combustion to air pollutant emissions”, PTDC/AMB/65706/2006 (BIOEMI) funded by the Portuguese Science Foundation (FCT).

This work was the result of the collaboration among several institutions. The University of Aveiro (Portugal) was responsible for the collection of the smoke samples from several wildfires. Members of the Portuguese team analysed the gaseous compounds, water-soluble ions, organic and elemental carbon and the organic constitution of the samples. All the analytical steps related to the detailed organic speciation were of my entire responsibility. The University of Huelva (Spain) and the Institute of Environmental Assessment and Water Research (Barcelona, Spain) were responsible for the analyses of elements included in Chapter 2. Finally, the Technological and Nuclear Institute (Lisbon, Portugal) performed the analyses of the elements comprised in Chapter 6.



Figure 1.5 Pictures of wildfires where smoke samples were collected during the summers of 2009 and 2010.

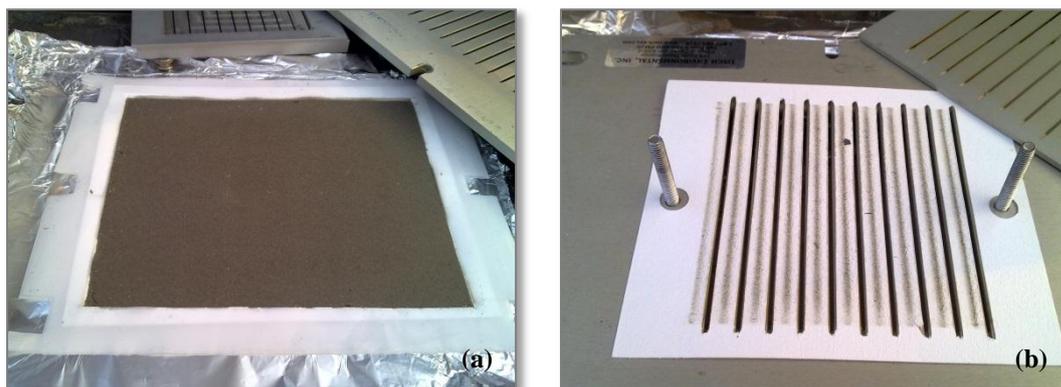


Figure 1.6 Pictures of quartz fibre filter used to collect the smoke samples during the summers of 2009 and 2010; (a) fine particles ( $PM_{2.5}$ ), (b) coarse particles ( $PM_{2.5-10}$ ).

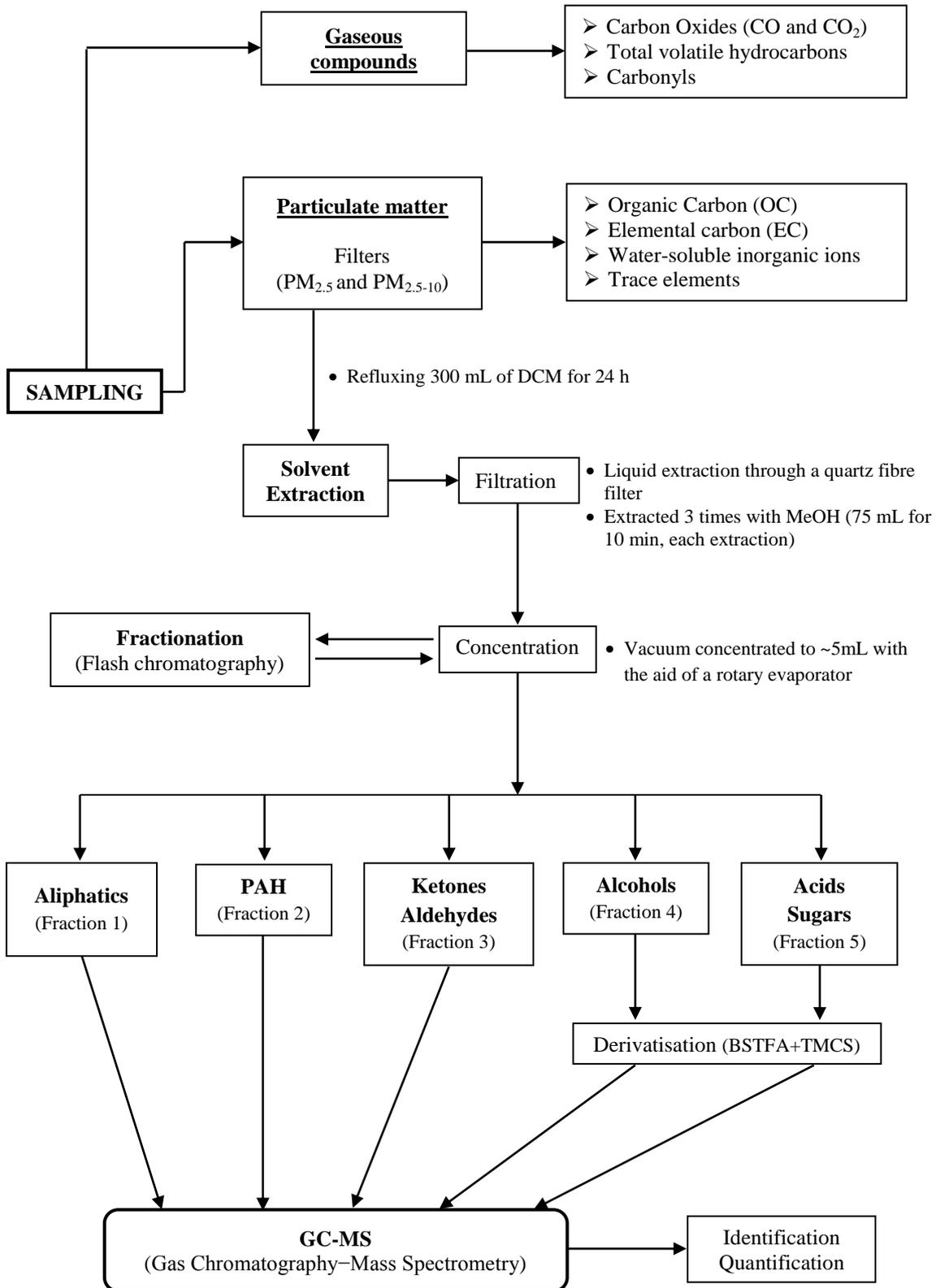


Figure 1.7 Scheme representing the sampling and analytical procedures for quantification of emission of trace gases and chemical characterisation of smoke particles (DCM – Dichloromethane; MeOH – Methanol; BSTFA+TMCS – *N,O*-bis(trimethylsilyl)-trifluoroacetamide + trimethylchlorosilane) (based on Alves, 2001; Oros and Simoneit, 2000).

## 1.5 General overview of the thesis

This thesis contains a collection of papers that have been published or submitted for publication in refereed journals.

The study reported in the first paper (Chapter 2) provides a characterisation of the gaseous compounds, emission factors of particles, and both their carbonaceous content and inorganic speciation for smoke samples collected in the plumes of several wildfires during summer 2009.

Chapter 3 includes an exhaustive description of methodologies used to collect the smoke samples and of all the analytical procedures carried out to obtain the organic speciation of particles. A very detailed characterisation of the first samples gathered during the field campaigns (wildfire in Sever do Vouga) is given. This fire was selected to be studied apart because it enabled the collection of samples representing the two most important combustion phases (smouldering versus flaming) and the quantification of a vast array of organic compounds in the smoke particles.

A comprehensive characterisation of smoke samples collected in the plumes of the wildfire with the highest burnt area in 2009 (Penedono) is provided in Chapter 4. This fire was studied independently due to the significant number of smoke samples collected, the variety of vegetation burned and the different combustion stages covered by the sampling, thus representing a good example of a typical wildfire and its behaviour.

Chapter 5 includes the organic speciation of particulate matter samples from all the wildfires characterised in Chapter 2, excepting Sever do Vouga and Penedono, which were discussed individually in separate chapters. The data discussed in this chapter complement the information presented in Chapter 2 for smoke samples collected during the campaign held in summer of 2009.

A complete data set for emissions of several wildfires, whose plumes were sampled during the field campaign of summer 2010, is presented in Chapter 6. Gaseous emissions and the inorganic and organic speciation of smoke particles are described and discussed in detail.

Finally, a compilation of the main conclusions of this study was included in Chapter 7. Suggestions for future research are also outlined.

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## **CHAPTER 2**



## Chapter 2. Summer 2009 in Portugal: emission of traces gases and aerosol composition

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### Abstract

In summer 2009, emissions of trace gases and aerosols from several wildfires occurring in Portugal were sampled. A portable high-volume sampler was used to collect sequentially, on quartz fibre filters, coarse ( $PM_{2.5-10}$ ) and fine ( $PM_{2.5}$ ) smoke particles. Tedlar air sampling bags have been used for complementary chemical characterisation of the gaseous phase. The carbonaceous content (elemental and organic carbon, EC/OC) of particulate matter was analysed by a thermal-optical transmission technique. The levels of almost 50 elements were quantified by inductively coupled plasma-mass spectrometry. The water-soluble ions were obtained by ion chromatography. Emission factors of species that are favoured by the smouldering phase (e.g. CO) were above the values reported in the literature for biomass burning in other ecosystems. The CO emission factors were  $231 \pm 117$  g  $kg^{-1}$  biomass (dry basis) burned. Emissions of compounds that are promoted in fresh plumes and during the flaming phase, such as  $CO_2$ , were generally lower than those proposed for savannah and tropical forest fires. The  $CO_2$  emission factors ranged from about 1000 to 1700 g  $kg^{-1}$ . Total hydrocarbons,  $PM_{2.5}$ ,  $PM_{10}$  and OC presented variable emissions, but in general substantially higher than values reported for wildfires in African and Amazonian biomes. The emission factors obtained in Portugal were as follows (in g  $kg^{-1}$  biomass, dry basis): 6-350 for total hydrocarbons, 0.5-42 for  $PM_{2.5}$ , 1-60 for  $PM_{10}$ , and

0.2-42 for OC (in  $PM_{10}$ ). The organic carbon-to-elemental carbon ratios measured in the present study largely exceeded those obtained by other researchers. The aerosol mass was dominated by organic matter ( $OC/PM_{2.5}=50\pm 18\%$ ,  $OC/PM_{2.5-10}=36\pm 18\%$ ). The metal elements represented, on average, 1.23 and 0.91%, while the measured water-soluble ions accounted for 2.6 and 2.1% of the  $PM_{2.5}$  and  $PM_{2.5-10}$  mass, respectively. Carbonates accounted for 0.15 to 3.1% (average = 0.83%) of  $PM_{2.5-10}$ . The dominant elements were B, Ti, Mn, Cu, Zn, Zr and Ba.

Keywords: wildfires, trace gases, carbonaceous particles, emission factors, water soluble ions, metals.

## 2.1 Introduction

Wildfires are a major contributor of trace gases and aerosol species (Andreae and Merlet, 2001; Lazaridis et al., 2008; Park et al., 2006; Yokelson et al., 2007), with a profound impact on visibility (Park et al., 2006; Wise, 2008), atmospheric chemistry and biogeochemical cycles (Crutzen and Andreae, 1990; Schimel and Baker, 2002), and climate (Langmann et al., 2009; Randerson et al., 2006). Pfister et al. (2005) showed that particularly intense wildfires in Alaska and Canada during the summer of 2004 emitted as much carbon monoxide as human activities in the continental United States during the same period. The fires also boosted ground-level ozone across the northern continental United States, even enhancing concentrations of this pollutant by 10% as far away as Europe. Smoke from wildfires has also been associated with both increased mortality (Vedal and Dutton, 2006) and morbidity (Bowman and Johnston, 2005). Expected changes in climate are predicted to result in considerable increases in fire intensity, frequency and area burned, which will result in increasing environmental impacts. In Portugal, future area burned is predicted to increase 478% under a CO<sub>2</sub> duplication scenario (Carvalho et al., 2010).

Model estimates of wildfire emissions and their impacts call for emission factors (EF) for both trace gases and aerosols. Since emissions vary with type of fuel burned and combustion stage (flaming versus smouldering), and taking also into account that atmospheric photochemistry, source apportionment and climate change models require detailed emissions factors, it is necessary to obtain regional emission databases reflecting the distinct burning conditions. EF have been estimated in some laboratory studies (e.g. Chen et al., 2007; Christian et al., 2003; McMeeking et al., 2009; Yokelson et al., 2008) and in field campaigns (e.g. Korontzi et al., 2003; McRae et al., 2006; Yokelson et al., 2007), but many uncertainties persist. Most of the studies reported in the literature present EF for American fuels (Battye and Battye, 2002; McMeeking et al., 2009), and for savannah/grassland, tropical and extratropical forests (Andreae and Merlet, 2001). In comparison, the Mediterranean area, where intense summer fires rage out of control more and more often, is particularly uncovered. As far as we know, only Alves et al. (2010) document detailed particle and trace gas EF for experimental fires in a Mediterranean

shrubland. Thus, the main goal of this study is to present a comprehensive set of measurements that include gas- and particulate-phase emissions, along with an indicator of combustion conditions, for several wildfires that occurred in Portugal during the 2009 summer season.

## 2.2 Methodology

In summer 2009, emissions of trace gases and aerosols from several wildfires occurring in Portugal (Table 2.1) were sampled. According to the Portuguese Forest Services (DGRF), from 1980 to 2009, the burnt area ranged from 17 244 (in 2008) to 425 726 ha (in 2003), averaging 108 550 ha/year. In 2009, about 86 020 ha of forest were burned. Most wildfires occur in central and northern Portugal. Thus, in terms of area burned and fuel types, the smoke sampling experiments in 2009 are representative of a “typical” summer fire season in Portugal.

A portable high-volume sampler (TE-5200, Tisch Environmental Inc.) operating at a flow of  $1.13 \text{ m}^3 \text{ min}^{-1}$  was used to collect sequentially, on pre-fired quartz fibre filters, coarse ( $\text{PM}_{2.5-10}$ ) and fine ( $\text{PM}_{2.5}$ ) smoke particles. A Tisch  $\text{PM}_{2.5}$  impaction plate was used to separate particles at  $2.5 \text{ }\mu\text{m}$ . The impaction system for removing particles  $> 10 \text{ }\mu\text{m}$  was designed at the University of Aveiro in accordance with the Marple and Rubow’s theory (1986). Sampling was performed at 1.5 m above ground, downwind from the burning area, at distances of 20-200 m from the flame. The sampler was connected only when impacted by the smoke plumes. As our samples were taken near the ground surface, these results represent freshly emitted fire aerosols that have not yet had time to undergo post-fire chemical or physical-chemical changes. In parallel with aerosol sampling, Tedlar bags previously flushed with  $\text{N}_2$  were used for the collection of gas samples. Pre-removal of water vapour from the air stream was carried out in a glass U tube filled with glass spheres, immersed in an ice bath. In addition, the air stream was filtered through a 47 mm quartz filter to remove particles before passing to the collection system, which also contained a Teflon-lined diaphragm pump connected to a needle valve and a calibrated rotametre operating at a flow rate of  $1 \text{ L min}^{-1}$ .

Total hydrocarbons (THC) and carbon oxides ( $\text{CO}_2$  and  $\text{CO}$ ) in the Tedlar bags were measured using automatic analysers with flame ionisation (Dyna-FID, model SE-

310) and non-dispersive infrared (Environnement, MIR 9000) detectors, respectively. Each gas analyser was calibrated with appropriate gas on zero and span points. The emissions of hydrocarbons are presented in methane-equivalents.

The carbonaceous content (organic and elemental carbon, OC and EC) of particulate matter was analysed by a thermal-optical transmission technique after a previous sample acidification to remove carbonates, following a short multi-step temperature protocol, first in an inert ( $N_2$ ) and then in an oxidising atmosphere ( $N_2/O_2$ ). Two 9 mm diameter filter punches, in the case of  $PM_{2.5}$  samples, or strips representing 1/20 of the total area, in the case of  $PM_{2.5-10}$  samples, were used in each analytical run. For each filter, two or three replicate analyses were done. The  $CO_2$  released during sample heating is measured by a non-dispersive infrared analyser. The anoxic heating conditions (OC quantification) follow a two-step temperature profile: 200°C for 200 seconds and 600°C for 600 seconds, respectively. After these steps, the anoxic gas stream is replaced by an oxidising atmosphere (4%  $O_2$ ) (EC quantification), and the sample is heated up to 850°C. However, thermally unstable organic compounds pyrolyse in the  $N_2$ -mode to form pyrolytic carbon, which then usually desorbs off the filter in the oxidising atmosphere, like native EC. To correct for pyrolysis, the optical properties of the sample are monitored during the analysis with a laser beam. During anoxic mode heating light transmission decrease while OC chars in the  $N_2$ -mode. When the pyrolytic carbon and EC are released from the filter in the  $N_2/O_2$ -mode, transmission increase again and the point at which the transmission reaches the pre-pyrolysis value is used to discriminate OC and EC (split point). Carbon carbonate present in aerosol samples was analysed throughout the release of  $CO_2$ , and measurement by NDIR, when a punch of filter is acidified with orthophosphoric acid in a free  $CO_2$  gas stream.

For the determination of soluble inorganic ions, small parts of the filters were extracted with ultra pure Milli-Q water. Dionex AS14 and CS12 chromatographic columns with Dionex AG14 and CG12 guard columns coupled to Dionex AMMS II and Dionex CMMS III suppressors, respectively for anions and cations, were used. A punch of each filter was digested in an acid media (2.5 ml  $HNO_3$ : 5 ml HF: 2.5 ml  $HClO_4$ ) following the method proposed by Querol et al. (2001). All the acids were of Suprapur quality.

Table 2.1 Wildfires episodes over Portugal in summer 2009 where smoke samples were collected.

Sampling locations	Latitude/Longitude Altitude (a.s.l.)	Date	Major types of biomass/Fire characteristics	Number of samples (PM <sub>2.5</sub> +PM <sub>2.5-10</sub> )	MCE
Sever do Vouga	40°35'59"N/8°22'10"W 255 m	31 May	<i>Acacia melanoxylon</i> / <i>Eucalyptus globulus</i>	8	0.78-0.97
Ovar	40°51'56"N/8°37'47"W 25 m	17 Jul.	<i>Acácia sp./Eucalyptus globulus</i>	6	0.66-0.87
Penedono	40°56'25"N/7°23'52"W 810 m	21 Jul.	<i>Pinus pinaster/Cytisus striatus/Rubus fruticosus</i>	14	0.60-0.86
Montemor-o-Velho	40°12'50"N/8°41'38"W 51 m	11 Aug.	<i>Pinus pinaster/Eucalyptus globulus</i>	6	0.52-0.75
Nariz (Aveiro)	40°32'52"N/8°35'30"W 25 m	27 Aug.	<i>Pinus pinaster/Acácia sp./Eucalyptus globulus</i>	4	0.58-0.78
Cinfães (Viseu)	40°59'04"N/8°07'12"W 619 m	30 Aug.	Creeping fire in a <i>Eucalyptus globulus</i> forest. Biomass burned: fallen twigs, <i>Erica</i> shrubs, <i>Eucalyptus</i> bark and dried leaves	2	0.79
Farejinha (Castro Daire)	40°55'55"N/7°51'03"W 822 m	31 Aug.	<i>Pinus pinaster/Cytisus striatus</i>	4	0.77-0.87
Quinta da Póvoa (Sabugal)	40°20'40"N/7°14'30"W 500 m	01 Sept.	<i>Cytisus striatus</i> (dominant); some isolated pine trees	4	0.77-0.87
Pendilhe (V. N. de Paiva)	40°53'34"N/7°49'48"W 825 m	06 Sept.	<i>Cytisus striatus/Pinus pinaster</i>	2	0.82

MCE – modified combustion efficiency

Major and trace elements were determined in the resulting digestion by means of Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). The mean precision and the accuracy fall under typical analytical errors (in the range of 3-10%), and were controlled by repeated analysis of a 1/4 of filter loads with 5 mg of SRM 1633b (coal fly ash) reference material (NIST, Gaithersburg, MD, USA). Blank filters were analysed simultaneously in the batches of their respective filter samples and the corresponding blank concentrations were subtracted for each sample.

The emission factor is a parameter that relates the emission of a particular species of interest to the amount of fuel burned. It is defined as the amount of a compound released per amount of dry fuel consumed, expressed in units of  $\text{g kg}^{-1}$ . The carbon combusted in a fire is emitted into the measurable portions of a smoke plume mainly in five forms of carbon:  $\text{CO}_2$ , CO, total hydrocarbons (including oxygenated volatile organic compounds), and total particulate carbon (TC=OC+EC). The emission factor of a species,  $n$ , is then obtained from the ratio of the mass concentration of that species to the total carbon concentration emitted in the plume. Thus, the emission factor is expressed in units of mass of species  $n$  emitted per unit mass of carbon burned. To convert this emission factor to the more frequently used grams of  $n$  produced per kg of dry matter burned, the previous ratio is multiplied by the mass fraction of carbon in the fuel (Reid et al., 2005):

$$EF_n = \frac{[n]}{[\text{CO}_2] + [\text{CO}] + [\text{THC}] + [\text{TC}]} \times \%C_{\text{fuel}} \quad (1)$$

It has been estimated that the dominant species in the Portuguese forest have a mean carbon content of  $48 \pm 2\%$  ( $\%C_{\text{fuel}}$ ) (Silva et al., 2008). It should be also noted that background levels have been subtracted from measurements in the smoke plumes. Since the carbon in the ashes was not included in the C-budget, the emission factors will be slightly elevated. To evaluate the completeness of combustion, it can be considered that  $>90\%$  of the carbon combusted in a fire is emitted in the form of  $\text{CO}_2$  and CO, and  $<10\%$  of carbon is in species such as hydrocarbons and particulate carbon. Keeping this in mind, the modified combustion efficiency (MCE) is calculated as follows:

$$\text{MCE} = \frac{[\text{CO}_2]}{[\text{CO}_2] + [\text{CO}]} \quad (2)$$

Pure smouldering usually has MCE below 0.85 (Yokelson, 2004). The flaming combustion usually exhibits the highest MCE (0.9-1) (Reid et al., 2005). Lower MCE values (<0.8) are found for wet fuels (Chen et al., 2007).

## 2.3 Results and Discussion

### 2.3.1 Emission of gases, particles and carbonaceous constituents

MCE values ranged from 0.52 to 0.97, but most of the values correspond to a greater predominance of smouldering than flaming combustions. Ground-level aerosol sampling during the flaming phase of a wildfire constitutes a very difficult task. The heat and flames from fires are obvious risk. Due to the high temperature of the flames, fire-emitted particles are directly injected into the atmosphere up to 3 to 4 km altitude. Thus, besides the danger, the thermal updraft of fire smoke plumes often render the obtaining of flaming emission samples unsuccessful. Generally, airborne measurements sample an integrated mixture of the emissions from both flaming and smouldering combustion, and even at the ground the separation is incomplete because both processes occur simultaneously in a given patch at most times (Andreae and Merlet, 2001).

The PM<sub>2.5</sub> and PM<sub>2.5-10</sub> smoke samples presented concentrations up to 45 400 µg m<sup>-3</sup> and 4 330 µg m<sup>-3</sup>, respectively. The gravimetric data confirmed that the PM<sub>10</sub> mass was dominated by PM<sub>2.5</sub> mass concentrations. PM<sub>2.5</sub> represented 86±8.8% of the PM<sub>10</sub> mass. Mass percentages of the same order have been obtained in previous works (Alves et al., 2010; McMeeking et al., 2009). Carbonates represented 0.15-3.1% (average = 0.83%) of PM<sub>2.5-10</sub>, whereas its contribution to the mass of fine particles was insignificant (Table 2.2). On average, 50±18% of the PM<sub>2.5</sub> mass emissions was composed of organic carbon, whilst the mass fraction for PM<sub>2.5-10</sub> was 36±18%. The OC mass fractions were in the range of values reported for biomass burning in grasslands, savannah, cerrado, boreal and tropical forests (Reid et al., 2005). On average, the OC concentrations were 10 times higher in PM<sub>2.5</sub> than in PM<sub>2.5-10</sub>. The carbonaceous fraction of smoke samples from any of the fires in this study was clearly dominated by organic carbon. A wide range of OC/EC ratios was

obtained. Most of the values are much higher than those reported for other biomass burning events (Andreae and Merlet, 2001; Reid et al., 2005). Very high OC/EC ratios were also determined for fires in a Mediterranean shrubland (Alves et al., 2010). The high OC production in fire plumes has been attributed to condensation of large hydrocarbons, enhanced isoprenoid emissions, acid-catalysed reactions and very rapid oxidation of low-volatility organic vapours (Grieshop et al., 2009; and references therein). Besides different proportions of smouldering to flaming-derived samples in the various investigations, it could be argued that dissimilarities between values of the current study and those reported in the literature may be a consequence of the utilisation of different methodologies for the OC and EC determination. It should be noted, however, that the comparison between the methodology of the University of Aveiro and the “European Supersites for Atmospheric Aerosol Research” (EUSAAR-2) protocol (Cavalli et al., 2009) gave similar results for OC and EC, without significant differences at a 95% confidence level (Nunes et al., 2010). Similar results were also obtained by the University of Aveiro in an international round robin test (Schmid et al., 2001).

Table 2.2 Mass fraction of carbonates, organic carbon and total carbon (TC=OC+EC) in the particulate matter, and organic-to-elemental carbon ratios.

Particle size	CO <sub>3</sub> <sup>2-</sup> /PM (%)	OC/PM (%)	TC/PM (%)	OC/EC
PM <sub>2.5</sub>	---	50±18	52±20	5-924 (avg = 90)
PM <sub>2.5-10</sub>	0.15-3.1 (avg = 0.83)	36±18	37±18	10-111922 (avg = 12275)

The PM<sub>2.5</sub> emission factors obtained for wildfires in Portugal were 19.3±15.1 g kg<sup>-1</sup>, lying in the ranges reported in the literature for other fires (Figure 2.1). Considering that MCE values higher or lower than 90% are characteristic of more flaming or smouldering combustion, respectively, Reid et al. (2005) obtained EF<sub>PM<sub>2.5</sub></sub> around 9 g kg<sup>-1</sup> for flaming combustion measurements, while an approximate value of 34 g kg<sup>-1</sup> was derived for smouldering stages. Yokelson et al. (2008) estimated a fine aerosol emission factor of 9.93 g kg<sup>-1</sup>, with global values ranging from 2.17 to 16.61 g kg<sup>-1</sup> for MCEs between 0.88 and 0.979. Ward and Hardy (1991) suggested an EF<sub>PM<sub>2.5</sub></sub> of 10 g kg<sup>-1</sup> for cured grasses, 15 g kg<sup>-1</sup> fuel for chaparral and palmetto/gallberry fires and 20-50 g kg<sup>-1</sup> for long-needled conifer fires. From open combustion of biomass in the laboratory, McMeeking et al. (2009) obtained EF<sub>PM<sub>2.5</sub></sub> g kg<sup>-1</sup> of 29.4±25.1 for montane, 18.9±13.9 for rangeland, 11.6±15.1 for

chaparral,  $23.4 \pm 18.7$  for coastal plain and  $12.7 \pm 11.3$  for boreal forest ecosystem species. In their review paper, Andreae and Merlet (2001) presented  $EF_{PM_{2.5}}$  of  $5.4 \pm 1.5 \text{ g kg}^{-1}$  (savannah and grassland),  $9.1 \pm 1.5 \text{ g kg}^{-1}$  (tropical forest) and  $13.0 \pm 7.0 \text{ g kg}^{-1}$  (extratropical forest). However, Yokelson et al. (2008) derived an Amazon-average  $EF_{PM_{2.5}}$  of  $16.8 \text{ g kg}^{-1}$ , which represents 85% more  $PM_{2.5}$  emissions for the region than using the Andreae and Merlet (2001) recommendation of  $9.1 \text{ g kg}^{-1}$ . The physical basis for this increase was the inclusion of a larger contribution from smouldering combustion. Kasischke et al. (2005) argued that most of the ground-layer organic matter is consumed during smouldering combustion, and this has to be accounted for when estimating forest fire emissions. Thus, taking into account the discrepancies observed, more measurements would be valuable.

Figure 2.2 shows the relationship between MCE and the pollutant emission factors. The linear regression between MCE and  $PM_{2.5}$  obtained in this study ( $EF_{PM_{2.5}} = 66.4 - 62.6 \times \text{MCE}$ ) is in good agreement with Ward and Hardy's relationship, who obtained  $EF_{PM_{2.5}} = 67.4 - 66.8 \times \text{MCE}$  for prescribed fires in the Pacific Northwest. It also approaches the empirical relationship estimated by Babbitt et al. (1994) for wildfires in Montana, Idaho and Oregon ( $EF_{PM_{2.5}} = 62.6 - 61.4 \times \text{MCE}$ ). However, the correlation ( $EF_{PM_{2.5}} = 336 - 341 \times \text{MCE}$ ) developed by McMeeking et al. (2009) in laboratory experiments with different types of biomasses differs significantly from the above-mentioned relationships. The discrepancy may be due to the inherent variability of emissions coupled with different fuels and burning conditions, as well as different ranges of MCE covered by the measurements. The lack of data in the literature over a broad range of MCE may result in biased estimates of particle emissions and properties. If the contribution of smouldering emissions is underestimated, the total  $PM_{2.5}$  emissions attributed to biomass combustion in current inventories are likely to be undervalued.

As observed in previous studies (McMeeking et al., 2009), the significance of the relationship between EC and MCE was weak. While OC increases considerably under smouldering conditions, EC emissions seem similar for flaming and smouldering conditions. This observation is in accordance with the inferences by Battye and Battye (2002) based on the compilation of several emission databases. However, it deviates from the reasoning that EC emissions enhance with flaming-phase combustion due to the dependency of soot formation mechanisms on temperature (Chen et al., 2007; McMeeking et al., 2009).

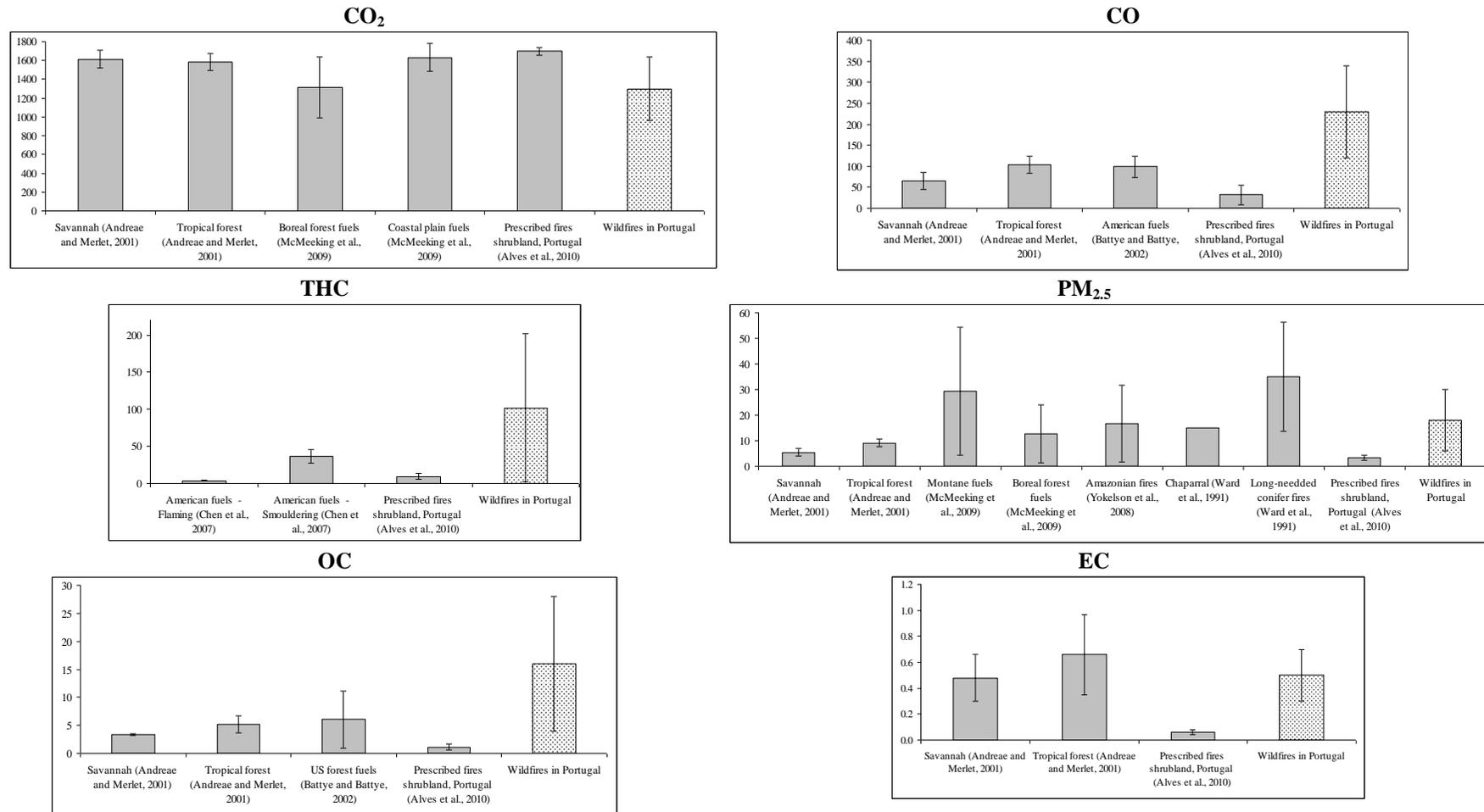


Figure 2.1 Comparison between emission factors (g kg<sup>-1</sup> fuel burned) for fires in Portugal and values published in the literature.

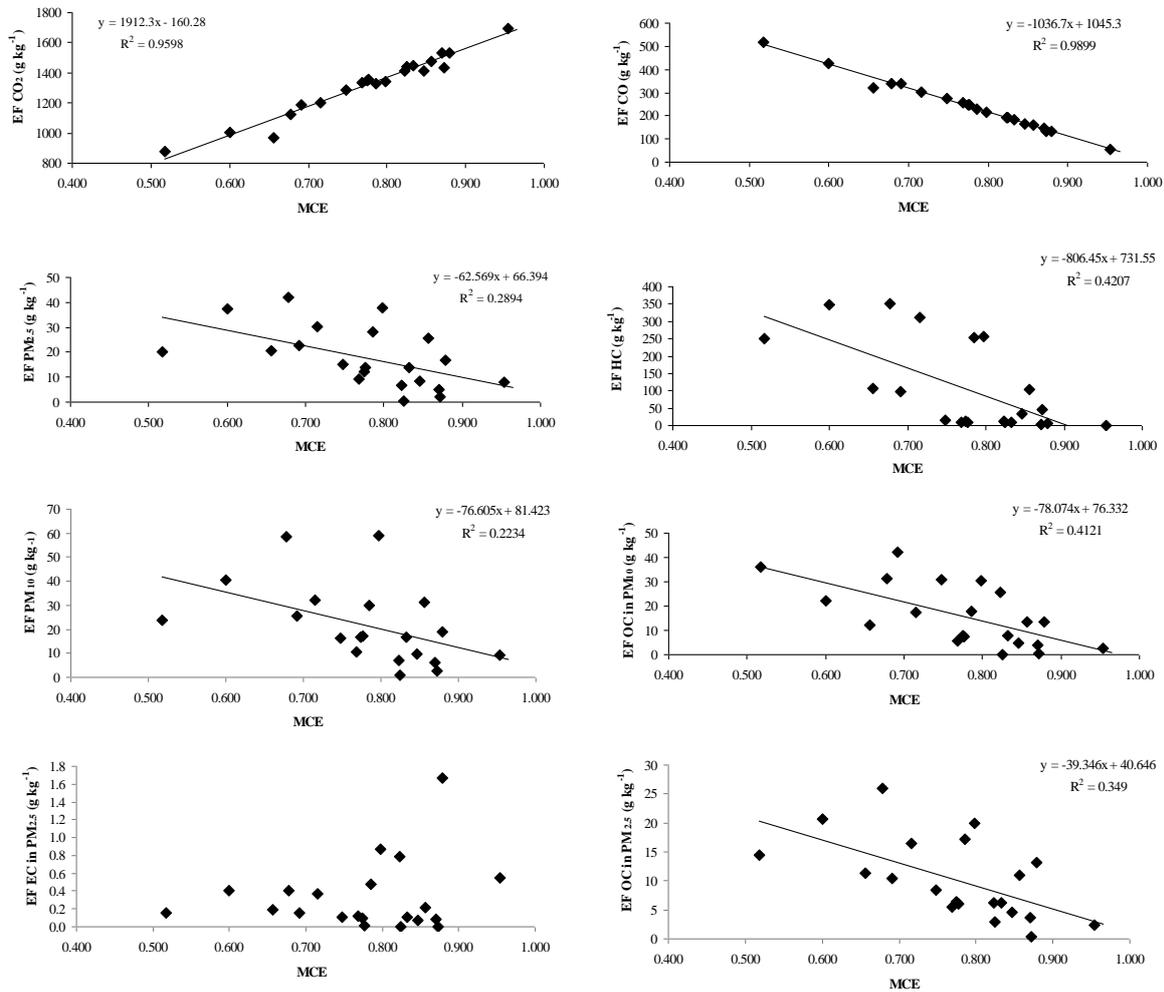


Figure 2.2 Emission factors as a function of MCE.

EC/TC ratios in PM<sub>2.5</sub> were less than 0.04 for MCE values below 0.90, and increased strongly for higher MCE values. The extreme EC/TC ratios were 0.012 for a sample collected during the smouldering fire with the lowest modified combustion efficiency (MCE = 0.52) and 0.18 for a sample collected during the flaming phase (MCE = 0.97). Battye and Battye (2002) reported EC/TC ratios of 0.06 (smouldering) and 0.16 (flaming) for airborne field studies with Ponderosa pine, while for chaparral species the ratios were 0.11 (smouldering) and 0.11-0.22 (flaming). McMeeking et al. (2009) obtained an EC/TC ratio of ~0 for a sample collected during only the smouldering phase of the fire (MCE = 0.80) and 0.5 for a sample collected during the flaming phase (MCE = 0.99). It should be noted that the EC/TC is not likely linear with MCE. Some studies show low

EC/TC ratios until MCE values of about 0.93-0.95 and then a very rapid increase (McMeeking et al., 2009).

In accordance with the results presented by Battye and Battye (2002), the ratio of OC to total PM<sub>2.5</sub> is very similar for smouldering and flaming conditions. Thus, OC appears to correlate well with total PM<sub>2.5</sub> over the full range of combustion efficiencies ( $EF_{OC}=1.94 \times EF_{PM_{2.5}}$ ;  $r^2=0.87$ ). OC emission factors ranged from 0.16 to 42 g kg<sup>-1</sup>, averaging 15.8 g kg<sup>-1</sup>. Andreae and Merlet (2001) reported  $EF_{OC}$  of  $3.4 \pm 1.4$  g kg<sup>-1</sup> (savannah),  $5.2 \pm 1.5$  g kg<sup>-1</sup> (tropical forest) and 8.6-9.7 g kg<sup>-1</sup> (extratropical forest). Battye and Battye (2002) gathered mean values from 1.96 to 25.6 g kg<sup>-1</sup> for different US forest biomass and burning stages.

On average,  $75.1 \pm 11.5\%$  of the carbon was emitted in the form of CO<sub>2</sub>, followed by CO ( $20.6 \pm 10.4\%$ ), hydrocarbons ( $3.37 \pm 3.04\%$ ), OC ( $1.15 \pm 1.09\%$ ) and EC ( $0.04 \pm 0.02\%$ ). CO is very important in the development of emissions inventories for many pollutants. Because CO is an indicator of smouldering combustion, its emission factor is often used to estimate emission factors for many other products of incomplete combustion (Battye and Battye, 2002). The  $EF_{CO}$  obtained for wildfires in Portugal ( $231 \pm 117$  g kg<sup>-1</sup>) are higher than the  $65 \pm 20$ ,  $104 \pm 20$  and  $107 \pm 37$  g kg<sup>-1</sup> compiled by Andreae and Merlet (2001) for fires in savannah, tropical and extratropical forests, respectively. Battye and Battye (2002) reported CO emission factors for different fire types in the ranges 99-232 g kg<sup>-1</sup> and 22-78 g kg<sup>-1</sup> for smouldering and flaming combustions, respectively, suggesting  $EF_{CO}$  of 125 g kg<sup>-1</sup> biomass consumed for both canopy fuel and shrubs and 158 g kg<sup>-1</sup> for duff. A high CO emission factor ( $459$  g kg<sup>-1</sup>) was measured for feathermoss/lichen in Scotch pine forests of Central Siberia with a low MCE of 0.59 (McRae et al., 2006). The average PM<sub>2.5</sub>/CO emission ratio was  $0.08 \pm 0.06$  g g<sup>-1</sup>. Janhäll et al. (2010) reported emission ratios of PM/CO= $(0.13 \pm 0.05)$  g g<sup>-1</sup> for forest, PM/CO= $(0.08 \pm 0.03)$  g g<sup>-1</sup> for savannah, and PM/CO= $(0.07 \pm 0.03)$  g g<sup>-1</sup> for grass. The PM/CO emission ratio has low MCE dependence and can be used to predict the level of one pollutant in a plume, when the concentration of the other is known. Moderate to high correlations between the CO and other pollutant emission factors were obtained:  $EF_{CO_2} = -1.79 \times EF_{CO} + 1755$  ( $r^2=0.92$ ),  $EF_{THC} = 0.764 \times EF_{CO} - 78.3$  ( $r^2=0.48$ ),  $EF_{PM_{2.5}} = 0.059 \times EF_{CO} - 3.63$  ( $r^2=0.42$ ), and  $EF_{OC} = 0.077 \times EF_{CO} - 2.78$  ( $r^2=0.52$ ).

The CO<sub>2</sub> emission factors obtained in this study ranged between a few values around 1000 and a maximum of 1697 g kg<sup>-1</sup>, reflecting the different contributions from smouldering and flaming fires. In laboratory experiments, McMeeking et al. (2009) obtained EF<sub>CO<sub>2</sub></sub> from 1311±325 g kg<sup>-1</sup> (boreal forest fuels) to 1632±150 g kg<sup>-1</sup> (coastal plain fuels). Andreae and Merlet (2001) suggested EF<sub>CO<sub>2</sub></sub> of 1613±95 g kg<sup>-1</sup> (savannah), 1580±90 g kg<sup>-1</sup> (tropical forest) and 1569±13 g kg<sup>-1</sup> (extratropical forest).

Total hydrocarbon emission factors ranged from 6 to 350 g kg<sup>-1</sup>, averaging 102 g kg<sup>-1</sup>. Chen et al. (2007) obtained average emission factors for HC from laboratory combustion of wildland fuels of 0.4-10.4 g kg<sup>-1</sup> (flaming) and 1.2-125 g kg<sup>-1</sup> (smouldering). These researchers observed higher and more variable emission factors for total hydrocarbons during the smouldering phase, especially for fuels containing substantial moisture.

### **2.3.2 Inorganic composition of smoke particles**

The concentrations of the water-soluble ions are listed in Table 2.3. On average, these constituents contribute to 2.6% and 2.1% of the fine and coarse particle mass, respectively. An excess of positive ions was observed, which correlates well with the concentrations of calcium ions, suggesting an origin, at least in part, on calcium carbonate from soil. In fact, when carbonates are taken into account in the ion balances, the excess of positive ions decreases substantially. The larger amounts of Mg<sup>2+</sup> generally observed in the coarse fraction could also come from soil dust entrained into the smoke aerosols. On the other hand, the excess of positive ions could also derive from the fact that not all the major anionic components were measured in the present study. It has been reported that biomass burning may contain significant amounts of water-soluble formate, acetate, oxalate and other organic anions, such as malonate, succinate and glutarate (Song et al., 2005). As observed in aerosols associated with savannah fires in southern Africa (Gao et al., 2003), the mass fractions of water-soluble ions vary widely from sample to sample. Besides the diversity of biomasses, the varying fire intensities could have contributed to the different mass fractions in distinct samples.

Table 2.3 Concentration ranges (and average) for water-soluble ions ( $\mu\text{g mg}^{-1}$  PM) in smoke particles from wildfires.

Wildfire	PM size	Na <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>	K <sup>+</sup>	Mg <sup>2+</sup>	Ca <sup>2+</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>
Sever do Vouga	PM <sub>2.5</sub>	bdl	bdl-5.14 (3.37)	bdl-13.2 (3.31)	bdl-0.49 (0.12)	bdl-4.67 (3.41)	bdl-7.01 (2.86)	bdl-4.21 (1.99)	4.24-6.48 (5.52)
	PM <sub>2.5-10</sub>	bdl	bdl	bdl-4.41 (1.94)	bdl-5.46 (2.33)	3.40-10.7 (6.52)	0.77-2.55 (1.49)	bdl-6.21 (2.70)	3.23-9.27 (5.89)
Ovar	PM <sub>2.5</sub>	bdl	22.4-25.9 (26.7)	bdl	bdl-2.85 (0.85)	4.90-23.0 (11.1)	20.2-29.2 (24.6)	0.50-0.59 (0.53)	4.65-16.3 (8.69)
	PM <sub>2.5-10</sub>	bdl	bdl-0.73 (0.24)	bdl -3.22 (1.43)	bdl-5.90 (2.88)	bdl-31.3 (14.5)	bdl-10.3 (6.00)	bdl-1.02 (0.56)	bdl-21.8 (10.0)
Penedono	PM <sub>2.5</sub>	bdl	0.20-3.74 (2.67)	bdl-3.17 (1.38)	bdl-1.77 (0.54)	bdl-7.01 (2.44)	1.09-2.25 (1.56)	0.11-0.29 (0.21)	1.80-4.19 (2.35)
	PM <sub>2.5-10</sub>	bdl	bdl-1.55 (0.53)	1.65-14.8 (5.83)	1.41-8.77 (4.36)	2.47-9.83 (5.83)	bdl-2.14 (0.81)	0.08-1.38 (0.29)	2.40-10.0 (5.12)
Montemor-o-Velho	PM <sub>2.5</sub>	bdl	3.34-3.72 (3.47)	bdl	bdl	1.74-2.91 (2.21)	2.23-2.39 (2.33)	0.49-0.72 (0.63)	1.73-2.29 (2.07)
	PM <sub>2.5-10</sub>	bdl	bdl-0.53 (0.29)	1.49-2.00 (1.71)	1.46-1.85 (1.64)	3.59-5.56 (4.44)	bdl-0.90 (0.58)	0.17-0.41 (0.30)	2.31-4.84 (3.62)
Nariz	PM <sub>2.5</sub>	bdl	bdl-4.57 (2.28)	bdl-9.30 (4.65)	1.57-7.23 (4.40)	7.32-13.2 (10.3)	1.22-1.63 (1.43)	0.40-0.58 (0.49)	6.82-13.6 (10.2)
	PM <sub>2.5-10</sub>	bdl	bdl-0.20 (0.10)	bdl-2.72 (1.36)	bdl-1.70 (0.85)	bdl-3.16 (1.58)	bdl-0.77 (0.39)	bdl-0.46 (0.23)	3.26-5.32 (4.29)
Cinfães	PM <sub>2.5</sub>	bdl	1.10	bdl	bdl	8.79	3.83	1.76	5.19
	PM <sub>2.5-10</sub>	bdl	bdl	0.26	bdl	bdl	bdl	bdl	4.38
Farejinha	PM <sub>2.5</sub>	bdl	4.01-5.78 (4.90)	bdl	1.59-2.07 (1.83)	4.03-6.14 (5.08)	1.95-2.72 (2.33)	1.64-2.66 (2.15)	4.87-8.14 (6.50)
	PM <sub>2.5-10</sub>	bdl	bdl-0.50 (0.25)	2.46-4.93 (3.70)	1.41-1.82 (1.61)	3.40-3.48 (3.44)	bdl	1.07-1.73 (1.40)	5.20-6.35 (5.77)
Sabugal	PM <sub>2.5</sub>	bdl	0.89-1.06 (0.98)	13.8-14.7 (14.3)	2.40-9.70 (6.05)	6.48-13.5 (9.98)	2.64-2.78 (2.71)	1.29-2.04 (1.66)	3.49-4.90 (4.20)
	PM <sub>2.5-10</sub>	bdl	bdl	10.6-10.8 (10.7)	9.40-10.3 (9.83)	7.96-10.3 (9.13)	bdl	2.17-2.47 (2.32)	7.04-7.85 (7.44)
Pendilhe	PM <sub>2.5</sub>	bdl	3.02	bdl	bdl	bdl	2.37	3.66	7.71
	PM <sub>2.5-10</sub>	bdl	bdl	1.46	bdl	4.20	bdl	1.58	4.01

bdl – below detection limit

The unexpected low potassium mass fractions for the wildfires could be due to the prevailing smouldering conditions. Yokelson et al. (2009) argued that the incorporation of potassium into particles depends strongly on the amount of flaming combustion, as may also be the case for other ions (e.g. chloride). Previous studies have also shown that the concentration of potassium in PM<sub>2.5</sub> smoke emissions may range from <1% of the mass for certain grasses, shrubs and softwood to values higher than 20% for sagebrush (Chen et al., 2007; Hildemann et al., 1991). The highest levels of Cl<sup>-</sup> and Mg<sup>2+</sup> were observed in smoke particles from a coastal wildfire (Ovar). This could reflect wet deposition of marine aerosol on the fuels (Yokelson et al., 2009). However, the Cl<sup>-</sup> and Mg<sup>2+</sup> content in one of the samples from this specific wildfire was below the detection limit, which might indicate that it was not burning hot enough to volatilise the fuel water-soluble ions efficiently. In fact, the MCE for this sample was 0.66, while values higher than 0.86 were obtained for the other samples.

The presence of SO<sub>4</sub><sup>2-</sup> in smoke aerosols can be the result of adsorption of SO<sub>2</sub> on black carbon particles through a catalytic effect in the gas to particle conversion of SO<sub>2</sub> to sulphate (Song et al., 2004). This effect occurs very fast (few seconds to minutes), allowing sulphate formation relatively close to the source. The presence of oxygen in air is important for SO<sub>2</sub> oxidation and the water vapour released from the vegetation fuel enhances the effect (Novakov et al., 1974). Aerosols of NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> must be produced in reactions of NO<sub>x</sub> and NH<sub>3</sub>, respectively, which are emitted during burning. Rocha et al. (2005) observed that nitrate concentrations increased during burning periods in Southeastern Brazil, with production of this ion across a broad particle size range. Previous measurements have shown that in addition to the instantaneous production of trace gases and particles resulting from the combustion of biomass matter, burning also enhances the biogenic emissions of nitric oxide and nitrous oxide from soil. Ammonium, a major nitrogen component of the burn ash, is the substrate in nitrification, which is the microbial process believed responsible for the production of nitric oxide and nitrous oxide. The enhanced biogenic soil emissions of nitric oxide and nitrous oxide may be comparable to or even surpass the instantaneous production of these gases during biomass burning (Levine et al., 1995). The variability in NH<sub>4</sub><sup>+</sup> levels may also be due to differing fire environments rather than different fuels. Moderate soil heating produces NH<sub>4</sub><sup>+</sup> from pyrolysis of organic matter. At higher temperatures more organic nitrogen is volatilised,

but less nitrogen accumulates as  $\text{NH}_4^+$ , since the  $\text{NH}_4^+$  and subsequent  $\text{NH}_3$  are oxidised to  $\text{NO}_x$  (Hegg et al., 1988).

For almost all water-soluble ionic components and trace elements, the relative concentrations increased with increasing values of MCE, which is in accordance with the observation of lower OC levels during the flaming phase compared to the smouldering stage. Almost 50 metal elements were detected in the smoke samples from wildfires, representing, on average, 1.23% and 0.91% of the  $\text{PM}_{2.5}$  and  $\text{PM}_{2.5-10}$  mass, respectively. In smoke aerosol from experimental fires in a Mediterranean shrubland with dominant flaming conditions, metal elements accounted for an average mass fraction close to 3% in  $\text{PM}_{10}$  (Alves et al., 2010).

The dominant elements were B, Ti, Mn, Cu, Zn, Zr and Ba (Figure 2.3). Boron is a micronutrient required for all plant nutrition. The main functions of boron relate to cell wall strength and development, cell division, fruit and seed development, sugar transport, and hormone development. Some functions of boron interrelate with those of nitrogen, phosphorus, potassium and calcium in plants. Manganese is necessary in photosynthesis, nitrogen metabolism and to form other compounds required for plant metabolism. Zinc is an essential component of various enzyme systems for energy production, protein synthesis, and growth regulation (Simoglou and Dordas, 2006). Titanium shows beneficial effects on various physiological parameters at low doses (e.g. biomass yield, essential element contents, and chlorophyll contents) (Kužel et al., 2003). Copper is an essential metal for normal plant growth and development, participating in numerous physiological processes. It is an essential cofactor for many metalloproteins (Yruela, 2005). Zirconium is ubiquitous, being present in nature in amounts higher than most trace elements. It is taken up by plants from soil and water and accumulated in certain tissues (Ghosh et al., 1992). Barium is naturally present in soils at relatively high concentrations, but it seems that, at high doses, it inhibits plant growth. However, some plant species have adapted to high concentrations of heavy metals and are able to survive in adversely impacted barite environments (Suwa et al., 2008). Biomass burning may result in the volatilisation of these trace metals which then undergo condensation or gas-to-particle type reactions, adsorbing on the surface of pre-existing aerosols. In addition, plant debris or partially combusted foliage ash may contribute to the detection of trace metals, principally in coarse aerosol particles (Alves et al., 2010).

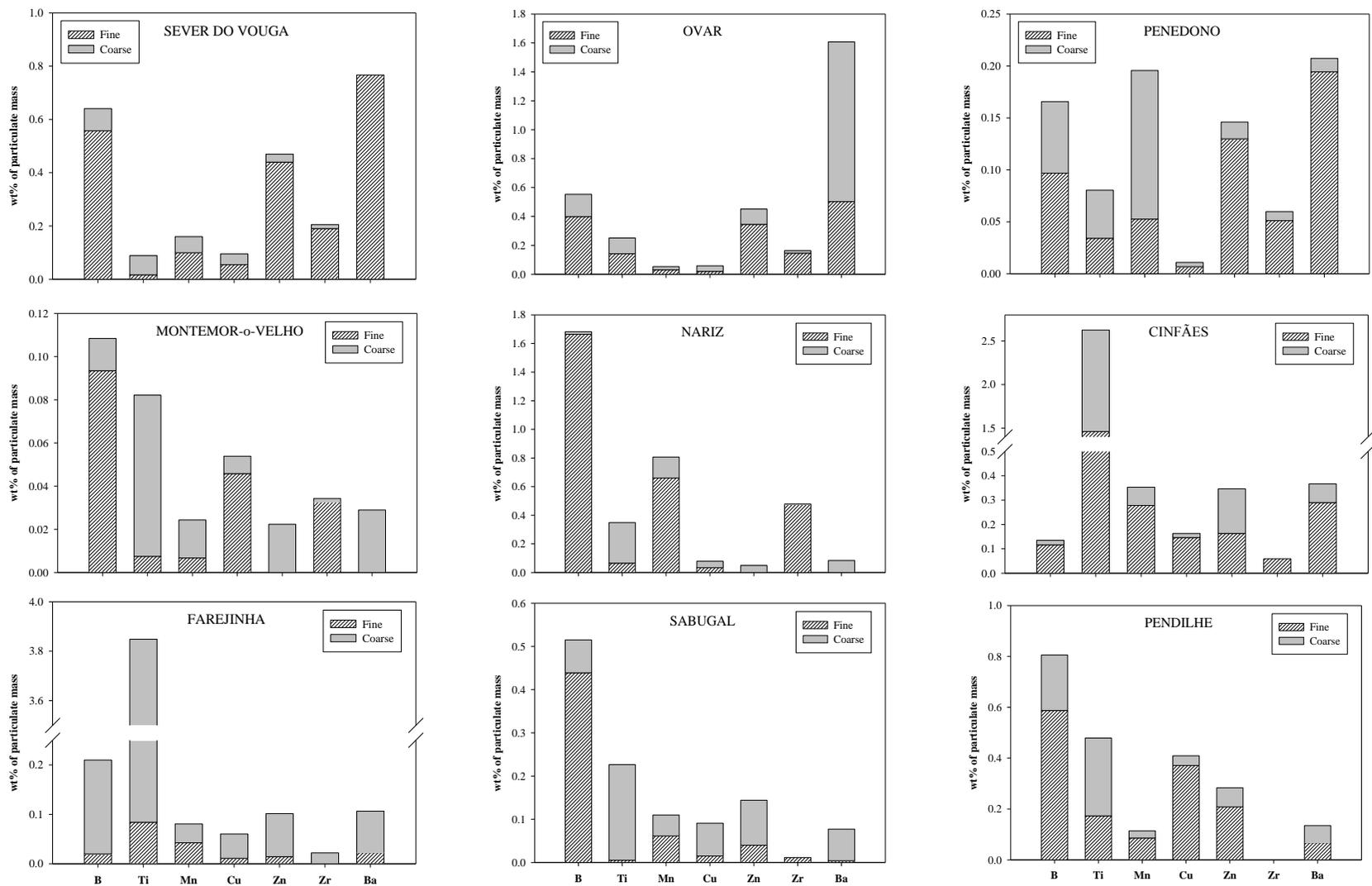


Figure 2.3 Major trace elements found in fine (PM<sub>2.5</sub>) and coarse (PM<sub>2.5-10</sub>) particles sampled in the plume from various wildfires.

Rare earth elements (e.g. La, Ce, Nd, Pr, Sm, Tb, Tm, Yb) were also detected in smoke aerosols as minor constituents. These elements take part in plant physiological and soil microbial processes (Babula et al., 2008). Other minor constituents in smoke particles, previously detected in plant tissues (e.g. Kogo et al., 2009; Caplan et al., 1987), were elements that may yield medium and long-lived radionuclides (e.g. Sc, Cr, Rb, Cs, U, etc.). The percentage concentrations of PM<sub>2.5</sub> and PM<sub>2.5-10</sub> weight for the minor metal elements can be found in annex (Table A1, supplementary material A1).

Previous studies have pointed out Mn, Cu and Zn as specific tracers for savannah burning emissions (Ferek et al., 1998; Gaudichet et al., 1995) and it has been established that the contribution of forest fires should be taken into account to understand the biogeochemical cycles of these elements. Ferek et al. (1998) estimated the percent contributions of savannah plus tropical forest biomass burning in the global emissions of Mn, Cu and Zn as 5%, 2% and 3%, respectively. Gaudichet et al. (1995) concluded that, for Zn, the biomass burning from African savannah could correspond to 4-11% of the worldwide estimates of anthropogenic emissions. However, the stability of these or other potential elemental tracers should be confirmed by other field studies to establish under which conditions they may constitute a profile and could be used as a fingerprint of a specific ecosystem. Due to the scarceness of measurements, it would be desirable to obtain a quantitative heavy metal screening in smoke particles from different biomasses, other than the Mediterranean area.

## 2.4 Conclusions

This study covers a comprehensive set of measurements that include gas-phase and particulate-phase emissions, along with an indicator of combustion conditions, for several wildfires that occurred in Portugal during the 2009 summer season. Parameterisations for the CO<sub>2</sub>, CO, total hydrocarbons, particulate matter and OC emission factors as a function of modified combustion efficiency were obtained:  $EF_{CO_2} (g\ kg^{-1}) = (1912 \times MCE - 160)$ ,  $EF_{CO} (g\ kg^{-1}) = (-1037 \times MCE + 1045)$ ,  $EF_{THC} (g\ kg^{-1}) = (-806 \times MCE + 73)$ ,  $EF_{PM_{2.5}} (g\ kg^{-1}) = (-63 \times MCE + 66)$  and  $EF_{OC\ in\ PM_{2.5}} (g\ kg^{-1}) = (-39 \times MCE + 41)$ . Taking into account that the smouldering phase may last for several hours to days, our results consolidate previous arguments that this combustion phase may contribute to significant amounts of

atmospheric pollutants and the corresponding emission factors should be considered when calculating the global wildfire emissions. Approximately 50% of the particulate mass was composed of organic carbon. The EC values obtained in this study are much lower than those reported in the literature for the laboratory combustion of wildland fuels or for fires in other regions. Since EC is an aerosol component that plays a key role in radiative forcing, and taking into account the discrepancies between the various studies, the magnitude of the emission factor for EC remains a significant uncertainty in estimates of the climate impacts of biomass burning and deserves further investigation. A screening of trace metals and water-soluble ions in particulate matter was performed, and some dominant elements were found. However, additional studies are required to define the use of these elements as potential tracers of biomass burning. The comprehensive database obtained is potentially very useful for numerical models to evaluate the impact of wildfires on the microscale to regional scale atmosphere in the Mediterranean region, which is not particularly well studied. Moreover, since source apportionment models require detailed emission factors, this investigation may also contribute to estimate the input of wildfires to the atmospheric levels measured currently at monitoring sites.

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## **CHAPTER 3**



## Chapter 3. Emission of trace gases and organic components in smoke particles from a wildfire in a mixed-evergreen forest in Portugal

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### Abstract

On May 2009, both the gas and particulate fractions of smoke from a wildfire in Sever do Vouga, central Portugal, were sampled. Total hydrocarbons and carbon oxides (CO<sub>2</sub> and CO) were measured using automatic analysers with flame ionisation and non-dispersive infrared detectors, respectively. Fine (PM<sub>2.5</sub>) and coarse (PM<sub>2.5-10</sub>) particles from the smoke plume were analysed by a thermal-optical transmission technique to determine the elemental and organic carbon (EC and OC) content. Subsequently, the particulate samples were solvent extracted and fractionated by vacuum flash chromatography into different classes of organic compounds. The detailed organic speciation was performed by gas chromatography-mass spectrometry. The CO, CO<sub>2</sub> and total hydrocarbon emission factors (g kg<sup>-1</sup> dry fuel) were 170±83, 1485±147, and 9.8±0.90, respectively. It was observed that the particulate matter and OC emissions are significantly enhanced under smouldering fire conditions. The aerosol emissions were dominated by fine particles whose mass was mainly composed of organic constituents, such as 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), monosaccharide derivatives from cellulose, steroid and terpenoid biomarkers, and polycyclic aromatic hydrocarbons (PAHs). The most abundant PAH was

retene. Even carbon number homologs of monoglycerides were identified for the first time as biomarkers in biomass burning aerosols.

Keywords: wildfire, emission factors, particles, OC/EC, organic tracers.

### 3.1 Introduction

Hot and dry conditions over the Mediterranean countries, Australia, California, or in many other regions, have contributed to an increasing number of wildfires. These fires release into the atmosphere tons of gaseous and particulate pollutants (e.g. 220-13500 Tg CO<sub>2</sub> yr<sup>-1</sup>, 120-680 Tg CO yr<sup>-1</sup>, ~ 38 Tg PM<sub>2.5</sub> yr<sup>-1</sup>) with a strong effect at the regional scale (Alves et al., 2010a; Balasubramanian and See, 2006; Jaffe et al., 2008; Liu et al., 2009; McMeeking et al., 2006) and also at sites thousands of kilometres from the source (Duck et al., 2007; Jaffe et al., 2004; Lewis et al., 2007; Petzold et al., 2007). Future climate changes are expected to result in more frequent and intense wildfires with far reaching consequences for visibility, air quality and the global carbon cycle. Using a chemical transport model, Spracklen et al. (2009) calculated that climate change will increase summertime organic carbon (OC) aerosol concentrations over the western United States by 40% and elemental carbon (EC) concentrations by 20% from 2000 to 2050. Most of this increase (75% for OC, 95% for EC) will be caused by larger wildfire emissions. While OC aerosols are known as important light scattering atmospheric components contributing to atmospheric cooling, EC has more recently gained attention as major light absorbing aerosol species exerting a positive radiative forcing and reinforcing the atmospheric warming due to increases in the greenhouse gases (Chen and Bond, 2010; Chung and Seinfeld, 2005). The eventual climate effects from carbon aerosols will depend on their physical and chemical composition, as well as their lifetime and distribution in the atmosphere (Jacobson, 2001). Besides the climate interactions, wildland forest fire smoke can have profound adverse health effects (Fowler et al., 2003; Jayachandran, 2009; Potera, 2009).

There are still many unknown aspects related to the emissions of trace gases and aerosol from wildfires. Part of this is due to the unpredictability and dangerousness of fires, which hampers systematic field studies. The molecular speciation of organic aerosols from fire plumes is practically nonexistent. Previous papers dealing with the smoke composition of prescribed fire plumes (Alves et al., 2010a; Lee et al., 2005; Yan et al., 2008) or laboratory combustion of wildland fuels (e.g. Inuma et al., 2007; Mazzoleni et al., 2007; Oros and Simoneit, 2001a,b) indicate that organic constituents represent a very significant

fraction of the particulate aerosol mass, which is formed by a complex mixture of hundreds of compounds. Since emissions vary with type of fuel burned and combustion stage (flaming versus smouldering) (Alves et al., 2010a), and taking also into account that atmospheric photochemistry, source apportionment and climate change models require detailed emissions factors, it is necessary to obtain emission databases reflecting the distinct burning conditions. Due to the higher combustion efficiency common to flaming fires, primary organic compounds, such as anhydrosugars, can decompose to smaller secondary species (Engling et al., 2006). Milder combustion conditions associated with smouldering fires in addition to an oxygen-rich environment have been shown to generate higher particulate emissions, in general, and of anhydrosugars, in particular (Engling et al., 2006). Thus, from smouldering fires mainly low molecular weight pyrolysis products are released in contrast to flaming fires in which soot and inorganic ash components are major components of the pyrogenic aerosol (Hoffer et al., 2005). Given that smouldering fires can be latent for long periods of time, they can emit enormous quantities of pollutants, which are not known in detail or properly quantified. The aim of the present study was to obtain a comprehensive characterisation of the carbonaceous constituents in smoke particles from a wildfire in Portugal, including smouldering and flaming samples.

## 3.2 Experimental

### 3.2.1 Sampling

On May 31<sup>st</sup>, 2009, smoke particles were sampled from the plume of a wildfire that took place in Sever do Vouga (~40°35'58.88"N and 8°22'10.06"W), central Portugal. The vegetation cover was composed by evergreen trees, mainly blue gum (*Eucalyptus globulus*) and Australian blackwood (*Acacia melanoxylon*). The creeping vegetation consisted predominantly of bracken (*Pteridium aquilinum*), heathers (*Erica* and *Calluna* spp.) and gramineae. A tripod high-volume sampler (TE-5200, Tisch Environmental Inc.) operating at a flow of 1.13 m<sup>3</sup> min<sup>-1</sup> was used to collect sequentially, on pre-baked quartz fibre filters, coarse (PM<sub>2.5-10</sub>) and fine (PM<sub>2.5</sub>) smoke particles. A total of 8 samples (PM<sub>2.5</sub> plus PM<sub>2.5-10</sub>) were obtained. The impaction system for removing PM<sub>10</sub> was designed at the University of Aveiro in accordance with the Marple and Rubow's theory (1986). Sampling was performed at 1.5 meters above ground, downwind from the burning area, at distances

of 5-500 meters from the fire. Sampling times ranged from 12 to 40 minutes, depositing 10-60 mg on the filters. The sampler was connected only when impacted by the smoke plume. In parallel, Tedlar bags previously flushed with N<sub>2</sub> were used for the collection of gas samples. Pre-removal of water vapour from the air stream was carried out in a glass U tube filled with glass spheres, immersed in an ice bath. In addition, the air stream was filtered through a 47 mm quartz filter to remove particles before passing to the collection system, which also contained a Teflon-lined diaphragm pump connected to a needle valve and a calibrated rotametre operating at a flow rate of 1 L min<sup>-1</sup>. It should be noted that the Teflon line to collect air samples in Tedlar bags was attached to the PM sampler support pan (structure where the filter holder hangs in the rectangular hole). Thus, the air sample inlet was positioned at a distance of about 6 cm from the filter holders, guaranteeing the collection of particles and gases at the same time and from the same air masses. Both sampling systems were connected to the same socket, so that they could be plugged and unplugged simultaneously. Since the wildfire occurred in a mountainous area, we took advantage of the natural relief and placed the equipment at elevated points in order to obtain samples from the core of the smoke plumes. When the smoke plume changed its direction, the equipment was moved to another point. Considering the difficulties in obtaining representative samples under very tricky field conditions and because smoke plumes are dynamic in nature, measurement bias may have occurred. Although our samples represent freshly emitted fire aerosols, it should be taken into account that emissions can undergo very fast volatilisation, and oxidation of low-volatility gas phase species may rapidly generate organic aerosol (Robinson et al., 2007). In addition, compounds such as plant oils volatilise at the higher temperatures and hastily condense as the plume cools.

### **3.3 Analysis of Samples**

#### **3.3.1 Measurement of hydrocarbons and carbon oxides in gas samples**

Total hydrocarbons and carbon oxides (CO<sub>2</sub> and CO) in the Tedlar bags were measured using automatic analysers with flame ionisation (Dyna-FID, model SE-310) and non-dispersive infrared (Environnement, MIR 9000) detectors, respectively. Each gas

analyser was calibrated with appropriate gas on zero and span points. The hydrocarbon concentrations were determined in methane-equivalents.

### 3.3.2 Organic carbon and elemental carbon measurement

The carbonaceous content (EC and OC) of particulate matter was analysed by a thermal-optical technique. Two 9 mm diameter filter punches, in the case of PM<sub>2.5</sub> samples, or strips representing 1/20 of the total area, in the case of PM<sub>2.5-10</sub> samples, were used in each analytical run. For each filter, two or three replicate analyses were done. Controlled heating in anoxic conditions was performed to separate OC into two fractions of increasing volatility. The first fraction corresponds to the volatilisation at T<200°C of lower molecular weight organics (OC<sub>1</sub>). The second fraction is related to decomposition and oxidation of higher molecular weight species at temperatures ranging from 150 to 600°C (OC<sub>2</sub>). The last fraction of OC is identified by transmittance and corresponds to pyrolysed organic carbon (PC) produced in the previous heating steps. Separation between OC and EC was achieved by initially heating the filter punches under an inert atmosphere to evaporate first the OC fraction. The remaining fraction is sequentially evaporated/burnt under a gas flow containing O<sub>2</sub>. This last carbon fraction contains initial EC plus OC that has pyrolysed during heating under an inert atmosphere. The interference between PC and EC can be controlled by continuous evaluation of the blackening of filter using a laser beam and a photodetector measuring the filter light transmittance.

### 3.3.3 Extraction and analysis of particulate organic compounds

Approximately ¼ of each filter was cut into small pieces and extracted by refluxing 300 mL of dichloromethane for 24 h. After filtration, the pieces of filter were then extracted 3 times with methanol (75 mL for 10 min, each extraction) in an ultrasonic bath. After filtration, all the extracts were combined, vacuum concentrated and dried under a gentle nitrogen stream. The total organic extracts were separated into different fractions by flash chromatography with silica gel (230-400 mesh, 60 Å Merck Grade 9385) and various solvents of increasing polarity. The following solvents (Merck SupraSolv<sup>®</sup>) were used to elute the different compound classes: (1) 22.50 mL *n*-hexane (fraction 1, aliphatics); (2) 22.50 mL toluene–*n*-hexane (8.40:14.10) (fraction 2, polycyclic aromatic hydrocarbons (PAHs)); (3) 22.50 mL *n*-hexane–dichloromethane (11.25:11.25) (fraction 3, carbonyl

compounds); (4) 30.00 mL ethyl acetate–*n*-hexane (12.00:18.00) (fraction 4, *n*-alkanols, sterols and other hydroxyl compounds); and (5) 30.00 mL solution of pure formic acid in methanol (4%, v/v) (fraction 5, acids and sugars). After each elution, the different fractions were vacuum concentrated (25–30°C under reduced pressure) and evaporated by a gentle ultra pure nitrogen stream. Fractions that include more polar compounds, such as alcohols, acids and sugars, were derivatised in sealed vials before injection with *N,O*-bis(trimethylsilyl)trifluoroacetamide + trimethylchlorosilane (99:1, v/v; Supelco 33149-U). The fractionated extracts were analysed by gas chromatography-mass spectrometry (GC-MS from Hewlett-Packard, models 9890 and 7883, respectively, quadrupole) with a TRB-5MS 60 m × 0.25 mm × 0.25 µm column. Data were acquired in the electron impact (EI) mode (70 eV). The oven temperature program was as follows: 60°C (1 min); 60–150°C (10°C min<sup>-1</sup>), 150–290°C (5°C min<sup>-1</sup>), 290°C (30 min) and using helium as carrier gas at 1 mL min<sup>-1</sup>. Standards and samples of fractions 1, 3, 4 and 5 were both co-injected with tetracosane D50 (Aldrich 45.177-0) and 1-chlorohexadecane as internal standards. In the case of PAHs, a mixture of deuterated internal standards was used: 1,4-dichlorobenzene-D4, naphtalene-D8, acenaphthene-D10, phenanthrene-D10, chrysene-D12 and perylene-D12 (Sigma-Aldrich). Compound identification was based on comparison of resulting mass spectra with the Wiley spectral library, co-injection with authentic standards and analysis of fragmentation patterns. A description of recovery efficiency tests for several compounds can be found elsewhere (Gogou et al., 1998; Oliveira et al., 2007). Every organic extract was injected in triplicate or quadruplicate (3 or 4 different dilutions), consecutively in the single ion monitoring and total ion chromatogram modes. The GC-MS calibration was based on a total of about 200 standards (Sigma-Aldrich, TSI, Chiron and Carbosynth) in five different concentration levels with relative response factors (RRF) determined individually to the majority of compounds. For those compounds for which no authentic standards were available, RRF were calculated as an average of the RRF from the overall homologous series or from compounds of similar chemical structure and retention time. Concentrations of organic compounds were normalised to OC (mass compound per mass OC).

## 3.4 Results and Discussion

### 3.4.1 Emission factors

The emission factor (EF) is a parameter that relates the emission of a particular species of interest to the amount of fuel burned. It is defined as the amount of a compound released per amount of dry fuel consumed, expressed in units of  $\text{g kg}^{-1}$ . The carbon combusted in a fire is emitted into the atmosphere mainly in four forms of carbon:  $\text{CO}_2$ , CO, hydrocarbons, and total particulate carbon ( $\text{TC}=\text{OC}+\text{EC}$ ). The emission factor of a species,  $n$ , is then obtained from the ratio of the mass concentration of that species to the total carbon concentration emitted in the plume. Thus, the emission factor is expressed in units of mass of species  $n$  emitted per unit mass of carbon burned. To convert this emission factor to the more frequently used grams of  $n$  produced per kg of dry matter burned, the previous ratio is multiplied by the mass fraction of carbon in the fuel (Reid et al., 2005), which, for the dominant species in the Portuguese forest was estimated to be 48% (Silva et al., 2008). The modified combustion efficiency (MCE) is used to characterise the burning conditions. It is defined as the amount of carbon released as  $\text{CO}_2$  divided by the amount of carbon released as  $\text{CO}_2$  plus CO. Pure smouldering usually has MCE below 0.85, while flaming combustion exhibits the highest values (0.9-1) (Alves et al., 2010a).

Particle concentrations were in the ranges  $158\text{-}2592 \mu\text{g m}^{-3}$  and  $113\text{-}956 \mu\text{g m}^{-3}$  for  $\text{PM}_{2.5}$  and  $\text{PM}_{2.5-10}$ , respectively. Fine particles represented, on average, 77% of the  $\text{PM}_{10}$  mass. Mass percentages of the same order have been obtained in previous works (Alves et al., 2010a; McMeeking et al., 2009). Organic carbon represented 31 to 55% of the  $\text{PM}_{2.5}$  mass, whereas its contribution to coarse particles ranged between 13 and 49%. The OC-to-EC ratios ranged from a minimum of 5, obtained in a sample collected during the flaming phase of the wildfire (MCE=0.97), to a maximum of 713 for smouldering particles. These values are higher than those reported for fires in savannah and tropical forest (Reid et al., 2005). It was observed that the particulate matter and OC emissions enhanced considerably under smouldering conditions. On the contrary, the EC emissions increased with increasing MCE values (Figure 3.1). It should be noted that MCE ranged from 0.77 to 0.97. The emission factors for particulate matter, its carbonaceous constituents and trace gases are presented in Table 3.1. As expected, the  $\text{CO}_2$  emission factors increased with the completeness of the combustion, whereas the opposite was registered for CO and

hydrocarbons. The discrepancies observed between this study and the values reported in the literature may be due to the inherent variability of emissions coupled with different fuels and burning conditions, as well as different ranges of MCE covered by the measurements.

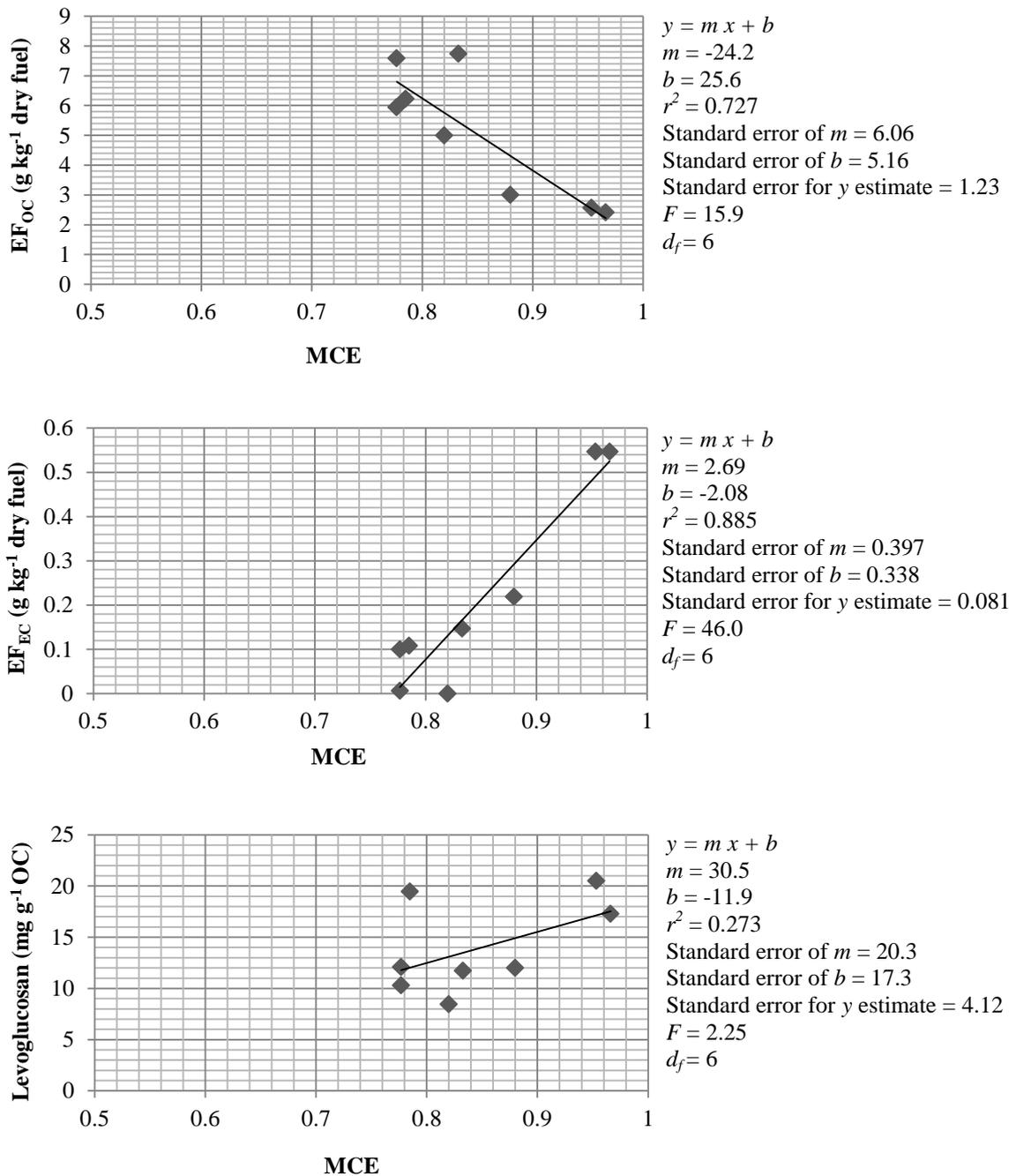


Figure 3.1 Correlation between the modified combustion efficiency and aerosol constituents emitted.

The PM<sub>2.5</sub> emission factors obtained for this wildfire are in the ranges reported in the literature for other fires. EF<sub>PM<sub>2.5</sub></sub> varying from 3.5 to 16 g kg<sup>-1</sup> have been obtained in various types of measurements in the Amazonian region (Neto et al., 2009; and references therein). Yokelson et al. (2008) estimated, for the tropical forest, a fine aerosol emission factor of 9.93 g kg<sup>-1</sup>, with global values ranging from 2.17 to 16.61 g kg<sup>-1</sup> for MCEs between 0.88 and 0.979. Ward and Hardy (1991) proposed an EF<sub>PM<sub>2.5</sub></sub> of 10 g kg<sup>-1</sup> for cured grasses, 15 g kg<sup>-1</sup> fuel for chaparral and palmetto/gallberry fires and 20-50 g kg<sup>-1</sup> for long-needled conifer fires. In their review paper, Andreae and Merlet (2001) reported EF<sub>PM<sub>2.5</sub></sub> of 5.4±1.5 g kg<sup>-1</sup> (savannah and grassland), 9.1±1.5 g kg<sup>-1</sup> (tropical forest) and 13.0±7.0 g kg<sup>-1</sup> (extratropical forest). In laboratory biomass burning experiments, McMeeking et al. (2009) obtained EF<sub>PM<sub>2.5</sub></sub> g kg<sup>-1</sup> of 29.4±25.1 for montane, 18.9±13.9 for rangeland, 11.6±15.1 for chaparral, 23.4±18.7 for coastal plain and 12.7±11.3 for boreal forest ecosystem species.

Table 3.1 Emission factors (mean ± standard deviation). Values are given in g kg<sup>-1</sup> fuel burned (dry basis).

CO	CO <sub>2</sub>	Total hydrocarbons	PM <sub>2.5</sub>	PM <sub>10</sub>	OC	EC
170±83	1485±147	9.8±0.90	12±3.3	14±4.5	6.0±2.9	0.27±0.25

The OC emission factors determined for the wildfire in central Portugal are also comparable to those published in the literature. Andreae and Merlet (2001) reported EF<sub>OC</sub> of 3.4±1.4 g kg<sup>-1</sup> (savannah), 5.2±1.5 g kg<sup>-1</sup> (tropical forest) and 8.6-9.7 g kg<sup>-1</sup> (extratropical forest). Battye and Battye (2002) gathered mean values from 1.96 to 25.6 g kg<sup>-1</sup> for different US forest biomass and burning stages.

Perhaps due to a greater predominance of smouldering samples, the EF<sub>CO</sub> obtained for wildfires in Sever do Vouga are higher than those compiled by Andreae and Merlet (2001). These authors presented EF<sub>CO</sub> of 65±20, 104±20 and 107±37 g kg<sup>-1</sup> for fires in savannah, tropical and extratropical forests, respectively. Battye and Battye (2002) reported values in the ranges 99-232 g kg<sup>-1</sup> and 22-78 g kg<sup>-1</sup> for the smouldering and flaming combustion phases of wildland fires in the USA, respectively. A very high CO emission factor (459 g kg<sup>-1</sup>) was measured for fires with a low MCE (0.59) of feathermoss/lichen in Scotch pine forests of Central Siberia (McRae et al., 2006).

The  $EF_{CO_2}$  lie in the ranges reported in the literature for other fires. McMeeking et al. (2009) obtained  $EF_{CO_2}$  from  $1311 \pm 325 \text{ g kg}^{-1}$  (boreal forest fuels) to  $1632 \pm 150 \text{ g kg}^{-1}$  (coastal plain fuels). Andreae and Merlet (2001) published  $EF_{CO_2}$  of  $1613 \pm 95 \text{ g kg}^{-1}$  (savannah),  $1580 \pm 90 \text{ g kg}^{-1}$  (tropical forest) and  $1569 \pm 13 \text{ g kg}^{-1}$  (extratropical forest). Neto et al. (2009) reported  $EF_{CO_2}$  of  $1631\text{-}1625 \text{ g kg}^{-1}$  (ignition),  $1690\text{-}1741 \text{ g kg}^{-1}$  (flaming) and  $1540\text{-}1548 \text{ g kg}^{-1}$  (smouldering) for an Amazonian forest clearing fire. Measurements of smoke emissions with high combustion efficiency in grasslands and woodland savannah in Africa supplied average  $EF_{CO_2}$  of  $1701 \text{ g kg}^{-1}$  (Ward et al., 1996). In accordance with the results from our study, Chen et al. (2007) obtained, from laboratory combustion of wildland fuels, average emission factors for total hydrocarbons in the gas phase of  $0.4\text{-}10.4 \text{ g kg}^{-1}$  (flaming) and  $1.2\text{-}125 \text{ g kg}^{-1}$  (smouldering).

### 3.4.2 Organic composition of aerosols in the smoke plume

The relative distribution of the quantifiable organic compounds in the smoke particles is presented in Figure 3.2. The chromatographically resolved organics were dominated by phenolic compounds and their alteration products, acids, aliphatics and sugar constituents, accounting for about 45 and 25% of the OC mass in the fine and coarse particles, respectively. The organic compounds that were not extractable or not detectable by GC-MS, such as oligomeric humic-like substances and biopolymeric material, likely represented a major fraction of the unidentified organic matter. On the other hand, it should be noted that, besides carbon atoms, the organic matter has an important contribution of other atomic species, such as oxygen, hydrogen, nitrogen, chloride and sulphur, which are not accounted for in the thermal-optical analysis. It has been estimated that the organic matter-to-organic carbon (OM/OC) ratio for smoke particles is around 1.9 (Alves et al., 2010a; and references therein). By applying this ratio, it can be concluded that  $85.5 \pm 5.7\%$  of the  $PM_{2.5}$  mass, which constitutes the majority of the smoke particle emissions, is composed of organic matter. In general, the concentrations for the different classes of organic compounds were higher in samples obtained during the smouldering phase of the fire compared to those collected during the flaming stage.

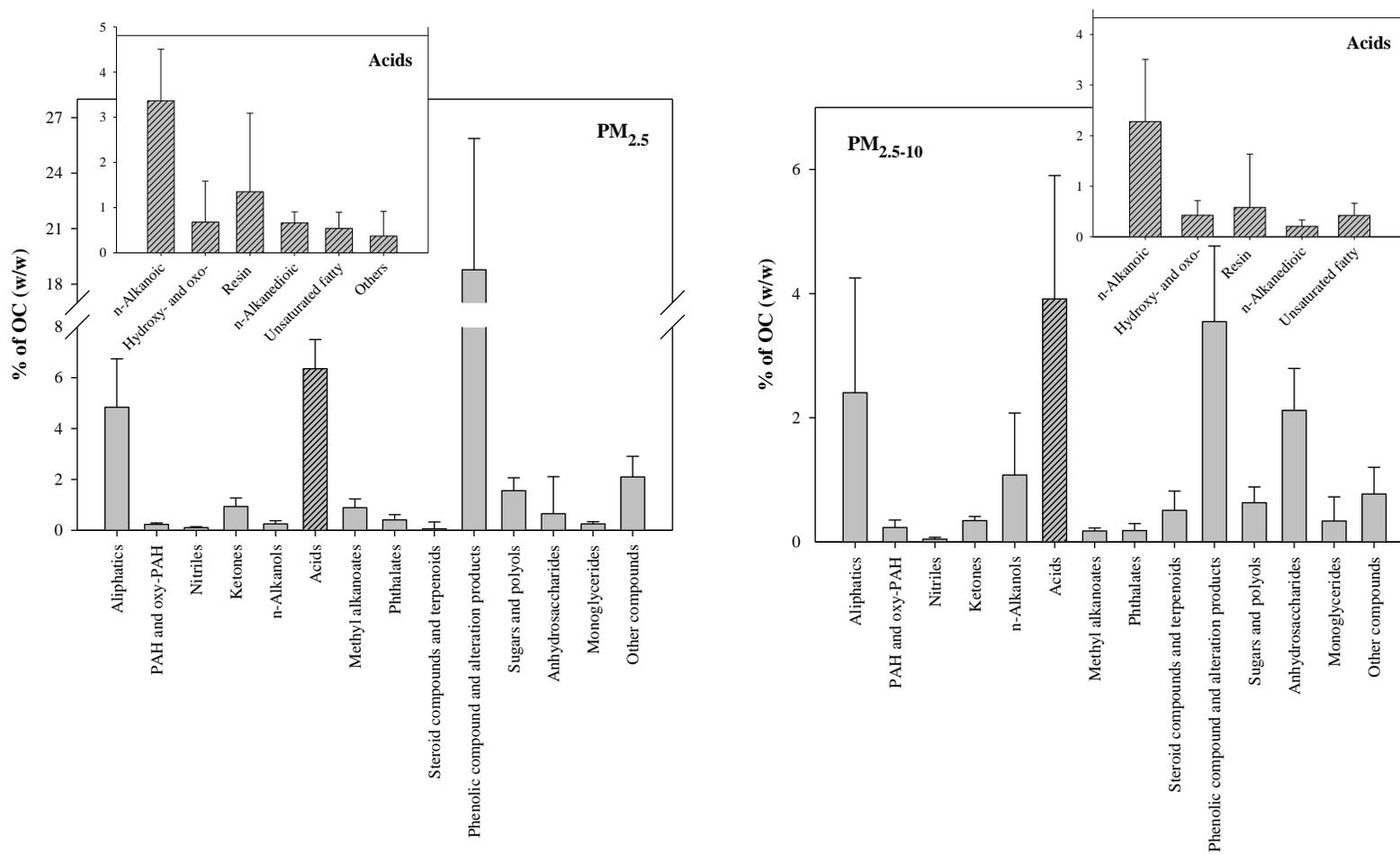


Figure 3.2 Contribution of the chromatographically resolved organic compounds to the OC in the fine and coarse smoke particles.

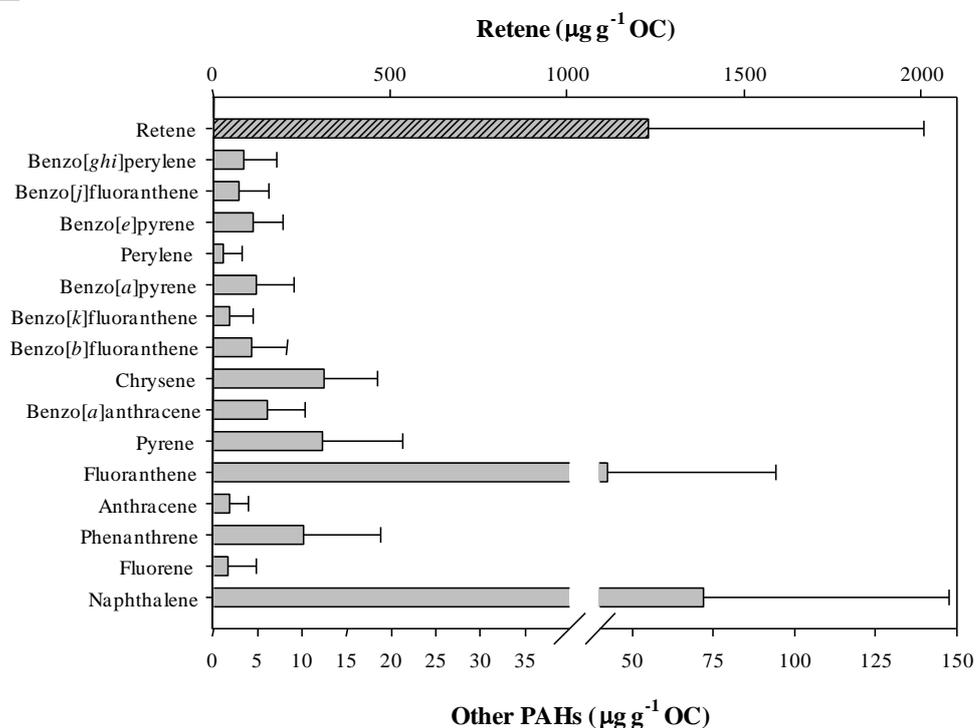
### 3.4.2.1 Aliphatic and aromatic hydrocarbons

The homologous series of *n*-alkanes (C<sub>12</sub>-C<sub>34</sub>) showed an odd carbon number predominance, maximising, in general, in the C<sub>25</sub>-C<sub>33</sub> interval, which have been described as vegetation wax components (Oros and Simoneit, 2001a). The *n*-alkene homologs ranged from tetradecene to octacosene. Since these olefinic compounds are not major components of plant waxes, it has been supposed that they may be produced by the thermal dehydration of *n*-alkanols and, to a lesser extent, from *n*-alkanes by oxidation during incomplete combustion (Oros and Simoneit, 2001a).

The OC-normalised PAH concentrations are depicted in Figure 3.3. The most abundant PAH was retene (1-methyl-7-isopropylphenanthrene), a well-known biomarker of wood combustion (Ramdahl, 1983). It has been argued that it is usually formed during smouldering combustion (Koziriski and Saade, 1998). However, in this study, the retene concentrations were two- to four-fold higher in the flaming samples. It has been discussed that retene is primarily formed by thermal degradation of resin compounds in the biomass, a formation mechanism different from that of other polyaromatic compounds (Otto and Simoneit, 2001). The mechanism involves cracking of organic compounds to smaller, unstable molecules. These fragments, mostly radicals, recombine to larger aromatic ring systems by pyrosynthesis (Koziriski and Saade, 1998). The ratio of benzo[e]pyrene to benzo[e]pyrene plus benzo[a]pyrene [BeP/(BeP+BaP)] has been proposed as a source assignment tool and as an index of the particle ageing, since BaP is easily decomposed by light and oxidants (Alves, 2008). As expected, the ratios obtained in this study (0.53±0.11 for PM<sub>2.5</sub> and 0.49±0.07 for PM<sub>2.5-10</sub>) match the value proposed in the literature for freshly emitted plumes (0.50) and deviates from those reported for vehicular sources (0.60-0.80) (Alves, 2008). Curiously, BeP/(BeP+BaP) ratios ranged from 0.5 to 0.75 for non weathered samples of paleowildfires (Marynowski and Simoneit, 2009). The presence of widespread wildfire records in the Upper Triassic and Lower Jurassic of Central Europe was based on the co-occurrence of charcoal fragments and elevated concentrations of pyrolytic PAHs. The fluoranthene to fluoranthene plus pyrene [Flu/(Flu+Pyr)] ratios of 0.65±0.26 and 0.56±0.13 for PM<sub>2.5</sub> and PM<sub>2.5-10</sub>, respectively, fall within the ranges reported for biomass burning sources (Alves et al., 2010b). The highest Flu/(Flu+Pyr) values were achieved under flaming conditions. The benzo[ghi]perylene to benzo[e]pyrene

(BghiP/BeP) diagnostic ratio ranged between 0.34 (smouldering sample) and 1.04 (flaming sample). Previous studies indicated that the BghiP/BeP ratio is generally higher in gasoline exhausts and lower in wood burning smoke. BghiP/BeP ratios of 0.8 and 2.02 have been used to identify non-traffic sources and traffic emissions (Nielsen, 1996). Okuda et al. (2002) reported values of  $1.0 \pm 0.7$  for wood burning, and  $2.2 \pm 1.1$  for gasoline vehicles. The benzo[ghi]perylene to benzo[a]pyrene (BghiP/BaP) diagnostic ratio increased with increasing MCE values, ranging from 0.37 to 0.75. An average ratio of 0.85 was obtained for prescribed fires in a Mediterranean shrubland with very strong flaming conditions (Alves et al., 2010b). Much higher values of this ratio have been recommended for traffic emissions (Alves, 2008). The benzofluoranthenes to benzo[ghi]perylene (BFs/BghiP) ratio was  $3.6 \pm 0.66$ . Similar ratios were obtained in the above-mentioned shrubland fires (Alves et al., 2010b). The values of this diagnostic ratio can be easily differentiated from those of other combustion sources. In fact, vehicular exhausts produce much lower values, whereas industrial emissions (e.g. cement plants) present the highest ratios (Alves, 2008).

### PM<sub>2.5</sub>



**PM<sub>2.5-10</sub>**

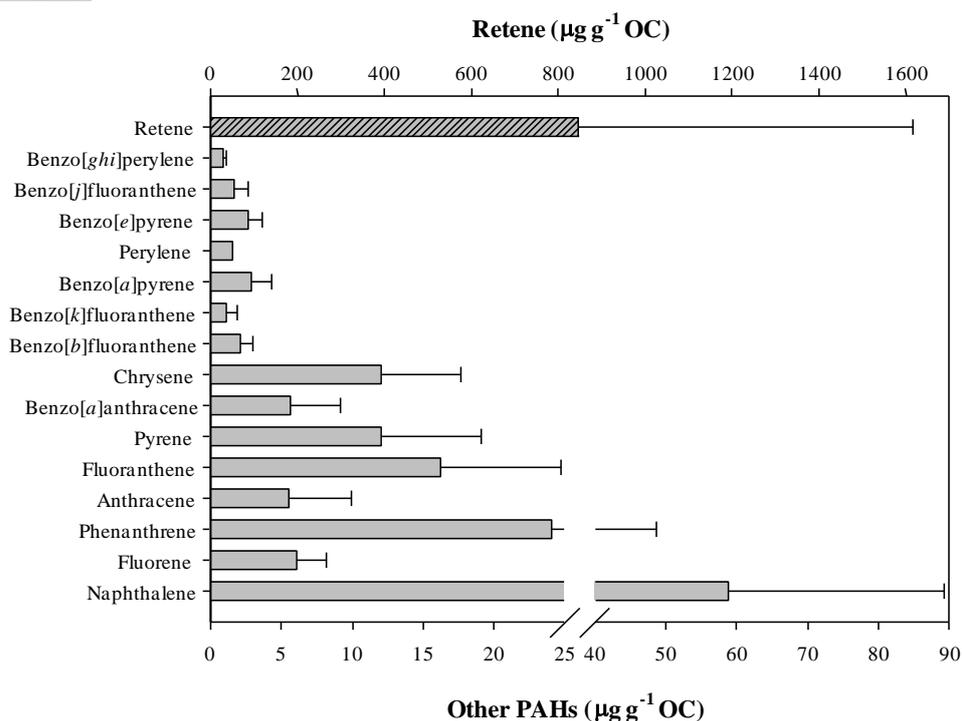


Figure 3.3 Normalised particulate OC emissions of PAH species.

**3.4.2.2 Alkyl nitriles and other nitrogen compounds**

A homologous series of alkyl nitriles (cyanides), generally higher than tetradecanenitrile, were detected in the aerosol phase, presenting higher concentrations in PM<sub>2.5</sub> and in smouldering samples. It has been suggested that fatty acids react with ammonia during biomass burning to form nitriles, which can be applied as useful biomarker tracers (Simoneit et al., 2003). Pyridin-3-ol (3-hydroxypyridine) was another nitrogen-bearing organic species found in smoke particles at mass concentrations between 2.87 and 18.2 mg g<sup>-1</sup> OC in PM<sub>2.5</sub> and from trace levels to 4.60 mg g<sup>-1</sup> OC in PM<sub>2.5-10</sub>. Concentrations increased with decreasing MCE values. This heterocyclic compound has been previously detected in aerosols emitted from agricultural fires (Ma and Hays, 2008).

**3.4.2.3 n-Alkanones and n-alkanols**

The *n*-alka-2-ones ranged from C<sub>13</sub> to C<sub>18</sub>, showing an enrichment in fine particles, especially from the smouldering combustion phase. It has been proposed that straight chain ketones are chiefly originated from the partial combustion of aliphatic precursors (Oros and Simoneit, 2001a). The isoprenoid ketone 6,10,14-trimethyl-2-pentadecanone was

detected at OC-normalised concentrations of 409-2219 and 434-1048  $\mu\text{g g}^{-1}$  in  $\text{PM}_{2.5}$  and  $\text{PM}_{2.5-10}$ , respectively. The minimum values corresponded to flaming samples.

The *n*-alkanol homologous series ranged from  $\text{C}_{12}$  to  $\text{C}_{30}$ , presenting an even-to-odd carbon number predominance characteristic of plant epicuticular waxes (Oros and Simoneit, 2001a,b). On average, the *n*-alkanol content in coarse particles was 3 times higher than that in fine particles. Plant debris or partially combusted foliage ash may have contributed to the detection of higher levels in  $\text{PM}_{2.5-10}$ .

#### 3.4.2.4 Terpenic and steroid compounds

Some sesquiterpenic constituents were present in the wildfire smoke samples (Table 3.2). Sesquiterpenes have become target analytes in biogenic emission analyses because their reactivity make them more efficient secondary organic aerosol precursors than other volatile organic compounds, playing an important role in the oxidative capacity of the atmosphere (Bouvier-Brown et al., 2009). Eudalene (1-methyl-7-(1-methylethyl)naphthalene) is a dehydrogenation product from a starting material containing 15 carbon atoms formed by the loss of one carbon atom. Cadalene is another naphthalene-type sesquiterpene (4-isopropyl-1,6-dimethylnaphthalene). It is a polycyclic aromatic hydrocarbon with a cadinane structural skeleton, which is ubiquitous in higher plants (Otto and Wilde, 2001). Naphthalene derivatives are generated by thermal aromatisation of phytosterols and sesquiterpenes (Gonzalez-Vila et al., 1991). A derivative of azulene, guaiazulene (1,4-dimethyl-7-isopropylazulene), is a bicyclic sesquiterpene that is a constituent of some essential oils. Aromadendrene belongs to the class of aromadendranes, structurally characterised by a dimethyl cyclopropane ring fused to a hydroazulene skeleton. It is present in the essential oils of *Eucalyptus* trees (Lamers, 2003). Gurjunene has been described as a lipophilic extractive of the inner and outer barks of *Eucalyptus globulus* (Freire et al., 2002). It has also been identified as a chemical constituent of the essential oils from the leaves (Song et al., 2009) and the fruits (Pereira et al., 2005) of this tree species. Many sesquiterpenoids have been identified in the vapour phase of ambient samples, but due to their poor retention on filters of high volume air samplers only limited data have been reported for sesquiterpenoids on aerosol particles (Elias et al., 1997).

Table 3.2 Concentration range for terpenoid compounds in smoke particles ( $\mu\text{g g}^{-1}$  OC).

Compound	Formula	PM <sub>2.5</sub>	PM <sub>2.5-10</sub>
Eudalene	C <sub>14</sub> H <sub>16</sub>	bdl-12.2	bdl-23.4
Cadalene	C <sub>15</sub> H <sub>18</sub>	bdl-80.6	bdl-87.6
Guaiazulene	C <sub>15</sub> H <sub>18</sub>	bdl-58.3	bdl-238
Aromadendrene	C <sub>15</sub> H <sub>24</sub>	nd	bdl-20.6
Gurjunene	C <sub>15</sub> H <sub>24</sub>	nd	bdl-719

bdl – below detection limit; nd – not detected

The sterols, generally comprised of the C<sub>29</sub> or C<sub>30</sub> phytosterol compounds (Table 3.3), are components of plant lipid membranes and waxes. The sterol biomarkers are present in all coniferous and deciduous tree smoke samples (Oros and Simoneit, 2001a,b). In general, the sterol components loads were lower in flaming samples than in the smouldering-derived aerosols, while the highest concentrations of their degradation products (e.g. stigmasta-3,5-dien-7-one) were observed in smoke samples resulting from more efficient burning. The steroid ketone 4-cholesten-3-one was only detected in fine particles. It has been described as a hydrous pyrolysis product resulting from the oxidation (dehydrogenation) of cholesterol (Rushdi et al., 2003), which was previously found in smoke from pine, oak, eucalyptus and shrub burning (Alves et al., 2010b; Nolte et al., 2001). Trendione (estra-4,9,11-triene-3,17-dione) is a steroid hormone detected in soils upon mixing with manure (Khan and Lee, 2010). Its presence in coarse particles may be related to soil lofting. Urs-12-en-3-one is a pentacyclic triterpene derived from  $\alpha$ -amyrin, which has been considered as tracer for angiosperm waxes, especially in their gums and mucilages (Oros and Simoneit, 2001a,b). The biosynthesis proceeds from squalene-2,3-epoxide to the basic ursane skeleton and further oxidative steps lead to the pentacyclic oxygenated compound (Alves, 2008).

Table 3.3 Steroid compounds in smoke particles ( $\mu\text{g g}^{-1}$  OC).

Compound	Formula	PM <sub>2.5</sub>	PM <sub>2.5-10</sub>
Stigmasterol	C <sub>29</sub> H <sub>48</sub> O	19.4±13.3	19.6±13.5
$\beta$ -Sitosterol	C <sub>29</sub> H <sub>50</sub> O	723±353	nd
$\alpha$ -Tocopherol	C <sub>29</sub> H <sub>50</sub> O <sub>2</sub>	1601±670	1743±1350
Lupeol	C <sub>30</sub> H <sub>50</sub> O	19.1±12.0	52.9±17.1
Taraxasterol	C <sub>30</sub> H <sub>50</sub> O	nd	1913±205
Trendione	C <sub>18</sub> H <sub>20</sub> O <sub>2</sub>	nd	446±280
4-Cholesten-3-one	C <sub>27</sub> H <sub>44</sub> O	37.6±11.3	nd
Stigmasta-3,5-dien-7-one	C <sub>29</sub> H <sub>46</sub> O	686±675	475±350
Urs-12-en-one	C <sub>30</sub> H <sub>48</sub> O	532±390	788±540

nd – not detected

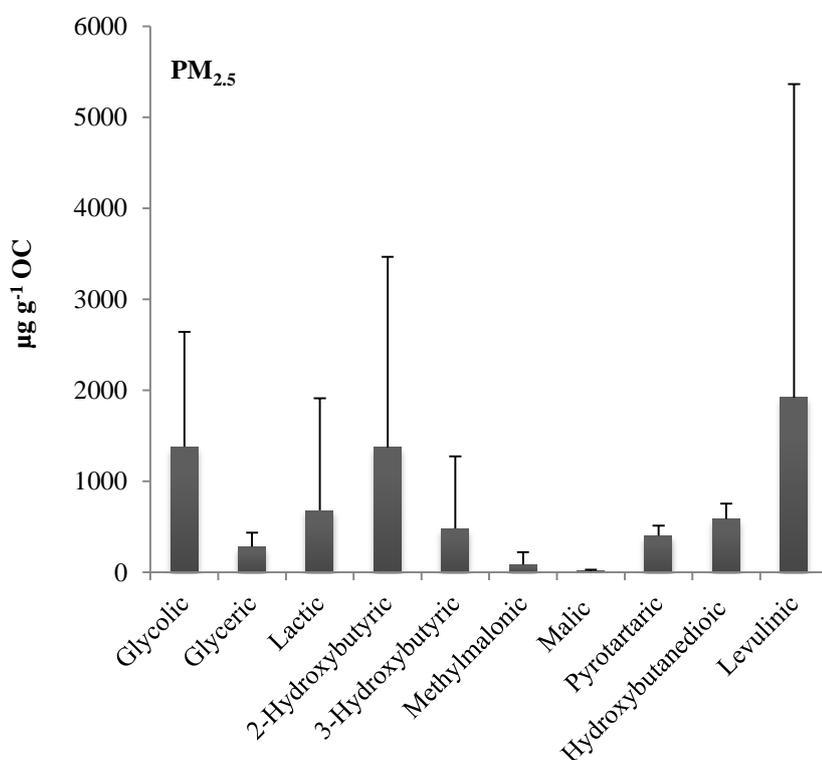
### 3.4.2.5 Acids

The *n*-alkanoic acid homologous series ranged from C<sub>8</sub> to C<sub>31</sub>, peaking at C<sub>14</sub>, C<sub>16</sub>, C<sub>22</sub> or C<sub>24</sub> for PM<sub>2.5</sub>, and at C<sub>16</sub>, C<sub>18</sub> or C<sub>22</sub> for PM<sub>2.5-10</sub>, and presenting a strong even-to-odd carbon number predominance. These compounds have been described as basic units of plant fats, oils and phospholipids (Oros and Simoneit, 2001a). Two unsaturated and polyunsaturated C<sub>18</sub> fatty acids (oleic and linoleic acids) were present in the smoke samples, accounting for, on average, 4331 and 3368  $\mu\text{g g}^{-1}$  OC in PM<sub>2.5</sub> and PM<sub>2.5-10</sub>, respectively. These constituents are important components of plant oils (Lísa et al., 2009). In addition, a series of *n*-alkanoic acid methyl esters with an even carbon number predominance were detected in the wildfire aerosols. Various alkanoates were also identified in PM<sub>2.5</sub> emissions from residential wood combustion (Fine et al., 2004), and in aerosols resulting from prescribed fires in a shrubland (Alves et al., 2010b). Schnelle-Kreis et al. (2007) found *n*-alkanoic acid methyl esters in the PM<sub>2.5</sub> aerosol of Augsburg, Germany, attributing the presence of these constituents to variable influences of wood and coal combustion.

It has been recognised that biomass burning is an important source of dicarboxylic acids and related compounds (e.g. ketocarboxylic acids) (Kundu et al., 2010). In this study, the glycolic (hydroxyacetic), lactic (hydroxypropanoic), hydroxybutyric (hydroxybutanoic) and levulinic (oxopentanoic) acids were the most abundant compounds (Figure 3.4). In general, concentrations were substantially higher in smouldering than in flaming samples. The usefulness of low vapour pressure particle-phase dicarboxylic and related acids as

atmospheric tracers of source emissions is suspicious because they can be formed as secondary organic aerosols by oxidation or emitted from motor exhausts (Legrand et al., 2007). However, its determination is very important for atmospheric studies since they affect cloud microphysical properties and hence precipitation patterns and cloud albedo (Kundu et al., 2010).

Resin acids constituted another group of naturally occurring compounds present in smoke aerosols. They embody a group of diterpenoid carboxylic acids present mainly in softwoods, which can be directly volatilised during combustion (Alves et al., 2010b). This group included the isopimaric, pimaric, abietic and dehydroabietic acids. However, only dehydroabietic acid occurred in all samples, ranging from 0.217 mg g<sup>-1</sup> OC in a smouldering PM<sub>2.5</sub> sample to a maximum of 28.4 mg g<sup>-1</sup> OC in aerosols derived from the flaming combustion phase. Its mass was much more abundant in fine particles. The other resin acids only took place in flaming samples, reaching mass concentrations of 3.50 (isopimaric), 2.83 (pimaric) and 3.05 (abietic) mg g<sup>-1</sup> OC in PM<sub>2.5</sub>. The respective maximum concentrations in PM<sub>2.5-10</sub> were 1.88, 1.38 and 1.38 mg g<sup>-1</sup> OC. The total OC-normalised concentrations of resins acids were 37.6±12.6 mg g<sup>-1</sup> and 21.6±7.66 mg g<sup>-1</sup> for coarse and fine flaming particles, respectively.



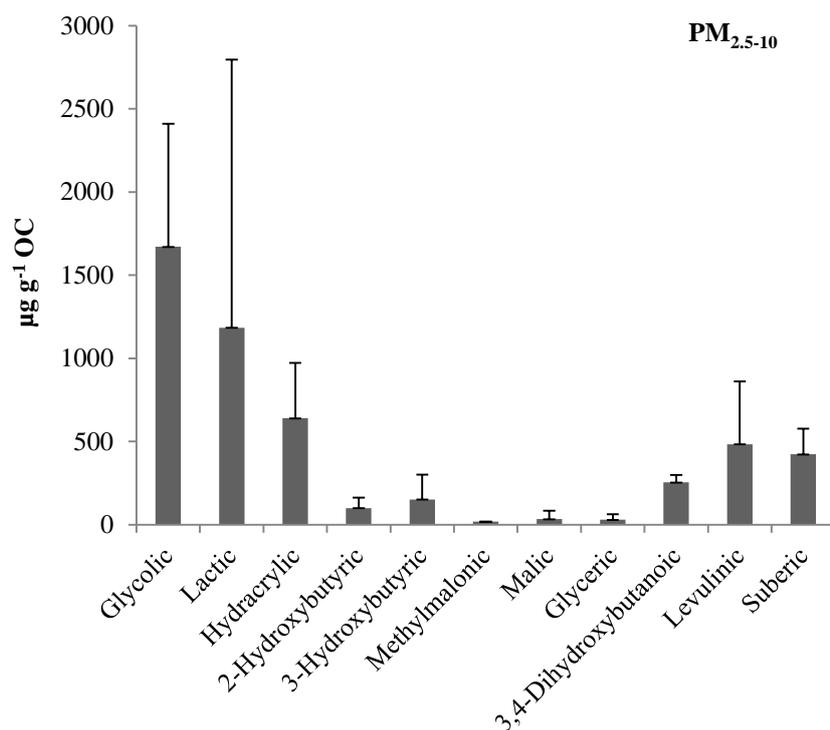


Figure 3.4 Mass concentrations of dicarboxylic, keto- and hydroxy-acids in smoke aerosols.

Some plasticisers, such as phthalic acid (1,2-benzenedicarboxylic acid), dibutyl phthalate, isooctyl phthalate, dioctyl phthalate and isobutyl phthalate, were detected in both fine and coarse particles. The presence of dialkyl esters of benzene-dicarboxylic acids (phthalates) in the wildfire smoke samples may be related to wind-blown plastic litter that is collected in clumps. These compounds volatilise by steam stripping during open burning followed by adsorptive deposition on pre-existing particles (Alves, 2008).

#### 3.4.2.6 Sugars, polyols and monoglycerides

The pyrolysis decomposition product of cellulose, levoglucosan (L), and its stereoisomers mannosan (M) and galactosan (G) were detected in fine particles at average levels of 13.4, 7.59 and 5.20 mg g<sup>-1</sup> OC, whereas in coarse particles the levels were 12.8, 5.65 and 2.80 mg g<sup>-1</sup> OC, respectively. The levoglucosan/OC ratios measured in this study approaches the value of 12.3 mg g<sup>-1</sup> reported by Graham et al. (2003) for the dry season aerosol in Rondonia and the value of 10.5 mg g<sup>-1</sup> measured by Lee et al. (2005) in PM<sub>2.5</sub> aerosols from a prescribed pine forest fire in southeast USA. Alves et al. (2010b) found a ratio of 43 mg g<sup>-1</sup> in experimental fires in a Mediterranean shrubland. Higher ratios were obtained for PM<sub>2.5</sub> aerosols from burning of savannah grasses (324-336 mg g<sup>-1</sup>), Montana

grass (1368 mg g<sup>-1</sup>), Ponderosa pine needles (98-186 mg g<sup>-1</sup>) and duff (525 mg g<sup>-1</sup>) (Engling et al., 2006). The relative amounts of the individual anhydrosaccharides in smoke aerosols can be used to distinguish different biomass burning sources (Fabbri et al., 2009). In this study, average values of 1.77 and 1.05 were obtained for the L/M and L/(M+G) ratios, respectively. Engling et al. (2006) reported values for the L/M ratio between 2.6 and 5.0 for softwood smoke, while the 13.8-52.3 range was pointed out as typical for hardwood. The same authors published L/(M+G) ratios of 2.4-2.8 and 4.5-39.3 for soft- and hardwood smoke, respectively. Values in the 1.4-2.2 and 3.7-4.8 ranges were obtained for the L/M and L/(M+G) ratios, respectively, in aerosols from Chinese shrub burning (Wang et al., 2009). Levoglucosan, mannosan, and galactosan are emitted in varying ratios, probably due to differences in the relative content of cellulose and hemicellulose in different types of biomass. Different combustion conditions also result in levoglucosan emissions that vary with fire regime (flaming versus smouldering combustion phase) and the burn direction/slope (heading versus backing fires) (Engling et al., 2006). In our study, a moderate positive correlation between the levoglucosan-to-OC ratio and the MCE values was registered (Figure 3.1). It has been observed that levoglucosan is also less stable than mannosan concerning chemical degradation in the atmosphere (Sandradewi et al., 2008; and references therein). Possibly, higher combustion temperatures and stronger acidic emissions associated with these wildfires in comparison to those registered in combustion experiments in the laboratory (e.g. Engling et al., 2006), may have led to the decomposition of levoglucosan via chemical processes such as acid-catalysed hydrolysis. This could partly explain the low L/G and L/(M+G) ratios obtained in this study.

Some monosaccharides, disaccharides, and polyols also occurred in the smoke samples. The monosaccharides comprised erythrose (C<sub>4</sub>), arabinose (C<sub>5</sub>), ribose (C<sub>5</sub>), galactose (C<sub>6</sub>), glucose (C<sub>6</sub>), mannose (C<sub>6</sub>), fructose (C<sub>6</sub>), and rhamnose (C<sub>6</sub>). Among these, only erythrose was detected in all samples. This sugar presented similar mass concentrations in fine (3236±1020 µg g<sup>-1</sup> OC) and coarse particles (3006±236 µg g<sup>-1</sup> OC), and did not differ appreciably between smouldering and flaming samples. Two disaccharides (C<sub>12</sub>) were observed in PM<sub>2.5</sub>, but absent from the PM<sub>2.5-10</sub> samples: sucrose and maltose. Their OC-normalised concentrations ranged from values below the detection limit to 74.6 or 752 µg g<sup>-1</sup>, respectively. The polyols encompassed glycerol (C<sub>3</sub>), erythritol (C<sub>4</sub>), arabitol (C<sub>5</sub>), mannitol (C<sub>6</sub>), and inositol (C<sub>6</sub>). These were always present at

individual mass concentrations lower than  $120 \mu\text{g g}^{-1} \text{OC}$ . The occurrence of monosaccharides, disaccharides, and polyols in smoke aerosols has been attributed to the direct volatilisation from vegetation material or to the breakdown of polysaccharides. Some of the sugars may also be formed by hydrolysis of the parent anhydrosugars under the acidic atmospheric conditions created by biomass combustion. Suspended biogenic detritus (e.g. plant debris, fungi, spores, etc.) has been pointed out as an additional, non-prevailing, source (Graham et al., 2002).

A series of monoglycerides, comprising the even carbon number homologs from 2,3-dihydroxypropyl docosanoate to 2,3-dihydroxypropyl octadecanoate, were detected in both  $\text{PM}_{2.5}$  and  $\text{PM}_{2.5-10}$  samples. The  $\text{C}_{16}$  (1-palmitin) and  $\text{C}_{18}$  (1-stearin) monoglycerides have been previously detected in meat smoke (Nolte et al., 1999). Some monoglycerides have also been listed as chemical components of lipophilic extractives from vegetation stems (Coelho et al., 2007), but, as far as we know, these biomarkers are reported for the first time in biomass burning aerosols. The typical fragments of the *TMS* derivatives are 73, 103, 129 and 147 and a base peak at the molecular weight of the compound plus 41.

#### **3.4.2.7 Lignin pyrolysis products**

Combustion of wood and other biomass fuels produces source-specific organic compounds arising from pyrolysis of lignin, including substantial amounts of 4-substituted methoxylated phenolic compounds, which, as it occurs with anhydrosugars or resin acids, have been used as atmospheric markers to determine the contribution of wood smoke to ambient atmospheric fine particulate matter (Simpson et al., 2005). Gymnosperm smoke is made up almost solely from 4-hydroxy-3-methoxy-phenyl (guaiacyl or vanillyl) compounds. Angiosperms generate both vanillyl and 4-hydroxy-3,5-dimethoxyphenyl (syringyl) constituents. Nonwoody tissue of both gymnosperms and angiosperms can be distinguished from woody tissue by their lower yields of vanillyl and syringyl phenols and by the characteristic production of phenylallyl (cinnamyl) phenols. Grasses give rise essentially to 4-hydroxyphenyl (coumaryl) products (Alves et al., 2010b; and references therein). In this study, many phenolic compounds were detected (Table 3.4). Vanillin was the most abundant methoxyphenolic compound in the smoke. In spite of the predominance of hardwood trees (angiosperms) in the forest, syringyl phenols were present at much lower concentrations compared to those of the vanillyl units. Previous laboratory pyrolysis

experiments with wood specimens revealed a preferential thermal degradation of syringic phenols, with the elimination of one of the 3- or 5-methoxyl group, thus entailing an increase in vanillic units at the expense of syringic ones (Ohta and Venkatesan, 1992). The vanillyl phenols formed from the thermal demethoxylation of syringyl phenol moieties would reflect the inputs of gymnosperms to a large extent, rather than the original angiosperms, which are relatively rich in syringyl phenols. Hence, demethoxylation may be a crucial reaction in biomass burning processes, because it can directly modify the substitution pattern of phenolic residues in original lignins, confounding the information about the plant source. The higher proportion of vanillyl than syringyl constituents may also have been influenced by the contribution of the creeping vegetation. An earlier chemical characterisation of the bracken and heather litter showed the dominance of vanillyl moieties (Anderson and Hetherington, 1999).

Table 3.4 Concentration range for phenols and alteration products in smoke particles ( $\mu\text{g g}^{-1}$  OC).

Compound	Formula	PM <sub>2.5</sub>	PM <sub>2.5-10</sub>
<i>Syringyl-type</i>			
Syringol	C <sub>8</sub> H <sub>10</sub> O <sub>3</sub>	nd-28.7	nd-743
Syringaldehyde	C <sub>9</sub> H <sub>10</sub> O <sub>4</sub>	nd-176	nd
Syringic acid	C <sub>9</sub> H <sub>10</sub> O <sub>5</sub>	538-8690	0.384-3.93
Sinapic acid	C <sub>11</sub> H <sub>12</sub> O <sub>5</sub>	7.84-48.0	nd-8.50
Sinapyl alcohol	C <sub>11</sub> H <sub>14</sub> O <sub>4</sub>	19.7-24.6	0.903-8.53
<i>Vanillyl-type</i>			
Vanillin	C <sub>8</sub> H <sub>8</sub> O	9345-130558	4378-15380
Isovanillin	C <sub>8</sub> H <sub>8</sub> O <sub>3</sub>	nd-339	nd-774
Vanillic acid	C <sub>8</sub> H <sub>8</sub> O <sub>4</sub>	1639-6479	1433-4014
Homovanillic acid	C <sub>9</sub> H <sub>10</sub> O <sub>4</sub>	nd-2147	nd-1123
Coniferyl aldehyde	C <sub>10</sub> H <sub>10</sub> O <sub>3</sub>	nd	5.59-820
Coniferyl alcohol	C <sub>10</sub> H <sub>12</sub> O <sub>3</sub>	18.6-72.4	5.58-49.8
3-Vanillylpropanol	C <sub>10</sub> H <sub>14</sub> O <sub>3</sub>	1244-2102	829-1675
<i>Coumaryl-type</i>			
<i>p</i> -Coumaric acid	C <sub>9</sub> H <sub>8</sub> O <sub>3</sub>	nd-500	nd

*Other compounds*

Hydroquinone	C <sub>6</sub> H <sub>6</sub> O <sub>2</sub>	895-2407	355-1550
Catechol	C <sub>6</sub> H <sub>6</sub> O <sub>2</sub>	1254-10407	nd-4150
Resorcinol	C <sub>6</sub> H <sub>6</sub> O <sub>2</sub>	1277-12924	894-4800
3-Methylcatechol	C <sub>7</sub> H <sub>8</sub> O <sub>2</sub>	nd-1571	nd-1388
4-Methylcatechol	C <sub>7</sub> H <sub>8</sub> O <sub>2</sub>	1046-6950	nd-2000
Pyrogallol	C <sub>9</sub> H <sub>14</sub> O <sub>3</sub>	1948-3834	nd-743
Isoeugenol	C <sub>10</sub> H <sub>12</sub> O <sub>2</sub>	nd-903	nd-464
4-Formylphenol	C <sub>7</sub> H <sub>6</sub> O <sub>2</sub>	nd-2140	nd-645
2- <i>tert</i> -Butylphenol	C <sub>10</sub> H <sub>14</sub> O	36.4-173	20.9-178
2,4-di- <i>tert</i> -Butylphenol	C <sub>14</sub> H <sub>22</sub> O	505-1086	214-1036
Benzaldehyde	C <sub>7</sub> H <sub>6</sub> O	23.8-623	2.25-176
Benzoic acid	C <sub>7</sub> H <sub>6</sub> O <sub>2</sub>	157-12584	223-1454
3-Hydroxybenzoic acid	C <sub>7</sub> H <sub>6</sub> O <sub>3</sub>	nd-1244	nd-743
4-Hydroxybenzoic acid	C <sub>7</sub> H <sub>6</sub> O <sub>3</sub>	210-1345	nd-493
2,3-Dihydroxybenzoic acid	C <sub>7</sub> H <sub>6</sub> O <sub>4</sub>	935-1582	nd-6350
Benzyl alcohol	C <sub>7</sub> H <sub>8</sub> O	34.8-789	63.0-549
3,5-Dimethyl-4-hydroxybenzaldehyde	C <sub>9</sub> H <sub>10</sub> O <sub>2</sub>	nd-12162	nd-3456
<i>p</i> -Hydroxyacetophenone	C <sub>8</sub> H <sub>8</sub> O <sub>2</sub>	400-575	nd-670
Phenylacetic acid	C <sub>8</sub> H <sub>8</sub> O <sub>2</sub>	28.5-53.8	nd-148
<i>trans</i> -Cinnamic acid	C <sub>9</sub> H <sub>8</sub> O <sub>2</sub>	119-1006	138-823
4-Hydroxyhydrocinnamic acid	C <sub>9</sub> H <sub>10</sub> O <sub>3</sub>	nd-449	nd-280
Ferulic acid	C <sub>10</sub> H <sub>10</sub> O <sub>4</sub>	nd-487	nd-87.5

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nd – not detected

Alkylphenols, such as 2-*tert*-butylphenol and 2,4-di-*tert*-butylphenol, have large variety of usage areas, e.g. as antioxidants, UV-stabilisers, lubricants, hardeners, etc. However, besides the anthropogenic origin, it has been argued that they may also be formed from biomass combustion (Remberger et al., 2003). Emissions of alkylphenols from residential biomass burning have recently been estimated (Johansson et al., 2004).

Emissions occurred regardless of the fuel type (pellets or wood). Cold temperatures after emission may favour condensation of these substances onto atmospheric aerosols.

Burning of lignin and other biopolymeric plant materials yielded many other breakdown products, as dihydroxybenzenes, and phenolic aldehydes, ketones, acids and alcohols, generally with the retention of the original substituents (OH, OCH<sub>3</sub>) on the phenyl ring. In general, these compounds were more enriched in fine particles. Most of them were previously detected in biomass burning particles (Alves et al., 2010b; Oros and Simoneit, 2001a,b). In spite of a lower phenolic content, the flaming samples showed a wider variety of compounds than that observed in smouldering-derived particles. Plausible formation pathways based on the combustion phase and biofuel type remain to be evaluated.

### 3.5 Conclusions

This work presents some of the first measurements of emission factors for trace gases and particles from wildfires in southern Europe. Fine particles represented, on average, 77% of the PM<sub>10</sub> mass. Organic carbon accounted for almost 50% of PM<sub>2.5</sub> mass. The OC-to-EC ratios ranged from 5 to 713, and were found to increase with decreasing MCE values. Also, the distributions and abundances of the biomass smoke constituents are dependent on combustion temperature (smouldering versus flaming conditions), although this aspect deserves further research. The extractable and chromatographically resolved particulate organic matter was mainly composed of phenolic compounds and their alteration products, acids, aliphatics and sugar constituents. Polycyclic aromatic hydrocarbons were also detected as minor constituents. The PAH molecular ratios in this study differ from those of other combustion processes; thus, they may be taken as diagnostic tools in source assignment studies. The levoglucosan/OC (13.4 mg g<sup>-1</sup>) ratio, especially useful for the assessment of the contributions of biomass combustion to ambient aerosol concentrations, approaches the values obtained for prescribed forest fires and for the dry season in Amazonia, but deviates significantly from the ratios reported in the literature for other biomass types and burning regimes. Monoglycerides, which, up to now, have been used as tracers for assigning meat cooking, were also detected in the wildfire smoke particles. In spite of the predominance of angiosperms in the forest, syringyl

phenols were present at much lower concentrations compared to those of the vanillyl-type constituents. This observation corroborates previous laboratory studies that suggested the formation of vanillyl phenols from the thermal demethoxylation of syringyl moieties. However, the thermodynamic and chemical aspects related to these processes remain to be evaluated.

The comprehensive database obtained may be useful for numerical models to evaluate the impact of wildfires on the micro- to regional scale atmosphere in the Mediterranean region, which is particularly uncovered by these studies. Since source apportionment models require detailed emission factors, this investigation may also contribute to estimate the input of wildfires to the atmospheric levels currently measured at monitoring sites.

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## **CHAPTER 4**



## Chapter 4. Measurement of trace gases and organic compounds in the smoke plume from a wildfire in Penedono (central Portugal)

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### Abstract

Gas and particulate fractions were measured simultaneously from a wildfire in Penedono, central Portugal, which occurred in summer 2009. The total volatile hydrocarbons (THC) and carbon oxides (CO<sub>2</sub> and CO) collected in Tedlar bags were measured using automatic analysers with flame ionisation and non-dispersive infrared detectors, respectively. Carbonyls (formaldehyde and acetaldehyde) were sampled from the Tedlar bags in DNHP cartridges and analysed by high-performance liquid chromatography. Fine (PM<sub>2.5</sub>) and coarse (PM<sub>2.5-10</sub>) smoke particles were collected sequentially, on pre-fired quartz fibre filters, with a portable high-volume sampler. The detailed speciation of organic compounds in smoke samples was carried out by gas chromatography-mass spectrometry. The organic and elemental carbon content of particulate matter was analysed by a thermal-optical transmission technique. Average emission factors of 1.86±0.80 and 0.063±0.066 g kg<sup>-1</sup> (dry basis) were obtained for acetaldehyde and formaldehyde, respectively. The THC, CO, CO<sub>2</sub>, PM<sub>2.5</sub>, PM<sub>10</sub>, OC and EC emission factors (g kg<sup>-1</sup> fuel burned, dry basis) were 260±88, 268±92, 1200±172, 37±12.2, 40±12.6, 21±6.7 and 0.44±0.21, respectively. The chromatographically resolved organics included *n*-alkanes, *n*-alkenes, *n*-alkanoic acids, *n*-di-acids, unsaturated fatty

acids, phenolic compounds, ketones, steroids, di- and triterpenoids, PAHs, with retene as the major compound, oxygenated PAH and anhydrosugars.

Keywords: wildfire, organic compounds,  $PM_{2.5}$ ,  $PM_{2.5-10}$ , emission factors.

## 4.1 Introduction

Biomass burning is increasingly being recognised as an important source of radiative and chemically active trace gases and aerosols at the global scale (Langmann et al., 2009). Smoke aerosols are predominantly in the form of submicrometer, accumulation mode particles, which can affect the Earth's albedo, as well as decrease local and regional visibility, because of their light-scattering properties (Chand et al., 2006; Eck et al., 2003; Myhre et al., 2005). Future climate warming may enhance the occurrence and impact of forest fires on air quality (Schär et al., 2004).

Burnt area in Portugal increased in the last decades, contrarily to other southern European countries; although the number of wildfire ignitions is increasing in Portugal, Spain and Greece, in Portugal its occurrence density is much higher (Catry et al., 2007).

Unlike other anthropogenic sources, wildfire emissions are poorly quantified in the literature due to their unpredictability in space and time, dangerousness and, many times, inaccessibility, which difficult a correct sampling and measurement. Laboratory studies and prescribed fires have been used frequently as easier surrogates for wildfires, but it is doubtful that emission fluxes and composition in these conditions are fully representative of real fires. Trace gas emissions have been obtained from wild, prescribed or laboratory-simulated fires (e.g. Alves et al., 2010a; Andreae and Merlet, 2001; McMeeking et al., 2009; Yokelson et al., 2003, 2009). The knowledge about the detailed organic composition of smoke particles is much sparser (Alves et al., 2010b, 2011; Lee et al., 2005; Yan et al., 2007). It has been demonstrated, however, that more than 80% of the smoke aerosol mass is composed of organic matter (Alves et al., 2010b, 2011; Graham et al., 2002), and that the type of compounds may change appreciably with the combustion phase and biofuel characteristics (Alves et al., 2011; Engling et al., 2006).

The aim of this study was to characterise the emission of trace gases and particulate matter in the fresh smoke plume emitted during a wildfire, in order to contribute with new data to source apportionment and emission inventory methodologies, and to better understand the effects of these emissions on human health, climate change and air quality in the Southern European countries.

## 4.2 Methodology

### 4.2.1 Sampling

On July 21<sup>st</sup>, 2009, smoke particles were sampled from a wildfire in the municipality of Penedono, in the Guarda district (~40°56'25.19"N, 7°23'51.58"W, 810 m above sea level), central Portugal. The wildfire, of criminal origin, was ignited in the neighbour municipality of Sernancelhe, in the Viseu district, and lasted over 3 days, destroying a forest area of 680 ha. It was the biggest wildfire recorded in the 2009 fire season, which ended with a total area burned of about 86 000 ha. The vegetation in the region was composed predominantly of pine trees (*Pinus pinaster*), broom (*Cytisus striatus*), and brambles (*Rubus ulmifolius Schott*). Undergrowth vegetation and some isolated oaks (*Quercus pyrenaica*) and cork trees (*Quercus suber*) were also found. During the wildfire event, temperature and relative humidity ranged between 28 and 33°C and 17-23%, respectively.

A portable high-volume sampler (TE-5200, Tisch Environmental Inc.) operating at a flow of 1.13 m<sup>3</sup> min<sup>-1</sup> was used to collect sequentially, on quartz fibre filters, coarse (PM<sub>2.5-10</sub>) and fine (PM<sub>2.5</sub>) smoke particles. The quartz fibre filters were previously baked at 500°C for 6 hours. A total of seven groups of PM<sub>2.5</sub>/PM<sub>2.5-10</sub> samples were obtained. The average sampling volume was 14.7±1.79 m<sup>3</sup>, enabling the deposit of 225-750 mg of particles on the filters. In parallel with aerosol sampling, gaseous samples were co-collected from the same plume in Tedlar bags for later analysis in the laboratory. Background measurements, far away from the wildfire plume, were also carried out and the corresponding values were subtracted from those obtained in the smoke samples. A detailed description of the sampling procedure can be found elsewhere (Alves et al., 2011). Sampling was performed at 1.5 m above ground, downwind from the burning area, at distances of 10-50 m from the fire. The equipment was positioned at a higher elevation point in relation to the fire front in order to obtain samples from the core of the smoke plume. In spite of the 2-3 m heights of the flames at the leading edge of the fire front, a very large smouldering area behind this front and water discharges from aerial firefighting aircrafts (Canadair and helicopters) in the proximities, may have contributed to the collection of emissions that represent a combination of smouldering with periodic bursts of flames.

#### 4.2.2 Determinations in the laboratory

The total volatile hydrocarbons (THC) and carbon oxides (CO<sub>2</sub> and CO) in the Tedlar bags were measured within a few hours following the sampling using automatic analysers with flame ionisation (Dyna-FID, model SE-310) and non-dispersive infrared (Environment, MIR 9000) detectors, respectively. Each gas analyser was calibrated with appropriate gas on zero and span points. The hydrocarbon concentrations were determined in methane-equivalents.

The organic (OC) and elemental carbon (EC) content in smoke particles was analysed by a thermal-optical transmission technique (Alves et al., 2011). Two 9 mm diameter filter punches, in the case of the PM<sub>2.5</sub> samples, or strips representing 1/20 of the total area, in the case of PM<sub>2.5-10</sub> samples, were used in each analytical run. For each filter, two or three replicate analyses were done.

Approximately  $\frac{3}{4}$  of each filter were extracted by refluxing 300 mL of dichloromethane (Fisher Scientific) for 24 h. After filtration, the pieces of filter were extracted 3 times with methanol (Fisher Scientific) (75 mL for 10 min, each extraction) in an ultrasonic bath. All the 4 extracts were then combined, vacuum concentrated and dried under a gentle nitrogen stream. The total organic extracts were subsequently separated into five different organic fractions by flash chromatography with silica gel (230-400 mesh, 60 Å Merck Grade 9385) and various solvents of increasing polarity (Alves et al., 2011). Following each elution, the different fractions were vacuum concentrated and evaporated under an ultra pure nitrogen stream. Before injections, the fractionated extracts that included more polar compounds, were derivatised to trimethylsilyl ethers with BSTFA. Finally, the extracts were analysed by gas chromatography-mass spectrometry (GC-MS). The GC-MS calibration was based on a total of approximately 200 standards in different concentrations levels with relative response factors determined individually for the majority of compounds. The overall inaccuracy of the calibration procedure did not exceed 14% for the aliphatic fraction, 15% for polycyclic aromatic compounds, 13% for carbonyl compounds, 11% for *n*-alkanols and sterol compounds, 15% for acids and 12% for sugars. Compound identification was made by comparison with authentic standards, matching against Wiley and NIST spectral libraries and analysis of fragmentation patterns. For those compounds with no authentic standards available, relative response factors were obtained as an average from the overall homologous series or from compounds of similar chemical

structure and retention time. Standards and samples were both co-injected with two internal standards: tetracosane-d50 (Sigma-Aldrich), 1-chlorohexadecane or 1-chlorododecane (Merck). In the case of PAHs, the EPA 8270 semi-volatile internal standard mix (Supelco), with six deuterated compounds was used: 1,4-dichlorobenzene-D4, naphthalene-D8, acenaphthene-D10, phenanthrene-D10, chrysene-D12 and perylene-D12. To test the recoveries, blank filters previously spiked with known quantities (five different concentration ranges) of representative organic standards were extracted and analysed. For the whole procedure of extraction and analysis, reproducible results of  $95\pm 3.9\%$  and  $96\pm 5.8\%$  were, respectively, obtained for polar and non-polar compounds. In the case of levoglucosan (the main anhydrosugar from biomass burning), the extraction and fractionation procedure enabled a recovery of  $91\pm 11\%$ . Taking into account the high percent recoveries, any correction factors were applied to the analyte concentrations. The analytical procedure for the determination of organic compounds was described in detail by Alves et al. (2011).

Gaseous carbonyl compounds were collected from the Tedlar bags as their hydrazones by drawing air through silica cartridges coated with 2,4-dinitrophenylhydrazine (Sep Pak DNPH, Waters). The analytes were extracted with 3 mL of acetonitrile and analysed by high-performance liquid chromatography (HPLC). The analytical system consisted of a Jasco PU- 980 pump, a Rheodyne manual injection valve (sample loop of 20  $\mu\text{L}$ ), a Supelcosil LC-18 column (250 $\times$ 4.6 mm;  $\mu\text{m}$ ; Supelco) and a Jasco MD-1510 diode array detector, all connected in series. Isocratic elution at room temperature was performed using an acetonitrile/water solution (60/40, v/v) as the mobile phase at a flow rate of 1.5  $\text{mL min}^{-1}$ . The carbonyl concentrations were quantified with external calibrations curves constructed from standard solutions of TO11/IP6A carbonyl-DNPH mix derivatives in acetonitrile.

### 4.2.3 Calculation of emission factors and combustion efficiencies

The emission factor is a parameter that relates the emission of a particular species of interest to the amount of fuel burned. Usually it is defined as the amount of a compound released per amount of dry fuel consumed, expressed in units of  $\text{g kg}^{-1}$ . The carbon combusted in a fire is emitted into the atmosphere mainly in four forms:  $\text{CO}_2$ , CO, volatile hydrocarbons and total particulate carbon ( $\text{TC}=\text{OC}+\text{EC}$ ). The emission factor of a species,

$n$ , is then obtained from the ratio of the mass concentration of that species to the carbon concentration emitted in the plume. Thus, the emission factor is expressed in units of mass  $n$  emitted per unit mass of carbon burned. To convert this emission factor to the more frequently used grams of  $n$  produced per kg of dry matter burned, the previous ratio is multiplied by the mass fraction of carbon in the fuel (Reid et al., 2005). It has been estimated that the dominant species in the Portuguese forest have a mean carbon content of  $48\pm 2\%$  (Silva et al., 2008). The modified combustion efficiency (MCE) is calculated and used for each sampling event to define the relative amount of flaming and smouldering combustion for biomass burning (Yokelson et al., 2009). MCE is calculated dividing the amount of carbon released as  $\text{CO}_2$  by the amount of carbon released as  $\text{CO}_2$  plus  $\text{CO}$ . MCE values higher than or less than 0.9 indicate dominance of flaming or smouldering combustion, respectively (Reid et al., 2005).

## 4.3 Results and Discussion

### 4.3.1 Particle and trace gas emission factors

Particle concentrations were in the ranges  $15.1\text{--}45.4 \text{ mg m}^{-3}$  and  $2.09\text{--}4.73 \text{ mg m}^{-3}$ , for  $\text{PM}_{2.5}$  and  $\text{PM}_{2.5-10}$ , respectively. The gravimetric data confirmed that the  $\text{PM}_{10}$  mass was dominated by the  $\text{PM}_{2.5}$  fraction. Fine particles represented  $90\pm 4.6\%$  of the  $\text{PM}_{10}$  mass concentration. On average, OC accounted for  $53\pm 5.5 \%$  (w/w) of the  $\text{PM}_{2.5}$  mass and  $46\pm 13.0 \%$  (w/w) of  $\text{PM}_{2.5-10}$  mass. Alves et al. (2010b) reported mass percentages of the same order for smoke particles emitted from prescribed fires in a shrub-dominated forest in Portugal. If an organic matter-to-organic carbon (OM/OC) factor of 1.9 is assumed to compute the total organic mass concentration, accounting for associated O, H, N, and other elements, from the measured C mass concentrations attributed to OC (Alves et al., 2010a; McMeeking et al., 2009), then it can be concluded that around 90% of the smoke aerosol mass is composed of organic matter. The OC/EC ratio ranged from a minimum of 34 to a maximum of 76. The highest value was obtained in a sample collected during intense smouldering conditions (MCE=0.68). As observed in previous studies, EC emissions increased with increasing MCE values (e.g. McMeeking et al., 2009). The percentage of carbon emitted in the forms of  $\text{CO}$ ,  $\text{CO}_2$ , THC and particulate carbon are presented in

Table 4.1. As observed in other fires (Alves et al. 2011; Amiro et al., 2002), more than 90% of the carbon in biofuels was released as CO<sub>2</sub> and CO.

Table 4.1 Percentage of carbon emitted in various forms from the wildfire in Penedono.

% C emitted in the form of CO <sub>2</sub>	% C emitted in the form of CO	% C emitted in the form of THC	% C emitted in the form of PC
68±9.8	24±8.2	3.4±1.1	4.5±1.4

PC - particulate carbon

The emission factors calculated in this study are presented in Table 4.2. The CO, THC, PM<sub>2.5</sub>, PM<sub>10</sub> and OC emission factors are much higher than those reported in the literature (Alves et al., 2011; Andreae and Merlet, 2001). The emission values were inversely correlated with MCE. CO is an indicator of smouldering conditions, so its emission factor is commonly used to estimate emission factors for many other products of incomplete combustion (Battye and Battye, 2002). Taking this into account, CO has an important role in the development of emissions inventories for many pollutants. Moderate to high correlations between the CO and other pollutant emission factors were obtained:  $EF_{CO_2} = -1.85 \times EF_{CO} + 1696$  ( $r^2=0.97$ ),  $EF_{THC} = 0.837 \times EF_{CO} + 35.1$  ( $r^2=0.77$ ),  $EF_{OC \text{ in } PM_{2.5}} = 1.06 \times EF_{CO} + 0.528$  ( $r^2=0.98$ ),  $EF_{EC \text{ in } PM_{2.5}} = 21.6 \times EF_{CO} + 11.7$  ( $r^2=0.44$ ). The CO<sub>2</sub> emission factors were in the range 962-1446 g kg<sup>-1</sup> (dry basis). These values are similar to those compiled by Andreae and Merlet (2001) for savanna and grasslands and the emission factors obtained by Alves et al. (2011) from another wildfire in a mixed-evergreen forest in central Portugal. The discrepancies observed between the values reported in the literature and those in this study may be due to the inherent variability of emissions coupled with different fuel burned and burning conditions (flaming versus smouldering). The MCE values obtained in our study ranged from 0.60 to 0.86, reflecting a greater contribution from the smouldering combustion phase. Although sampling has been carried out near the fire front with flaming combustion taking place, an extensive smouldering zone behind the zone of the advanced fire front likely contributed to an integrated mixture of the emissions from both combustion phases. The lowest MCE value was achieved in a sample influenced by the emissions after water discharge from a Canadair in the vicinity of the sampling point.

Table 4.2 Emission factors ( $\text{g kg}^{-1}$  fuel burned, dry basis).

	CO	CO <sub>2</sub>	THC	PM <sub>2.5</sub>	PM <sub>10</sub>	OC	EC
This study	268±92	1200±172	260±88	37±12	40±13	21±6.7	0.44±0.21
Savanna and grassland <sup>a</sup>	65±20	1613±95	3.4±1.0	5.4±1.5	8.3±3.2	3.4±1.4	0.48±0.18
Tropical forest <sup>a</sup>	104±20	1580±90	8.1±3.0	9.1±1.5	6.5±11	5.2±1.5	0.66±0.31
Extratropical forest <sup>a</sup>	107±37	1569±131	5.7±4.6	13±7.0	18±6.4	8.6±9.7	0.56±0.19
Biofuel burning <sup>a</sup>	78±31	1550±95	7.3±4.7	7.2±2.3	9.4±6.0	4.0±1.2	0.59±0.37
Mixed-evergreen forest in Portugal <sup>b</sup>	170±83	1485±147	9.8±0.90	9.1±6.3	11±7.7	4.5±3.8	0.20±0.24

THC – Total volatile hydrocarbons; <sup>a</sup> Andreae and Merlet (2001; and references therein); <sup>b</sup> Alves et al. (2011)

Among other primary sources (e.g. natural vegetative process, vehicular emissions, power plants, etc.), aldehydes may also be emitted during biomass burning processes. In this study, the oxygenated volatile organic compounds measured were formaldehyde and acetaldehyde. Emission factors between 1.22 and 3.17  $\text{g kg}^{-1}$  were determined for acetaldehyde, while values in the range 0.012-0.17  $\text{g kg}^{-1}$  were obtained for formaldehyde. During combustion of vegetable matter (e.g. tobacco in the cigarette smoking), the emission factor of acetaldehyde is about one order higher than that of formaldehyde (Baker, 2006), whilst in vehicle exhausts formaldehyde prevails on acetaldehyde (Nelson et al., 2008; Westerholm et al., 1996). In residential wood burning experiments, acetaldehyde was emitted at the highest rate of all the carbonyls (1.18  $\text{g kg}^{-1}$ ), whereas formaldehyde was emitted at the next highest rate with an average emission of 0.841  $\text{g kg}^{-1}$  (Schauer et al., 2001). The inverse relationship obtained, in this study, between acetaldehyde and MCE was fairly good ( $r^2=0.80$ ). Formaldehyde emissions also increased with decreasing MCE values; however, the relationship with MCE was weaker. Christian et al. (2003) reported the same relationship between acetaldehyde and MCE for laboratory measurement of biomass burning emissions from different fuel types. The inverse relationship of formaldehyde versus MCE obtained in this study is in good agreement with results reported by Yokelson et al. (2003) in measurements of trace gases in smoke samples from African savanna fires.

#### 4.3.2 Particulate organic compounds

The organic compounds in smoke particles identified in this study included homologous series of *n*-alkanes, *n*-alkenes, *n*-alkanols and *n*-alkanoic acids, terpenoid

constituents (especially diterpenoids), carbonyls, phenolic components, PAHs and oxy-PAHs, carbohydrates and polyols (Figure 4.1) The OC-normalised concentrations of all these constituents can be found in appendix (Table A2, supplementary material A2).

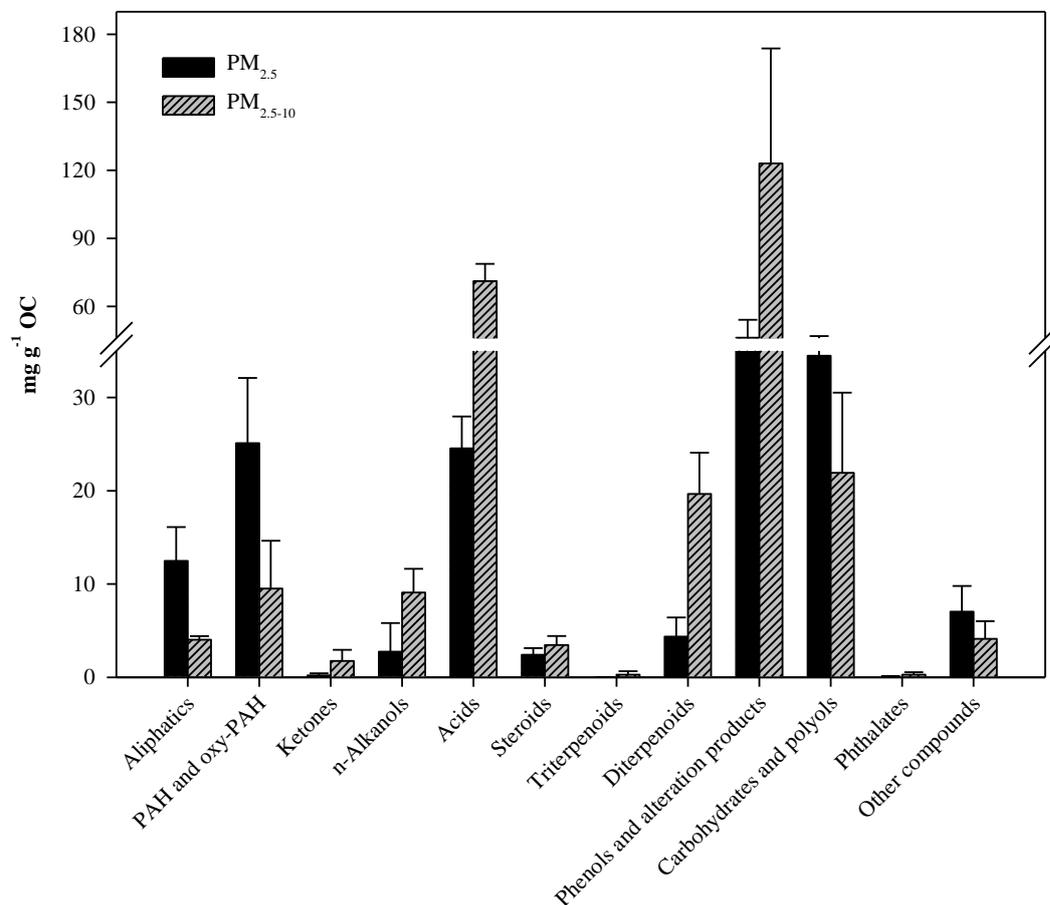


Figure 4.1 OC-normalised concentration of organic compounds detected in smoke samples.

#### 4.3.2.1 Aliphatic compounds

Aliphatic compounds comprised the *n*-alkane homologous series from C<sub>10</sub> to C<sub>35</sub> with an odd-to-even carbon predominance. The homologous series maximised at C<sub>29</sub> and C<sub>31</sub>, which have been assigned to the contribution from epicuticular waxes (Oros and Simoneit, 2001a). The determination of the carbon preference index (CPI) can be used to evaluate the contribution of anthropogenic and biogenic inputs. CPI values ranging between 1 and 2.0 are typically found in urban environments where vehicular emissions dominate, while values higher than 2.0 are characteristic of rural/forest environments, due to the contribution of biogenic sources. In this study, the CPI values of the homologous in the C<sub>26</sub>-C<sub>35</sub> range were 3.71±1.02 and 7.01±4.68 in fine and coarse particles, respectively, reflecting the strong input of biogenic material from plant wax constituents. The *n*-alkene

homologous series ranged from C<sub>14</sub> to C<sub>30</sub>. The *n*-alkenes are not major compounds in plant waxes. It has been assumed that they are formed primarily by the thermal dehydration of *n*-alkanols and, to a minor extent, from the *n*-alkanes by oxidation during incomplete combustion (Oros and Simoneit, 2001a). The homologous series of *n*-alkenes showed an even C number predominance, with C<sub>max</sub> at 24, which is in agreement with the Oros and Simoneit's description of organic constituents in biomass burning aerosols. The *n*-alkane and *n*-alkene contents in the wildfire smoke particles were in the ranges 1.00-8.73 mg g<sup>-1</sup> OC and 1.75-8.30 mg g<sup>-1</sup> OC, respectively. The relationship between the OC-normalised concentrations of aliphatic compounds (*n*-alkanes or *n*-alkenes) and MCE presented a negative slope (Figure 4.2), suggesting that the emission of these compounds is favoured by the smouldering phase of fires. A significant fraction of aliphatics, whose individual characterisation was not possible, was composed of 0.13, 0.48, 0.23 and 0.74 mg g<sup>-1</sup> OC of branched alkanes, other alkanes, branched alkenes and other alkenes, respectively. Hopanes were detected in both fine and coarse particles at very low concentrations (0.05±0.01 mg g<sup>-1</sup> OC and 0.02±0.01 mg g<sup>-1</sup> OC for PM<sub>2.5</sub> and PM<sub>2.5-10</sub>, respectively). Hopanes are biomarkers of fossil fuel utilisation, mainly from vehicular traffic (Simoneit, 2002). Probably, some fire vehicle circulation in the vicinity of the sampling point contributed to the detection of these pentacyclic triterpanes in both size fractions.

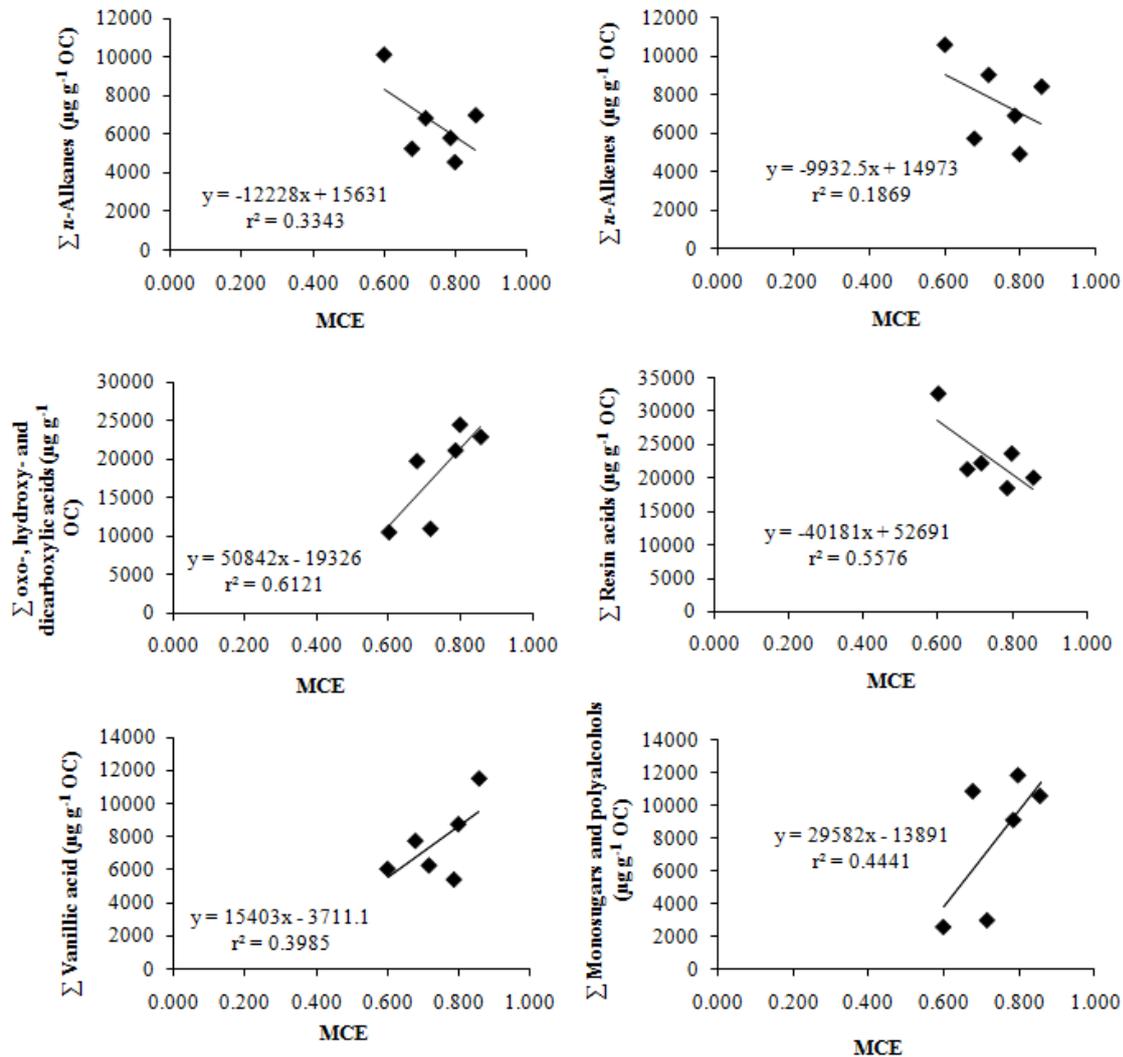


Figure 4.2 Correlations between organic compounds in  $\text{PM}_{10}$  and modified combustion efficiency.

#### 4.3.2.2 Polycyclic aromatic hydrocarbons

The average distribution of the PAH and oxy-PAH compounds for fine ( $\text{PM}_{2.5}$ ) and coarse ( $\text{PM}_{2.5-10}$ ) smoke particles are presented in Figure 4.3. Retene was the major aromatic hydrocarbon present in the fine and coarse particles ( $1.69 \pm 2.75 \text{ mg g}^{-1}$  OC and  $2.40 \pm 2.26 \text{ mg g}^{-1}$  OC, respectively). The values were higher than those reported by Otto et al. (2006) for a wildfire in Canada and by Hays et al. (2005) for the open burning of agricultural biomass. Retene results from the thermal degradation of resin compounds in softwood (Rogge et al., 1998), which is in accordance with the dominant vegetation type burned during this wildfire (conifer wood, especially pine trees). This origin is also

confirmed by the good correlation ( $r^2 = 0.97$ , at a significant level of 0.01) obtained for the  $PM_{2.5}$  fraction between retene and abietic acid (a resin acid). Besides retene, phenanthrene and fluoranthene were the most abundant PAHs found in both size fractions. Benzo[a]anthracene, benzo[a]pyrene and benzo[e]pyrene, components with high mutagenic and genotoxic potential (Medeiros and Simoneit, 2008), were also present, but as minor constituents. Benzo[a]pyrene concentrations were, on average, approximately 3 times higher than those of benzo[e]pyrene in both size fractions. The difference in concentrations may be related to the fact that samples were collected from the fresh smoke plume. Fine et al. (2004a) reported benzo[a]pyrene concentrations 2 times higher than those of benzo[e]pyrene in fine particles emissions from wood stove combustion. Benzo[a]pyrene is easily decomposed in a few minutes by light and in the presence of oxidants. Thus, its relationship with benzo[e]pyrene is affected by the strong reactivity of the former in the atmosphere (Cazaunau et al., 2010). Perylene was found at concentrations comparable to those of benzofluoranthenes and benzo[e]pyrene. Perylene has been found in emissions from boilers burning distillate fuel (Rogge et al., 1997), fine particles from residential wood combustion (Fine et al., 2004a; Rogge et al., 1998), particulate phase emissions from gasoline powered motor vehicles (Schauer et al., 2002), and emissions from waste incineration (Chen et al., 2003; Lee et al., 2002). However, in this type of emissions, perylene was generally found in lower concentrations than those of other PAH congeners. Perylene was identified by Spitzer (2008) as a component of lignite samples but it was not found in emissions from fossil fuel combustion. Thus, apart from the pyrogenic or petrogenic formation, it has been proposed that it is produced biologically and/or diagenetically under anaerobic conditions (Silliman et al., 1998). It is relatively abundant in sediment and soils, and has been associated with degradation of wood or vegetable matter (Grice et al., 2009; Yang et al., 2006). Grice et al. (2009) found considerable concentrations of perylene in sediment samples from the Holocene and hypothesised a relationship between the PAH and the activity of wood-degradation fungi. Wilcke et al. (2002) found high perylene concentrations in soils and suggested a recent biological source related to woody plants and termites. Taking into account that the concentrations of perylene obtained in this study were in the range of those of other PAH that have their origin in combustion processes, besides its pyrogenic contribution, an additional origin in soil dust entrained into the smoke aerosols should also be considered. The dominant oxy-

PAH in fine and coarse particles was 9-fluorenone. Unidentified PAHs represented up to 31.2 mg g<sup>-1</sup> OC. PAHs cannot be considered as specific markers for biomass combustion, because they also can be emitted from other combustion sources (Wang et al., 2009). The ratio of benzo[e]pyrene to benzo[a]pyrene plus benzo[a]pyrene [BeP/(BeP+BaP)] has been identified as a source assignment tool and as an indicator of the particle ageing, due to the relative short lifetime of BaP (decomposed very easily by light and oxidants). The increasing of the ratio can be considered as an index of the aging of the particles. In this study, the ratio was in the ranges 0.10-0.50 and 0.15-0.47, in PM<sub>2.5</sub> and PM<sub>2.5-10</sub>, respectively, which is in accordance with the value of 0.50 proposed in the literature for freshly emitted plumes (Alves, 2008). The fluoranthene to fluoranthene plus pyrene [Flu/(Flu+Pyr)] ratios ranged from 0.53 to 0.86 and from 0.48 to 0.93 for PM<sub>2.5</sub> and PM<sub>2.5-10</sub>, respectively. These values were in agreement with those reported in literature for biomass burning sources. Alves et al. (2010b) obtained ratios of 0.60±0.07 and 0.56±0.25, respectively, for fine and coarse particles emitted from prescribed fires in a shrubland. Oros and Simoneit (2001a) reported values in the range 0.16-0.88, for temperate climate conifer fuel burning. The ratio of benzo[ghi]perylene to benzo[e]pyrene (BghiP/BeP) has been used to differentiate between traffic (BghiP/BeP≈2.02) and non-traffic sources (BghiP/BeP≈0.80) (Nielsen et al., 1996). The diagnostic ratio obtained in this study was, on average, 0.87±0.63. Alves et al. (2010b) determined benzo[ghi]perylene to benzo[a]pyrene (BghiP/BaP) ratios of 0.37 and 0.75, respectively, for the smouldering and flaming phases of another wildfire in Portugal. In agreement with these results, the average value obtained in the present study was 0.34±0.15, reflecting the predominance of samples collected during the smouldering combustion phase (MCE in the range 0.60-0.86). Rogge et al. (1993) reported values up to 3.3 for traffic emissions. Thus, the BghiP/BaP ratio may also be used as a source assignment tool to separate vehicular and biomass burning emissions. Benzofluoranthenes to benzo[ghi]perylene (BFs/BghiP) ratios in the range 0.33-1.6 have been reported for traffic emissions (Alves, 2008). The ratio obtained in this study was much higher, varying from 3.53 to 9.59. These values are also similar to those obtained by Alves et al. (2010b, 2011) for other fires. According to the literature, CPAH/∑PAH ratios of the order of 0.4-0.5 are characteristic of vehicular emissions, while higher values are associated with various industrial processes (Alves, 2008). The results of

this study showed much lower values:  $0.12 \pm 0.09$  and  $0.023 \pm 0.012$  for fine and coarse particles, respectively.

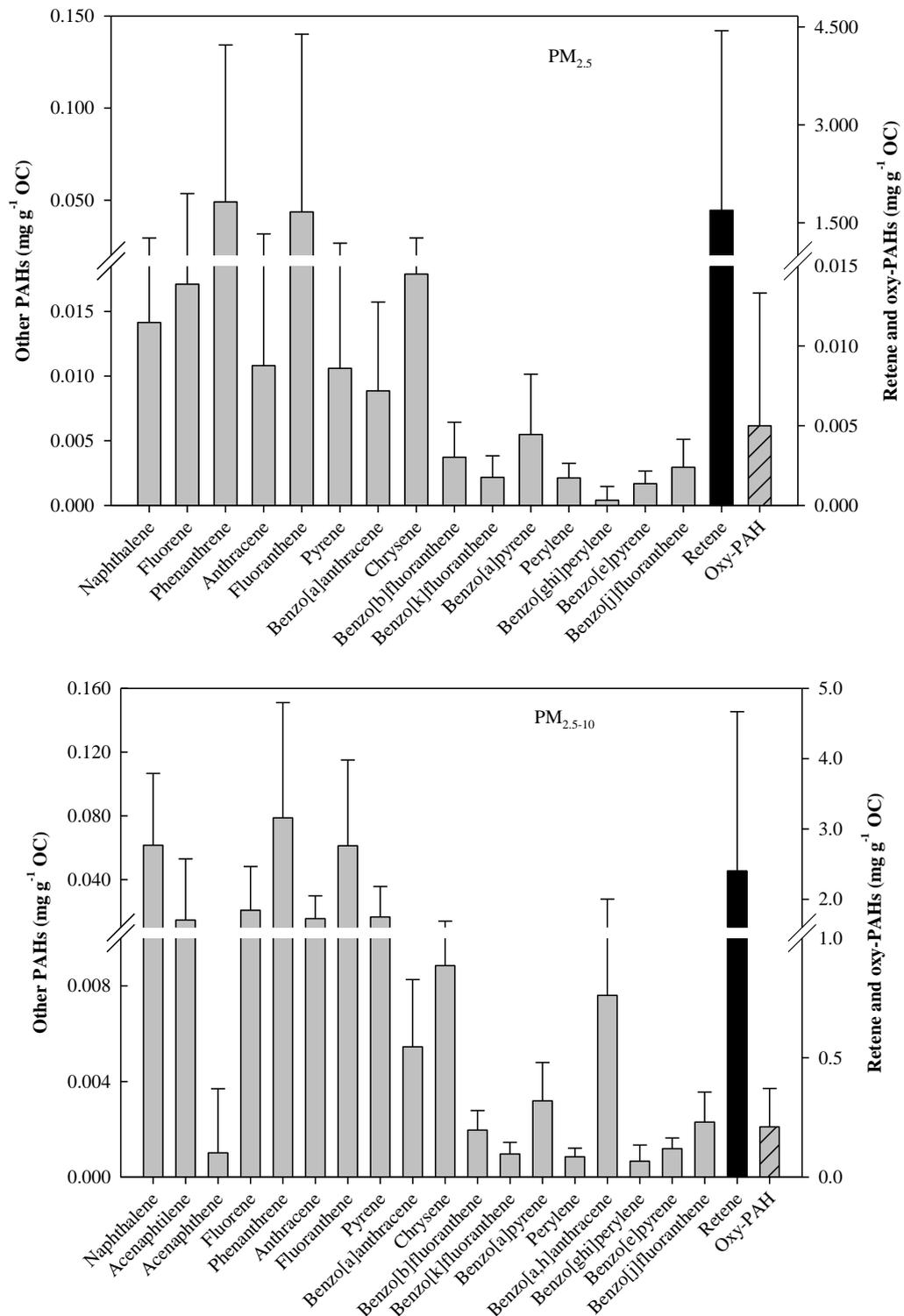


Figure 4.3 OC-normalised concentrations of PAHs and oxy-PAHs in fine and coarse PM fractions.

### 4.3.2.3 *n*-Alkanols and *n*-alkanones

A series of *n*-alkanols ranging from C<sub>10</sub> to C<sub>30</sub> were present in the smoke samples with the dominant homologous higher than C<sub>20</sub> and C<sub>max</sub> varying from C<sub>22</sub> to C<sub>30</sub>. The *n*-alkanols from C<sub>20</sub> to C<sub>30</sub> are major compounds of epicuticular waxes (Medeiros and Simoneit, 2008; Oros and Simoneit, 2001a). The *n*-alkanol content in the PM<sub>2.5-10</sub> particles was, on average, more than 3 times higher than that in the PM<sub>2.5</sub> particles (9.08±2.55 and 2.75±3.07 mg g<sup>-1</sup> OC, respectively).

The *n*-alka-2-one homologous series ranged from C<sub>13</sub> to C<sub>18</sub> with higher concentration in the coarse particles than in the fine particles. It has been proposed that *n*-alka-2-ones are chiefly derived from the partial combustion of aliphatic precursors (Oros and Simoneit, 2001a). The isoprenoid ketone 6,10,14-trimethylpentadecan-2-one was detected in both size fractions with concentrations of 0.0013-0.47 mg g<sup>-1</sup> OC and 0.14-0.29 mg g<sup>-1</sup> OC in fine and coarse particles, respectively. It has been reported that this compound is formed from phytol by oxidative processes (Abas et al., 2004). The phenyl ketone benzophenone was detected only in the coarse fraction with values ranging from 0.012 to 0.044 mg g<sup>-1</sup> OC.

### 4.3.2.4 Acids

The homologous series of *n*-alkanoic acids ranged from C<sub>6</sub> to C<sub>24</sub>, exhibiting a strong even-to-odd carbon number predominance. In PM<sub>2.5</sub> the carbon number peaked at C<sub>16</sub> with a second C<sub>max</sub> at C<sub>24</sub>, whereas in PM<sub>2.5-10</sub> the C<sub>max</sub> was at C<sub>24</sub>, followed by C<sub>22</sub> and C<sub>16</sub>. The *n*-alkanoic acids are basic units of plants fats, oils and phospholipids (Oros and Simoneit, 2001a). The *n*-alkenoic acids present in the smoke samples were the *cis*-9-octadecenoic acid (oleic acid), 9,12-octadecadienoic acid (linoleic acid) and *cis*-9-hexadecenoic acid (palmitoleic acid) (Figure 4.4). These constituents are important components of plant oils (Lísa et al., 2009). The unsaturated fatty acid that presented the highest concentration in the smoke samples was the oleic acid (C<sub>18:1</sub>) with a strong predominance in the coarse particles. A series of *n*-di-acids, ranging from C<sub>3</sub> to C<sub>16</sub>, were also present in the smoke samples. The heptanedioic acid (pimelic acid) was the most abundant constituent in fine particles (1.63-3.85 mg g<sup>-1</sup> OC), followed by nonanedioic acid (azelaic acid) and butanedioic acid (succinic acid). In the coarse fraction, all these three homologous constituents presented normalised concentrations in the range from 0.0745 to 1.07 mg g<sup>-1</sup> OC. Butanedioic and heptanedioic acids have been described as photo-

oxidation products of anthropogenic cyclic olefins (Stephanou and Stratigakis, 1993). Nonanedioic acid has been proposed as a photo-oxidation product of oleic and linoleic acids (Oros and Simoneit, 2001a; Stephanou and Stratigakis, 1993). Thus, the utilisation of these constituents as primary biomass burning tracers is questionable. In smoke samples, oxo- and hydroxy-acids were also identified. The most abundant compound was glycolic acid (hydroxyacetic), in both size fractions, and lactic (hydroxypropanoic) and levulinic acid (oxopentanoic) in coarse particles (Table 4.3). The relationship between the oxo-, hydroxy-, and dicarboxylic acids and MCE was represented in Figure 4.2. It seems that higher emissions of dicarboxylic acids and related compounds take place during the flaming phase.

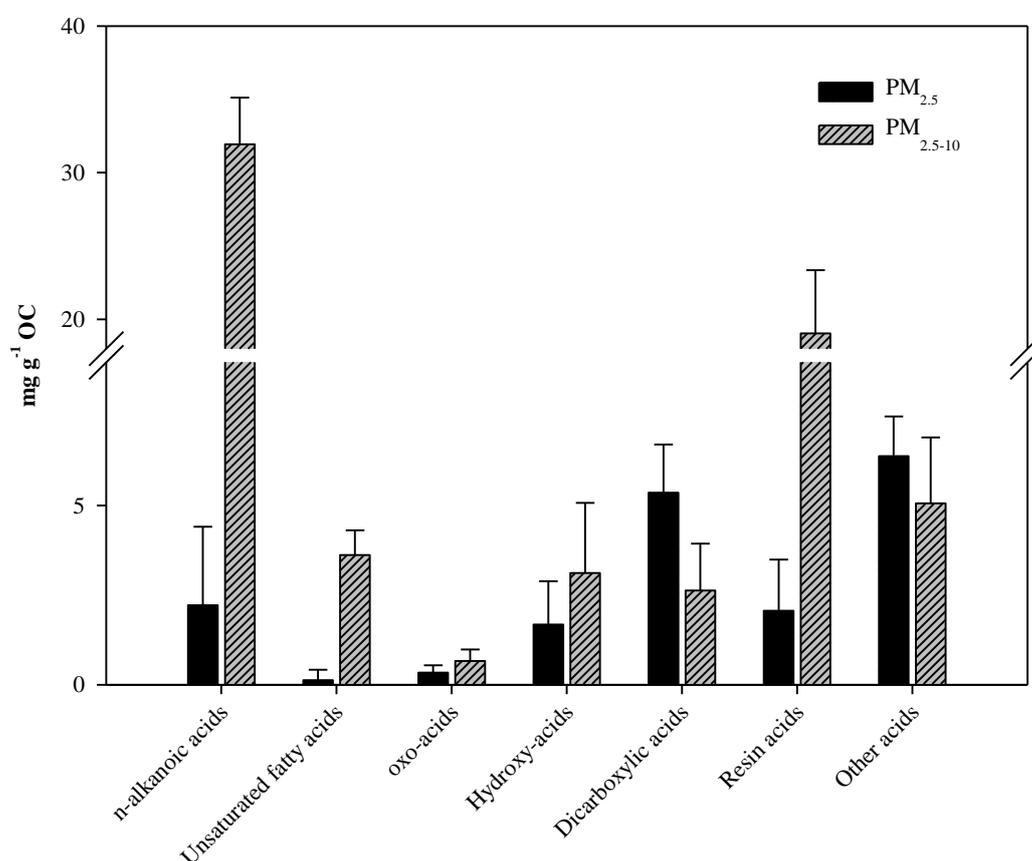


Figure 4.4 OC-normalised concentrations of acids in smoke aerosols.

Table 4.3 Concentration range (and average) for oxo-, hydroxy- and dicarboxylic acids in smoke particles ( $\text{mg g}^{-1}$  OC).

Compound	Formula	PM <sub>2.5</sub>	PM <sub>2.5-10</sub>
Levulinic acid	C <sub>5</sub> H <sub>8</sub> O <sub>3</sub>	0.13-0.65 (0.34)	0.21-1.1 (0.66)
Glycolic acid	C <sub>2</sub> H <sub>4</sub> O <sub>3</sub>	2.4-8.5 (5.5)	1.4-3.9 (2.1)
(R)-3-hydroxybutyric acid	C <sub>4</sub> H <sub>8</sub> O <sub>3</sub>	0.050-0.16 (0.089)	0.053-0.23 (0.10)
Lactic acid	C <sub>3</sub> H <sub>6</sub> O <sub>3</sub>	0.75-1.7 (1.1)	0.22-3.1 (0.85)
4-Hydroxybutyric acid	C <sub>4</sub> H <sub>8</sub> O <sub>3</sub>	nd-0.050 (0.0071)	nd-0.19 (0.039)
Methylmalonic acid	C <sub>4</sub> H <sub>6</sub> O <sub>4</sub>	0.0060-0.010 (0.0076)	0.0077-0.031 (0.013)
L(-)-Malic acid	C <sub>4</sub> H <sub>6</sub> O <sub>5</sub>	0.0032-0.010 (0.0068)	0.0010-0.0095 (0.0034)
Pyrotartaric acid	C <sub>4</sub> H <sub>6</sub> O <sub>6</sub>	nd-0.51 (0.35)	nd-0.82 (0.24)
Methylmaleic acid	C <sub>5</sub> H <sub>6</sub> O <sub>4</sub>	nd	nd-0.81 (0.12)
Propanedioic acid	C <sub>3</sub> H <sub>4</sub> O <sub>4</sub>	0.0038-0.0074 (0.0061)	nd-0.038 (0.0089)
Butanedioic acid	C <sub>4</sub> H <sub>6</sub> O <sub>4</sub>	0.36-1.3 (0.77)	0.074-0.87 (0.57)
Pentanedioic acid	C <sub>5</sub> H <sub>8</sub> O <sub>4</sub>	0.12-0.33 (0.23)	0.020-0.18 (0.12)
Hexanedioic acid	C <sub>6</sub> H <sub>10</sub> O <sub>4</sub>	0.055-0.14 (0.096)	nd-0.077 (0.050)
Heptanedioic acid	C <sub>7</sub> H <sub>12</sub> O <sub>4</sub>	1.6-3.8 (2.5)	0.29-1.1 (0.50)
Octanedioic acid	C <sub>8</sub> H <sub>14</sub> O <sub>4</sub>	nd-0.26 (0.26)	nd-0.28 (0.077)
Nonanedioic acid	C <sub>9</sub> H <sub>16</sub> O <sub>4</sub>	0.54-1.6 (1.1)	0.10-0.94 (0.56)
Decanedioic acid	C <sub>10</sub> H <sub>18</sub> O <sub>4</sub>	0.063-0.14 (0.099)	0.024-0.19 (0.099)
Hexadecanedioic acid	C <sub>16</sub> H <sub>30</sub> O <sub>4</sub>	0.0086-0.053 (0.026)	0.054-0.66 (0.28)

nd – not detected

#### 4.3.2.5 Steroids

Sterols were present in all smoke samples. They were generally comprised of the C<sub>28</sub> and C<sub>29</sub> phytosterol compounds, which have been described as constituents of plant lipid membranes and waxes (Oros and Simoneit, 2001a).  $\beta$ -sitosterol was the major compound detected in the smoke samples, followed by stigmasterol and campesterol. Nolte et al. (2001) also obtained high concentrations of  $\beta$ -sitosterol whether in wood smoke or in ambient atmosphere. The same author suggested that  $\beta$ -sitosterol can be an indicator for the possible presence of smoke aerosols from biomass burning. However, non-combustion sources, as plant wax detritus, may also inject this compound into the atmosphere. Stigmasterol is the precursor of several alteration products that have been identified in this study. Among them, stigmasta-3,5-dien-7-one was the one with the highest concentration, followed by stigmast-4-en-3-one and stigmastan-3,5-diene.

#### 4.3.2.6 Terpenoids

Triterpenoids are important constituents in gums and mucilages of many higher plants, especially of deciduous trees, and are major biomarker tracers (Oros and Simoneit, 2001b; Simoneit, 2002). These compounds occurred as minor constituents in the smoke samples. This low abundance may be related to the fact that biofuels were dominated by conifer trees. Cholesterol was the most abundant triterpenoid in coarse particles, while 4-cholesten-3-one prevailed in fine particles.

Among diterpenoids and their thermal alteration products, resin acids represented the major biomarkers detected in all smoke samples (Figure 4.5). They are constituents of many higher plants, mainly in softwood, in their resins (Oros and Simoneit, 2001a). The most abundant products were pimaric and abietic acids for fine and coarse particles, respectively. In the PM<sub>2.5</sub> fraction, methyl dehydroabietate was the thermal alteration product with the highest concentration ( $2.29 \pm 1.20$  mg g<sup>-1</sup> OC). The 7-oxodehydroabietic acid only occurred in the PM<sub>2.5</sub> size fraction. Dehydroabietic acid was the major resin product present in the coarse particles with an average concentration of  $13.6 \pm 3.62$  mg g<sup>-1</sup> OC. Abietic acid, methyl dehydroabietate and dehydroabietic acid occurred in all smoke samples. Emissions of resin acids increased with decreasing MCE values (Figure 4.2).

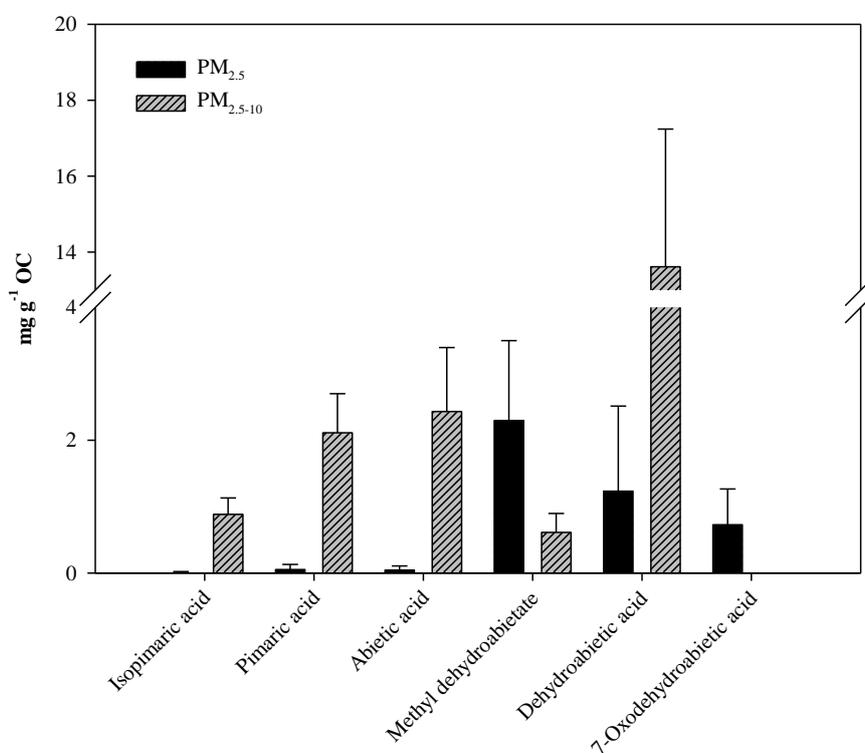


Figure 4.5 OC-normalised concentrations of diterpenoids and alteration products in smoke aerosols.

#### 4.3.2.7 Methoxyphenols

Methoxyphenols have been identified as products from the pyrolysis of lignin. They are abundant in wood smoke and have been suggested as potential molecular markers for biomass burning (Simpson et al., 2005). Pyrolysis of lignin yields the breakdown products of the biopolymer as phenols, aldehydes, ketones, acids and alcohols, usually with the retention of the original substituent on the phenyl ring (Simoneit, 2002). Smoke from hardwood and softwood burning can be distinguished by the relative proportions of substituted guaiacol (2-methoxyphenol) compared to syringol (1,3-dimethoxy-phenol) (Naehrer et al., 2007). In this study, many phenolic compounds were detected. Vanillin was the most abundant in both size fractions with average concentration of  $11.7 \pm 4.90 \text{ mg g}^{-1} \text{ OC}$  and  $92.7 \pm 41.5 \text{ mg g}^{-1} \text{ OC}$  for fine and coarse particles, respectively. Vanillic acid exhibited similar concentrations in both size fractions ( $3.96 \pm 1.16 \text{ mg g}^{-1} \text{ OC}$ ) and its emission increased with increasing MCE values (Figure 4.2). Syringaldehyde and syringic acid were also present in smoke samples. Isolated hardwood trees (cork and Holm oaks) burned during the wildfire probably contributed to the detection of syringic-type products. Grasses yield essentially coumaryl-type products, such as *p*-coumaric acid, which was present at minor amounts in the smoke samples. Some other phenolic compounds were identified in the smoke samples, including guaiacyl-type, benzenediol and benzenetriol. A fraction of phenols, not possible to characterise individually, contributed, on average, to  $0.95 \pm 0.62 \text{ mg g}^{-1} \text{ OC}$ .

#### 4.3.2.8 Sugar compounds

High concentrations of carbohydrates were detected in the smoke samples of this study. These compounds have been described as the major organic components of smoke particles produced during biomass combustion of cellulose and hemicelluloses. The anhydrosugar levoglucosan, and its stereoisomers mannosan and galactosan, constitute the main thermal alteration products and, therefore, are specific markers for wood combustion in ambient particulate matter (Medeiros and Simoneit, 2008; Simoneit et al., 1999). The strong correlation (at a significant level of 0.01) between levoglucosan and its stereoisomers mannosan ( $r^2=0.97$ ) and galactosan ( $r^2=0.96$ ), reflects the common origin in cellulose/hemicelluloses. As expected, levoglucosan was the most abundant anhydrosugar, followed by mannosan and galactosan. These compounds were detected in fine particles at average levels of  $13.9 \pm 5.12$ ,  $8.40 \pm 2.77$  and  $6.21 \pm 2.02 \text{ mg g}^{-1} \text{ OC}$ , while in coarse particles

the average values were  $9.65 \pm 4.17$ ,  $5.65 \pm 1.93$  and  $4.23 \pm 1.68$  mg g<sup>-1</sup> OC, respectively. The levoglucosan/OC ratio obtained in this study approaches the values of 13.4 mg g<sup>-1</sup> OC in PM<sub>2.5</sub> and 12.8 mg g<sup>-1</sup> OC in PM<sub>2.5-10</sub> reported by Alves et al. (2011) in smoke aerosols from a wildfire in Portugal and the value of 12.3 mg g<sup>-1</sup> OC measured by Graham et al. (2003) for the dry season aerosol in Rondonia. Puxbaum et al. (2007; and references therein) reported values ranging from 43 to 523 mg g<sup>-1</sup> OC for residential wood combustion in fireplaces and stoves. Since levoglucosan/OC ratios for wildfires are low compared with those obtained in domestic wood burning, different values should be taken into account in source apportionment studies. In this study, levoglucosan/OC ratios show no clear dependence on MCE. Sullivan et al. (2008) suggest that the levoglucosan/OC ratio is likely more dependent on the fuel component (branches, leaves, wood, etc.) being burned rather than the combustion efficiency. The levoglucosan-to-mannosan (L/M) and the levoglucosan-to-mannosan plus galactosan [L/(M+G)] ratios can be used to distinguish different biomass burning sources (Fabbri et al., 2009). In this study, the average L/M and L/(M+G) ratios were 1.66 and 0.95, respectively. Fine et al. (2004b) obtained an L/M ratio from fireplace combustion around 13-24 and 3.9-6.7 for hard- and softwood, respectively. The same author published L/(M+G) ratios of 10.4-14.2 and 2.9-5.0 for hard- and softwood. Engling et al. (2006) reported L/M and L/(M+G) ratios for PM<sub>2.5</sub> resulting from the burning of grasses in the ranges 108-202 and 54.2-66.1, respectively. The L/M and L/(M+G) average ratios obtained for a wildfire in a mixed-evergreen forest in Portugal were 1.77 and 1.05, respectively (Alves et al., 2011).

Other sugar compounds detected and identified in smoke samples encompassed monosaccharides (lyxose, ribose, galactose and glucose), disaccharides (sucrose and maltose) and polyols (inositol, arabitol, mannitol, xylitol, ribitol, glycerol, maltol and erythritol) (Figure 4.6). Many of these sugar compounds have been previously identified in smoke samples from controlled burning of green vegetation from temperate climate forests (Medeiros and Simoneit, 2008), in smoke aerosols emitted from experimental wildland fires in a Mediterranean ecosystem (Alves et al., 2010b) and in smoke particles from a wildfire in Portugal (Alves et al., 2011). Mannitol and glycerol were the only that appeared in both size fractions. Maltol was only detected in fine particles, while lyxose, xylitol, ribitol, erythritol and sucrose were exclusively found in coarse particles. Graham et al. (2002) suggested that many of these monosugar and polyalcohol constituents are primary

products of combustion formed whether through direct volatilisation from plant matter or as products of the breakdown of polysaccharides. Some of the sugars may also be formed by hydrolysis of the corresponding anhydrosugars under the acidic atmospheric conditions created by biomass burning. Emissions of monosugars and polyalcohols increased with increasing MCE values, indicating a dependence on the fire regime (Figure 4.2).

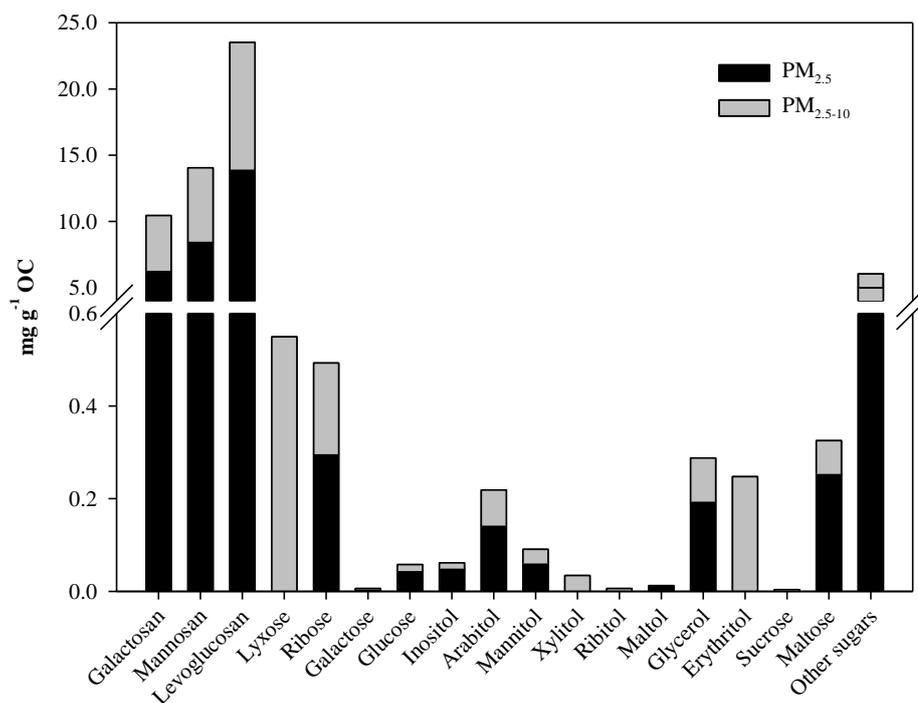


Figure 4.6 OC-normalised concentrations of anhydro-, mono-, disaccharides and polyols in smoke aerosols.

Phthalates, such as dibutyl, isooctyl and dioctyl phthalates, were detected in both fine and coarse smoke particles. Alves (2008) refers that the presence of these constituents in wildfire smoke samples may be related to wind-blown plastic litter that is collected in clumps. Another reason may be related to the discharge of plastic wastes directly into the forest.

#### 4.4 Conclusions

This study involved the simultaneous measurement of the gas and particle-phase emissions for a wildfire in central Portugal. The determination of carbon oxides (CO<sub>2</sub> and CO) enabled the determination of fire combustion conditions (MCE). Around 90% of the

PM<sub>10</sub> aerosol mass was represented by PM<sub>2.5</sub>. On average, OC accounted for 53±5.5 % and 46±13.0 of the PM<sub>2.5</sub> and PM<sub>2.5-10</sub> mass, respectively. Particle, OC and CO emission factors were significantly enhanced with low MCE values, while CO<sub>2</sub> emissions increase with increasing MCE values. The emission factor of CO was found to be a good predictor of emissions of other pollutants (e.g. CO<sub>2</sub>, THC, OC and EC). The OC/EC ratio ranged from 34 to 76 and increased during intense smouldering conditions, reflecting a much higher fraction of OC in emissions from biomass burning than that in vehicular exhausts.

Acetaldehyde mass concentration was thirty times higher than that of formaldehyde. Emissions of both compounds increase with decreasing MCE values. The main organic components in smoke particles were phenolic compounds and their alteration products, especially guaiacyl type, acids, carbohydrates, in particular levoglucosan, diterpenoids and PAHs. Some biomarker/OC ratios can be used as tracers to distinguish the fuel types being burnt. Retene, a biomarker of softwood smoke, was the dominant aromatic hydrocarbon identified in all samples. The polycyclic aromatic hydrocarbon diagnostic ratios obtained can be taken as indicative of vegetation burning in source apportionment studies. The BghiP/BaP values (0.34±0.15) support the fact that this ratio may be used as a tool to differentiate vehicular and biomass burning emissions in source assignment attempts. For most of the organic constituents in smoke particles, a dependence on the fire regime was observed. While emissions of di-, oxo-, and hydroxy-acids, monosugars, polyols and some phenolics like vanillic acid are promoted during the flaming phase, aldehydes, aliphatic compounds and resin acids are predominantly formed during the smouldering combustion phase. Thus, the combustion conditions exert a great influence on the formation pathways and emission rates of organic compounds.

Since estimation of wildfire emissions requires knowledge of fuel-appropriate emissions factors, the comprehensive database obtained in this study is potentially useful to improve the current emission inventories. It has been observed that the smouldering phase, which can occur simultaneously with the flaming front and continue for several hours to days, may contribute to significant amounts of atmospheric pollutants and the corresponding emission factors should be considered when calculating the global wildfire emissions. It has also been concluded that, besides the pyrogenic formation, some compounds may be derived from soil. Due to the lack of detailed emission profiles, the database can also be very helpful for receptor modelling in southern Europe.

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## **CHAPTER 5**



## Chapter 5. Organic speciation of aerosols from wildfires in central Portugal during summer 2009

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### Abstract

The aim of this study was the detailed organic speciation of fine ( $PM_{2.5}$ ) and coarse ( $PM_{2.5-10}$ ) particles and gaseous carbonyl compounds from plumes emitted by wildfires during the summer of 2009 in Portugal. Complementary characterisation of the smoke particulate inorganic fraction, along with emission factors of major trace gases, have already been published in Atmospheric Environment. The detailed speciation of organic compounds in particle samples was carried out by gas chromatography-mass spectrometry after multi-solvent extraction, flash chromatography on silica gel and appropriate derivatisation techniques.  $PM_{2.5}$  constitutes an important fraction of  $PM_{10}$  ( $PM_{2.5}/PM_{10} > 80\%$ ). Gaseous carbonyls were sampled from the Tedlar bags containing the smoke samples in DNHP cartridges and analysed by high-performance liquid chromatography. A clear predominance of carbonaceous constituents was observed, with OC concentrations always much higher than EC in both particle size fractions ( $OC/EC \gg 7$ ). The chromatographically resolved organics were dominated by diterpenoids, acids, sugars, phenols and aliphatic compounds in both size fractions. Retene, a biomarker of softwood smoke, was the dominant aromatic hydrocarbon in samples. The major anhydrosugar detected was levoglucosan, followed by mannosan and galactosan. Among the measured oxygenated volatile organic compounds, the most abundant was acetaldehyde with EFs (dry basis) between 1.03 and 1.87  $g\ kg^{-1}$ , followed by formaldehyde with values in the

range of 0.090-0.96 g kg<sup>-1</sup>. Propionaldehyde was the less abundant carbonyl, with values in the range of 0.032-0.17 g kg<sup>-1</sup>.

Keywords: wildfires, trace gases, particulate matter, emission factors, organic speciation.

## 5.1 Introduction

Wildfires are an important source of aerosol particles and trace gases, with strong impacts on human health, visibility, biogeochemical cycles, atmospheric chemistry and global and regional climate (Koppmann et al., 2005; Reid et al., 2005; Spracklen et al., 2007; Strada et al., 2012).

In Portugal, where most fire events occur in northern and central areas of the country, wildfires destroy every year thousands of hectares, with important losses in terms of environmental quality, economic disruptions and human lives. According to the National Forestry Authority (DGRF), during the period from 1999 to 2008, the mean area burnt by wildland fires in Portugal was higher than 145 000 ha, per year, with more than 25 000 forest fires/year. In 2009, 26 136 forest fires were registered with a total of 86 674 ha destroyed (DGRF, 2010).

Due to their important role on fire regimen, climate and weather are both key aspects that need to be taken into account in forest fires studies (Carvalho et al., 2008; Pereira et al., 2005). Summer heat-waves in southern Europe have become more frequent and are forecast to increase in association with projected global warming. Thus, changes in climate are predicted to result in considerable increases in fire intensity, frequency and area burned, which will lead to increasing environmental impacts. In Portugal, future area to be burned is predicted to increase 478% under a CO<sub>2</sub> duplication scenario (Carvalho et al., 2010).

The determination of emission factors (EFs) constitutes an important challenge and an unquestionable necessity to feed models (e.g. atmospheric photochemistry, source apportionment and climate change models). EFs have been estimated in field campaigns (Lee et al., 2005; Yokelson et al., 2007) and in some laboratory studies (Chen et al., 2007; Christian et al., 2003; McMeeking et al., 2009; Yokelson et al., 2008), but many uncertainties persist. Emissions from American fuels (the most representative on frequency and consumption in wild and prescribed fires in the US), and savannah/grassland, tropical and extratropical forest are the most deeply studied (Andreae and Merlet, 2001; McMeeking et al., 2009; Sinha et al., 2003). In the Mediterranean region and Atlantic transition areas, where forest fires are highly frequent during summer, less is known about

the emissions from the significant amounts of open biomass burning. Due to the extreme difficulties in obtaining smoke samples from uncontrolled fires and the posterior time-consuming analytical techniques associated with the organic speciation, articles reporting a comprehensive characterisation of chemical compounds are very scarce (Alves et al., 2011a; Alves et al., 2010b; Lee et al., 2005; Yan et al., 2008). During the summer of 2009 an intensive study was conducted in order to characterise emission factors of gases and particles for several wildfires occurring in Portugal. The emissions factors of gases and the inorganic composition (elements and water-soluble ions) were discussed in detail by Alves et al. (2011b). Since it has been observed that the aerosol mass was dominated by organic carbon, the aim of this study is to provide a comprehensive overview of the organic compounds in smoke aerosols particles from some of the most representative wildfires whose plumes were sampled in 2009. These results will complement the information already published about wildfires and experimental wildland fire emissions (Alves et al., 2010a; Alves et al., 2011a; Alves et al., 2011b; Vicente et al., 2011). Relationships between combustion conditions (flaming versus smouldering) and the chemical composition of smoke aerosols are explored. These results provide important information to reduce the lack of detailed biomass burning emission profiles for Southern Europe and to lower uncertainty estimates of fire contribution to ambient aerosol levels when applying receptor models.

## **5.2 Methodology**

### **5.2.1 Field work**

During the summer 2009, smoke particles were sampled from seven wildfires occurring in central Portugal (Figure 5.1 and Table 5.1). According to DGRF, during this season, the largest wildfire broke out at Sabugal, in Guarda district. This fire began on August 30 and lasted three days, with a total burned area of 9 976 ha. Part of this burned area corresponds to “Quinta da Póvoa”, one of the wildfires covered by this study. Fire occurrences were followed through the National Authority for Civil Protection of Portugal web-site ([www.prociv.pt](http://www.prociv.pt)). When a wildfire relatively close to the University of Aveiro occurred, the study team moved closer to the fire location using a four wheel drive vehicle, to where the measurement equipment was transported. After reaching the destination, the

fire brigades were contacted asking for permission and advice on a safe place of sampling. Sample collection was carried out as close as possible to the fire. Ground-level aerosol sampling, especially during the flaming phase of a wildfire, constitutes a very difficult task. The heat and flames from fires are obvious risks. Besides the danger, the thermal updraft of fire smoke plumes often renders difficult the collection of emissions samples. In this study, only a minority of field trips (~10%) enabled the collection of samples.

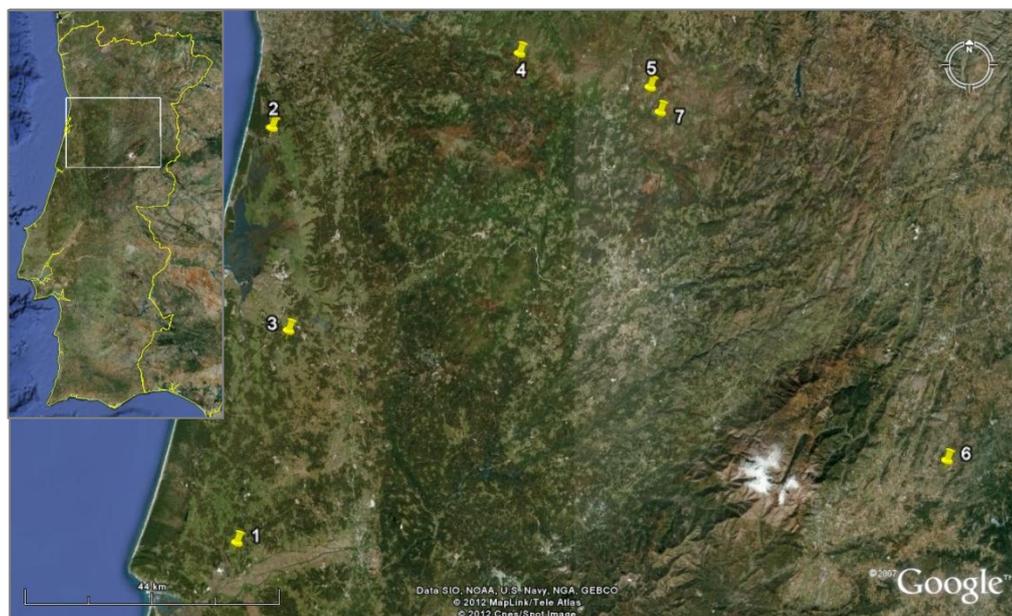


Figure 5.1 Location of wildfires during summer 2009 in Portugal where samples were collected.

A portable high-volume sampler (TE-5200, Tisch Environmental Inc.) operating at a flow of  $1.13 \text{ m}^3 \text{ min}^{-1}$  was used to collect simultaneously, coarse ( $\text{PM}_{2.5-10}$ ) and fine ( $\text{PM}_{2.5}$ ) smoke particles from the plumes. All the quartz fibre filters were previously pre-baked at  $500^\circ\text{C}$  for 6 hours to eliminate organic contaminants. A total of fourteen  $\text{PM}_{2.5}/\text{PM}_{2.5-10}$  sample pairs were obtained. Before and after sampling the gravimetric determination was performed with a microbalance. Filter weights were obtained from the average of three measurements, with a precision of 0.1 mg, before and after sampling, after 24 h of stabilisation in a clean humidity-controlled box. In parallel and simultaneously with aerosol sampling, Tedlar bags were used to collect gas samples, for later analysis in the laboratory. A detailed description of the sampling procedure can be found elsewhere (Alves et al., 2011a).

Table 5.1 Information about wildfires that broke out in central Portugal in 2009, where smoke samples were collected.

Sampling locations	Latitude/Longitude	Date	Major types of biomass/Fire characteristics	Number of samples (PM <sub>2.5</sub> +PM <sub>2.5-10</sub> )	Burnt area (ha)	MCE
	Altitude (a.s.l.)					
1 Montemor-o-Velho	40°12'50"N/8°41'38"W 51 m	11 Aug.	<i>Pinus pinaster/Eucalyptus globulus</i>	6	<100	0.52-0.75
2 Ovar	40°51'56"N/8°37'47"W 25 m	17 Jul.	<i>Acacia sp./Eucalyptus globulus</i>	6	<100	0.66-0.87
3 Nariz (Aveiro)	40°32'52"N/8°35'30"W 25 m	27 Aug.	<i>Pinus pinaster/Acacia sp./Eucalyptus globulus</i>	4	<100	0.58-0.78
4 Cinfães (Viseu)	40°59'04"N/8°07'12"W 619 m	30 Aug.	Creeping fire in a <i>Eucalyptus globulus</i> forest. Biomass burned: fallen twigs, <i>Erica</i> shrubs, <i>Eucalyptus</i> bark and dried leaves	2	368	0.79
5 Farejinha (Castro Daire)	40°55'55"N/7°51'03"W 822 m	31 Aug.	<i>Pinus pinaster/Cytisus striatus</i>	4	348	0.77-0.87
6 Quinta da Póvoa (Sabugal)	40°20'40"N/7°14'30"W 500 m	01 Sept.	<i>Cytisus striatus</i> (dominant); <i>Pinus pinaster</i>	4	9 976	0.77-0.87
7 Pendilhe (V. N. de Paiva)	40°53'34"N/7°49'48"W 825 m	06 Sept.	<i>Cytisus striatus/Pinus pinaster</i>	2	148	0.82

MCE = Modified combustion efficiency =  $(\Delta[\text{CO}_2])/(\Delta[\text{CO}_2]+[\text{CO}])$

Background measurements, in air masses not impacted by the wildfire plume, were also carried out during the campaign and the corresponding values were subtracted from those obtained in the smoke samples. Sampling was performed at 1.5 m above ground, downwind from the burning area, at distances of 10-50 m from the fire. The equipment was positioned at a higher elevation point in relation to the fire front in order to obtain samples from the core of the smoke plume. Most samples contain a mixture of smouldering and flaming emissions with a predominance of the smouldering production. The samplers were connected only when impacted by the smoke plume, sometimes benefiting from steep terrain declivities in mountain catchments under conditions of slope winds. Considering the unpredictable behaviour of wildfires and the very tricky field conditions, the plumes cannot be sampled always at the same distance from the fire. Thus, smoke samples at different levels of dilution and ambient temperatures are obtained, which may cause some bias. In fact, once emitted, many shorter-lived compounds undergo fast gas-particle interconversion processes, whose accounting is very difficult.

## **5.2.2 Laboratory analyses**

### **5.2.2.1 Gaseous compounds**

The total volatile hydrocarbons (THC) and carbon oxides (CO<sub>2</sub> and CO) in the Tedlar bags were measured using automatic analysers with flame ionisation (Dyna-FID, model SE-310) and non-dispersive infrared (Environment, MIR 9000) detectors, respectively. Each gas analyser was calibrated with appropriate gases, on zero and span points. The hydrocarbon concentrations were determined in methane-equivalents.

### **5.2.2.2 Carbonyl compounds**

Gaseous carbonyl compounds were collected from the Tedlar bags as their hydrazones by drawing air through silica cartridges coated with 2,4-dinitrophenylhydrazine (Sep Pak DNPH, Waters). The analytes were extracted with 3 mL of acetonitrile and analysed by high-performance liquid chromatography (HPLC). The analytical system consisted of a Jasco PU- 980 pump, a Rheodyne manual injection valve (sample loop of 20 µL), a Supelcosil LC-18 column (250×4.6 mm; µm; Supelco) and a Jasco MD-1510 diode array detector, all connected in series. Isocratic elution at room temperature was performed using an acetonitrile/water solution (60/40, v/v) as the mobile phase at a flow rate of 1.5

mL min<sup>-1</sup>. The carbonyl concentrations were quantified with external calibrations curves constructed from standard solutions of TO11/IP6A carbonyl-DNPH mix derivatives in acetonitrile.

### 5.2.2.3 Organic and elemental carbon

The carbonaceous content (OC and EC) of smoke particles was analysed by a thermal-optical transmission technique (Alves et al., 2011a). Two 9 mm diameter filter punches, in the case of the PM<sub>2.5</sub> samples, or strips representing 1/20 of the total area, in the case of PM<sub>2.5-10</sub> samples, were used in each analytical run. For each filter, two or three replicate analyses were done.

### 5.2.2.4 Organic speciation

Approximately ¾ of each filter was extracted by refluxing 300 mL of dichloromethane (Fisher Scientific) for 24 h. After filtration, the pieces of filter were extracted 3 times with methanol (Fisher Scientific) (75 mL for 10 min, each extraction) in an ultrasonic bath. All the 4 extracts were then combined, vacuum concentrated and dried under a gentle nitrogen stream. The total organic extracts were subsequently separated into five different organic fractions by flash chromatography with silica gel (230-400 mesh, 60 Å Merck Grade 9385) and various solvents of increasing polarity (Alves et al., 2011a). After elution, the different fractions were vacuum concentrated and evaporated by ultra-pure nitrogen stream. Before injection, the compounds with hydroxylic and carboxylic groups were converted into the corresponding trimethylsilyl derivatives by addition of *N,O*-bis(trimethylsilyl)-trifluoroacetamide (BSTFA): trimethylchlorosilane (TMCS) 99:1 (Supelco). Finally, the extracts were analysed by gas chromatography-mass spectrometry (GC-MS). The GC-MS calibration was based on a total of approximately 200 standards in different concentration ranges with relative response factors determined individually for the majority of compounds. Compound identification was made by comparison with authentic standards, matching against Wiley and NIST spectral libraries and analysis of fragmentation patterns. For those compounds with no authentic standards available, relative response factors were obtained as an average from the overall homologous series or from compounds of similar chemical structure and retention time. Standards and samples were both co-injected with two internal standards: tetracosane-d50 (Sigma-Aldrich), 1-chlorohexadecane or 1-chlorododecane (Merck). In the case of PAHs, the EPA

8270 semi-volatile internal standard mix (Supelco), with six deuterated compounds was used: 1,4-dichlorobenzene-D4, naphthalene-D8, acenaphthene-D10, phenanthrene-D10, chrysene-D12 and perylene-D12. The internal standards were added to the vials in prescribed amounts to eliminate the error caused by variation in injection volume. To test the recoveries of the whole procedure, blank filters previously spiked with known quantities (five different concentration ranges) of representative organic standards were extracted and analysed. About 50 different standards, including non-polar semi-polar and polar organic compounds spiked onto filters have been subjected to the same complete procedure applied to samples, including derivatisation of more polar constituents. For the whole procedure of extraction and analysis, reproducible results of  $95\pm 3.9\%$  and  $96\pm 5.8\%$  were, respectively, obtained for polar and non-polar compounds. In the case of levoglucosan (the main anhydrosugar from biomass burning), the extraction and fractionation procedure enabled a recovery of  $91\pm 11\%$ . Taking into account the high percent recoveries, no correction factors were applied to the analyte concentrations. The detailed description of the analytical procedure for the determination of organic compounds can be found in Alves et al. (2011a).

## 5.3 Results and Discussion

### 5.3.1 Particulate matter and gaseous compounds

The particle concentrations obtained in this study were in the range 0.67-7.5 for fine and 0.16-1.6  $\text{mg m}^{-3}$  for coarse particles. Fine particles represented  $87\pm 9.2\%$  of  $\text{PM}_{10}$  mass concentrations. On average,  $51\pm 22\%$  of the  $\text{PM}_{2.5}$  emissions consisted of organic carbon, whilst the OC mass fraction for  $\text{PM}_{2.5-10}$  was  $24\pm 18\%$ . The EFs of gaseous compounds and particulate matter obtained for all the wildfires studied during 2009 can be found in Alves et al. (2011b). The  $\text{PM}_{2.5}$  and  $\text{PM}_{2.5-10}$  EFs for plume samples that are the centre of this study ranged from 7.2 to 18 and from 5.9 to 20  $\text{g kg}^{-1}$  (dry basis) biomass burned, respectively (Figure A3.2, supplementary material A3). The OC and EC emission factors ranged between 2.9-34 and 0.1-2.4  $\text{g kg}^{-1}$  (dry basis), respectively (Figure A3.4, supplementary material A3). Andreae and Merlet (2001) reported  $\text{PM}_{2.5}$  emission factors ( $\text{g kg}^{-1}$  dry matter burned) for savannah and grassland, tropical forest and extratropical forest of  $5.4\pm 1.5$ ,  $9.1\pm 1.5$  and  $13.0\pm 7.0$ , respectively. The OC emission factors compiled by the

same authors for these three ecosystems were, accordingly,  $3.4\pm 1.4$ ,  $5.2\pm 1.5$  and  $8.6-9.7$ , whereas the average black carbon values were in the range  $0.48-0.56$  ( $\text{g kg}^{-1}$ , dry basis). In laboratory experiments, McMeeking et al. (2009) obtained  $\text{PM}_{2.5}$  emission factors ( $\text{g kg}^{-1}$  dry fuel) of  $29.4\pm 25.1$  for montane,  $18.9\pm 13.9$  for rangeland,  $11.6\pm 15.1$  for chaparral,  $23.4\pm 18.7$  for coastal plain and  $12.7\pm 11.3$  for boreal forest ecosystem species. Depending on the combustion efficiency and biomass type, the OC and EC emission factors determined in the laboratory combustion of these wildland fuels were, respectively, in the ranges  $1.5-50$  and  $0-8.1$  ( $\text{g kg}^{-1}$  dry fuel).

In the present study, a clear predominance of carbonaceous compounds was observed, with OC concentration always remaining much higher than EC in both size fractions ( $\text{OC/EC}\gg 7$ ). In the case of  $\text{PM}_{2.5}$ , the OC/EC ratios ranged from 7 to 69. For coarse particles, these ratios were even higher. Regarding gaseous compounds, the CO and  $\text{CO}_2$  EFs were in the ranges  $158-354$  and  $1046-1451$   $\text{g kg}^{-1}$  biomass burned (dry basis), respectively (Figure A3.3, supplementary material A3). These values are in accordance with those reported by Andreae and Maerlet (2001) for savannah and grassland ( $65\pm 20$  for CO and  $1613\pm 95$   $\text{g kg}^{-1}$ , dry matter burned, for  $\text{CO}_2$ ), tropical forest ( $65\pm 95$  for CO and  $1580\pm 90$   $\text{g kg}^{-1}$ , dry matter burned, for  $\text{CO}_2$ ) and extratropical forest ( $107\pm 37$  for CO and  $1569\pm 131$   $\text{g kg}^{-1}$ , dry matter burned, for  $\text{CO}_2$ ). For THC, EFs reached values up to  $61.4$   $\text{g kg}^{-1}$  (dry basis) (Figure A3.4, supplementary material A3). It should be noted that higher and more variable emission factors for total hydrocarbons and CO are observed during the smouldering phase, while emissions of  $\text{CO}_2$  dominate during the flaming phase.

The oxygenated volatile organic compounds measured in this study were formaldehyde, acetaldehyde and propionaldehyde. Among other primary sources, aldehydes may also be emitted during biomass burning. The most abundant compound was acetaldehyde with emission factors (dry basis) between  $1.03$  and  $1.87$   $\text{g kg}^{-1}$ , followed by formaldehyde with values in the range  $0.090-0.96$   $\text{g kg}^{-1}$ . Propionaldehyde was the less abundant ( $0.032-0.17$   $\text{g kg}^{-1}$ ) (Figure 5.2). The emission factors of aldehydes obtained in this study are in accordance with those reported by Schauer et al. (2001) for residential wood burning experiments, as well with those obtained by Vicente et al. (2011) for a wildfire in central Portugal. In vehicular emissions formaldehyde prevails over acetaldehyde (Nelson et al., 2008) and propionaldehyde (Westerholm et al., 1996). The emission factors of all three aldehydes increased with decreasing MCE values. The inverse

relationship between acetaldehyde and MCE values was more significant compared with formaldehyde and propionaldehyde. Christian et al. (2003) reported the same relationship between acetaldehyde and MCE for laboratory measurements of biomass burning emissions from different fuel types. As far as we know, the relationship between these carbonyls and MCE has never been established for wildfires.

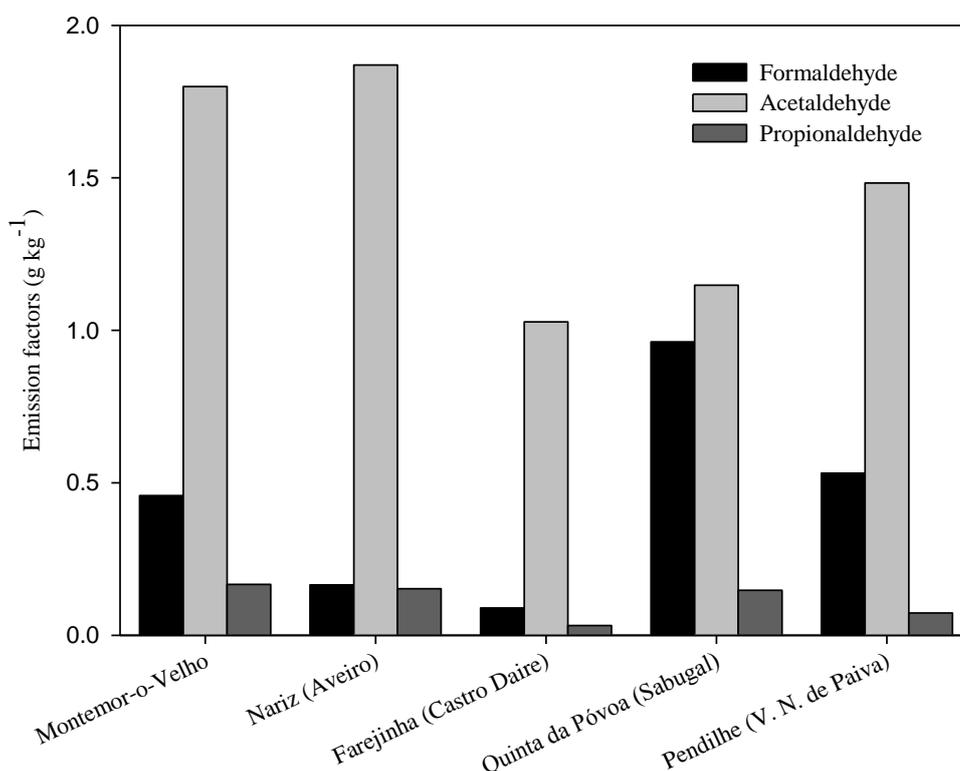


Figure 5.2 Average emission factors for formaldehyde, acetaldehyde and propionaldehyde ( $\text{g kg}^{-1}$  biomass burned, dry basis).

### 5.3.2 Particulate organic speciation

The particulate organic compounds identified in this study included homologous series of n-alkanes, n-alkenes, n-alkanols and n-alkanoic acids, terpenoid constituents, carbonyls, phenolic components, PAHs and oxy-PAHs, carbohydrates and polyols. The OC-normalised concentrations of all these constituents can be found in appendix (Table A3, supplementary material A3), as supplementary material. The chromatographically resolved organics were dominated by diterpenoids, acids, sugars, phenols and aliphatic compounds in both size fractions (Figure 5.3). A significant fraction of other compounds,

whose individual quantification was not possible to make with exactitude, has a large contribution to the OC of smoke particles.

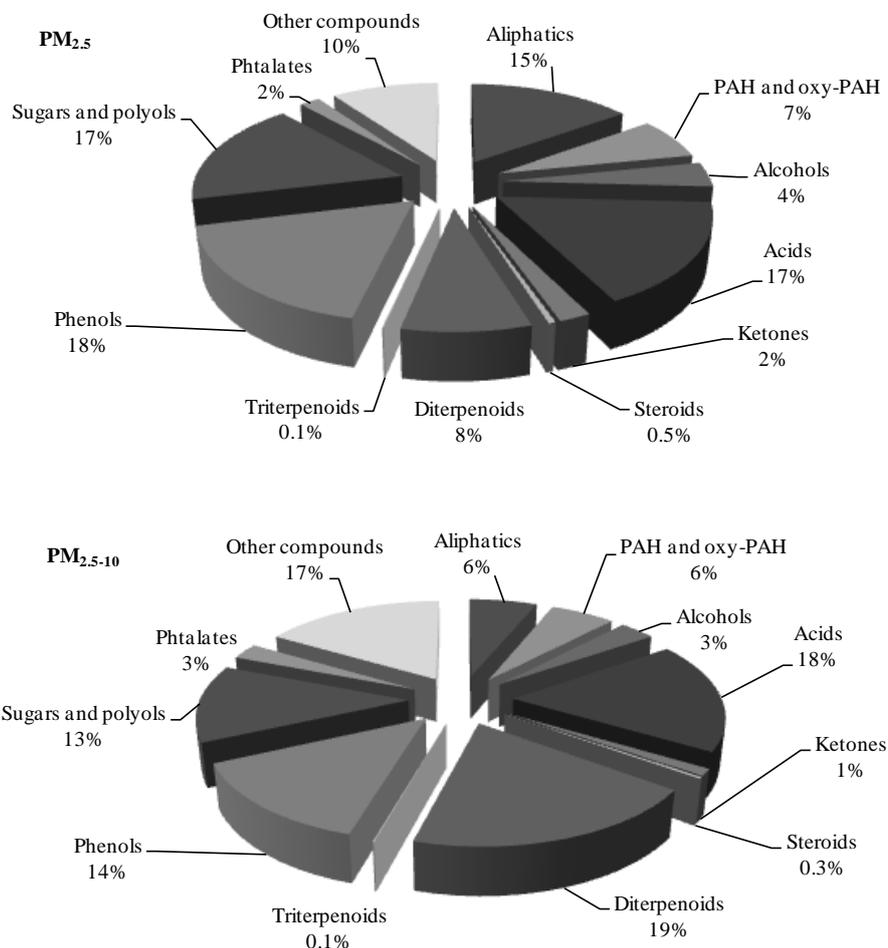


Figure 5.3 Percentage distribution of chromatographically resolved organic compounds detected in smoke samples.

### 5.3.2.1 Homologous compounds series

Aliphatic compounds comprised the *n*-alkane homologous series from C<sub>15</sub> to C<sub>34</sub> with an odd to even carbon predominance (Table 5.2). The homologues with the highest concentrations (C<sub>max</sub>) were C<sub>29</sub> and C<sub>31</sub>, for fine and coarse particles, respectively. Oros and Simoneit (2001) assigned this distribution to the contribution from epicuticular waxes. The *n*-alkenes homologous series ranged from C<sub>14</sub> to C<sub>30</sub>, with C<sub>max</sub> at C<sub>20</sub>, C<sub>24</sub> or C<sub>26</sub>, for both size fractions, and showed an even-to-odd carbon number predominance. The *n*-

alkenes derived mostly from the thermal dehydration of *n*-alkanols and in smaller amounts, from the oxidation of *n*-alkanes during incomplete combustion (Oros and Simoneit, 2001).

A series of *n*-alkanols ranging from C<sub>10</sub> to C<sub>30</sub> were present in the smoke samples with C<sub>max</sub> usually at C<sub>22</sub> and C<sub>24</sub> for both size fractions, showing an even to odd carbon predominance. The *n*-alkanols from C<sub>20</sub> to C<sub>30</sub> are major compounds of epicuticular waxes (Oros and Simoneit, 2001). The same distribution was observed by Vicente et al. (2011) in smoke samples from a wildfire in a mixed forest of central Portugal. The OC-normalised mass concentrations in PM<sub>2.5</sub> and PM<sub>2.5-10</sub> were, on average, 3.0±2.2 and 8.0±8.1 mg g<sup>-1</sup> OC, respectively. The *n*-alkanol content in coarse particles was, on average, more than 2 times higher than that in fine particles. Plant debris or partially burned foliage ash may have contributed towards the quantification of higher levels in PM<sub>2.5-10</sub>. Moreover, ground-level wind circulation generated by the heat released from the fire contributes to the emission of coarse particles, which rise into the atmosphere, transporting organic soil constituents and vegetation ashes. Some *n*-alkanols may also become associated with PM<sub>2.5-10</sub> by volatilisation from fine particles followed by condensation onto coarse particles.

The *n*-alka-2-one homologous series ranged from C<sub>7</sub> to C<sub>18</sub>, presenting higher OC-normalised concentrations in coarse than in fine particles. The most abundant homologue was C<sub>16</sub>, for both size fractions. It has been proposed that straight chain ketones are mainly derived from the partial combustion of aliphatic precursors (Oros and Simoneit, 2001).

A series of *n*-alkanoic acids were identified in the smoke of all samples, ranging from C<sub>8</sub> to C<sub>24</sub>. In PM<sub>2.5</sub> and PM<sub>2.5-10</sub>, the carbon number peaked usually at C<sub>16</sub>, followed by C<sub>22</sub> and C<sub>24</sub>. The long-chain *n*-alkanoic acids are basic units of plants fats, oils and phospholipids (Oros and Simoneit, 2001), while short-chain homologs (<C<sub>16</sub>) have been mainly reported as minor constituents of fungi and insects (Otto et al. 2006, and references therein). Uncompleted burned or volatilised biological material may have contributed to the detections of this type of compounds. The alkenoic acid presenting the highest concentration in all smoke samples was *cis*-9-octadecenoic acid (oleic acid), followed by 9,12-octadecadienoic acid (linoleic acid) and *cis*-9-hexadecenoic acid (palmitoleic acid). These constituents are important components of plant oils (Lísa et al., 2009). The concentration of unsaturated fatty acids in coarse particles was, on average, more than 2 times higher than that in fine particles. A series of *n*-di-acids, ranging from C<sub>3</sub> to C<sub>16</sub>, were

also present in the smoke samples. The pentanedioic acid (glutaric acid) was the most abundant constituent in coarse particles, ranging from 0.0071 to 11 mg g<sup>-1</sup> OC. The second most abundant was butanedioic acid (succinic acid). In the fine fraction, butanedioic acid and nonanedioic were the dominant di-acids, with concentrations ranging from 0.038 to 0.54 mg g<sup>-1</sup> OC and from 0.014 to 1.0 mg g<sup>-1</sup> OC, respectively. A series of *n*-alkanedioic acids ranging from C<sub>4</sub> to C<sub>10</sub> have also been detected in particle emissions from domestic biomass burning (Fine et al., 2004), combustion of foliar fuels (Hays et al., 2002), and prescribed fires in pine forests (Lee et al., 2005). Stephanou and Stratigakis (1993) described butanedioic acid as a product from the photo-oxidation of cyclic olefins. Nonanedioic acid has been proposed as a photo-oxidation product of oleic and linoleic acids (Oros and Simoneit, 2001; Stephanou and Stratigakis, 1993). Thus, as these low vapour pressure particle-phase dicarboxylic acids can also be secondarily formed, their utilisation as tracers of biomass burning emissions is questionable.

It should be noted that a significant fraction of other acids, whose individual quantification was not possible, has a large contribution to the OC of smoke particles. Those other acids are mostly dicarboxylic acids and related compounds, hydroxy-acids (e.g. malic acid) and oxo-acids (e.g. levulinic acid). In fact, in various cases, the individual quantification of some acids could not be done due to co-elution problems. In other cases, typical mass fragments of dicarboxylic, hydroxyl- or oxo-acids enabled the classification of each type of acid, but did not allow the accurate identification of individual compounds. The quantification of these compounds was based on the application of chromatographic relative response factors determined for constituents of similar chemical structure and retention time.

The utility of most of the homologous compounds as atmospheric tracers of biomass burning is doubtful because, generally, they are ubiquitous constituents of many aerosol types. Thus, the application of OC or PM normalised concentrations of these compounds in source apportionment methodologies should be done in conjugation with specific biomarkers.

Table 5.2 OC-normalised concentrations of homologous compound series in smoke samples from different wildfires (mg g<sup>-1</sup>OC).

	Ovar		Montemor-o-Velho		Nariz (Aveiro)		Cinfães (Viseu)		Farejinha (Castro Daire)		Quinta da Póvoa (Sabugal)		Pendilhe (V. N. de Paiva)	
	PM <sub>2.5</sub>	PM <sub>2.5-10</sub>	PM <sub>2.5</sub>	PM <sub>2.5-10</sub>	PM <sub>2.5</sub>	PM <sub>2.5-10</sub>	PM <sub>2.5</sub>	PM <sub>2.5-10</sub> <sup>a</sup>	PM <sub>2.5</sub>	PM <sub>2.5-10</sub>	PM <sub>2.5</sub>	PM <sub>2.5-10</sub>	PM <sub>2.5</sub>	PM <sub>2.5-10</sub>
Alkanes														
<i>n</i> -Alkanes	19	5.5	5.1	5.1	0.35	1.9	0.046		0.68	4.4	0.0045	2.7	0.53	4.9
Branched alkanes	0.20	1.6	0.058	1.2	0.21	0.69	1.9		0.56	14.9	0.27	4.0	0.30	8.8
Other alkanes	0.72	0.48	0.15	0.35	0.066	0.17	0.42		0.15	3.0	0.0078	1.4	0.16	2.7
$\sum$ Alkanes	20	7.6	5.4	6.6	0.63	2.7	2.3		1.4	22	0.28	8.1	0.99	16
C <sub>max</sub>	C <sub>29</sub>	C <sub>21</sub>	C <sub>31</sub>	C <sub>21</sub>	C <sub>21</sub> , C <sub>22</sub>	C <sub>21</sub>			C <sub>29</sub> , C <sub>31</sub>	C <sub>17</sub> , C <sub>31</sub>	C <sub>33</sub>	C <sub>34</sub>	C <sub>21</sub>	C <sub>24</sub> , C <sub>25</sub> , C <sub>34</sub>
Alkenes														
<i>n</i> -Alkenes	11	4.7	2.8	2.2	0.78	2.3	0.82		0.61	2.2	0.023	1.0	1.8	2.4
Branched alkenes	1.7	1.2	0.056	0.21	0.071	0.12	0.042		0.031	0.13	0.00025	0.32	0.033	0.060
Other alkenes	7.9	4.0	2.2	1.5	0.43	+	0.70		0.45	1.7	0.0098	0.43	1.3	3.9
$\sum$ Alkenes	21	9.9	5.0	3.9	1.3	2.45	1.6		1.1	4.1	0.033	1.8	3.2	6.3
C <sub>max</sub>	C <sub>20</sub>		C <sub>24</sub>	C <sub>20</sub> , C <sub>21</sub>	C <sub>20</sub>	C <sub>20</sub> , C <sub>21</sub>	C <sub>24</sub> , C <sub>26</sub>		C <sub>24</sub> , C <sub>26</sub>	C <sub>20</sub>	C <sub>21</sub> , C <sub>24</sub>	C <sub>21</sub> , C <sub>30</sub>	C <sub>24</sub> , C <sub>26</sub>	C <sub>21</sub>
Alka-2-one														
<i>n</i> -alka-2-one	1.5	1.9	0.19	0.93	0.29	0.26	0.055		0.076	0.35	0.0032	0.044	0.11	0.23
Other alka-2-ones	2.5	3.5	0.96	1.2	0.46	0.45	0.26		0.22	0.42	+	+	0.44	0.95
$\sum$ Alka-2-ones	3.9	5.4	1.2	2.1	0.75	0.71	0.32		0.30	0.77	0.0032	0.044	0.55	1.2
C <sub>max</sub>	C <sub>16</sub>		C <sub>16</sub>		C <sub>16</sub>		C <sub>16</sub>		C <sub>16</sub>		C <sub>16</sub>			C <sub>16</sub>
Alkanols														
<i>n</i> -Alkanol	5.4	8.1	1.3	5.3	4.8	3.2	2.7		1.4	6.2	0.19	1.3	5.6	24
C <sub>max</sub>	C <sub>22</sub> , C <sub>24</sub>	C <sub>22</sub>	C <sub>22</sub>	C <sub>22</sub> , C <sub>24</sub>	C <sub>20</sub> , C <sub>24</sub>	C <sub>18</sub>	C <sub>30</sub>		C <sub>22</sub> , C <sub>24</sub>	C <sub>24</sub> , C <sub>26</sub>	C <sub>22</sub> , C <sub>24</sub> , C <sub>26</sub>	C <sub>12</sub> , C <sub>14</sub>	C <sub>22</sub> , C <sub>24</sub>	C <sub>24</sub> , C <sub>26</sub>

Chapter 5

<i>n</i> -Acids													
<i>n</i> -Alkanoic acids	16	18	14	32	14	35	8.6	6.0	32	0.91	11	15	86
$C_{\max}$	C <sub>14</sub> , C <sub>16</sub> , C <sub>24</sub>	C <sub>16</sub>	C <sub>16</sub>	C <sub>22</sub> , C <sub>24</sub>	C <sub>24</sub>	C <sub>22</sub> , C <sub>24</sub>	C <sub>14</sub> , C <sub>16</sub>	C <sub>16</sub> , C <sub>24</sub>	C <sub>16</sub>	C <sub>16</sub> , C <sub>24</sub>	C <sub>16</sub> , C <sub>18</sub>		C <sub>16</sub>
<i>n</i> -Di-acids	0.79	0.50	2.2	3.5	0.76	0.28	1.9	0.37	3.9	0.42	10	1.3	14
$C_{\max}$	C <sub>4</sub> , C <sub>9</sub>	C <sub>8</sub>	C <sub>4</sub> , C <sub>7</sub> , C <sub>9</sub>	C <sub>4</sub>	C <sub>4</sub> , C <sub>5</sub>	C <sub>8</sub> , C <sub>9</sub>	C <sub>4</sub> , C <sub>9</sub>	C <sub>4</sub> , C <sub>7</sub> , C <sub>9</sub>	C <sub>4</sub> , C <sub>5</sub>	C <sub>4</sub> , C <sub>5</sub>		C <sub>4</sub>	C <sub>4</sub> , C <sub>5</sub>
$\sum$ <i>n</i> -Acids	17	18	17	35	14	35	10	6.3	36	1.3	21	16	100

<sup>a</sup> damaged sample; (+) not detected

### 5.3.2.2 Polycyclic aromatic hydrocarbons

More than twenty PAHs and oxy-PAHs were quantified in the smoke samples. This group of compounds is formed as a result of incomplete combustion or thermal decomposition (pyrolysis) of the organic material.

The sum of OC-normalised concentrations of all identified PAH compounds for coarse and fine smoke particles are presented in Figure 5.4. Retene was the dominant polyaromatic hydrocarbon found in both particle sizes. It is the fully aromatised thermal alteration product of the resin acids present in conifer woods (Ramdahl, 1983). Major degradation processes of abietane diterpenes, which are particularly abundant among cone-bearing seed plants, are defunctionalisation (cleavage of acid and hydroxyl groups), demethylation, methylation and the progressive aromatisation via loss of hydrogen. The degradation of several abietane precursors yields the same degradation products with the ultimate generation of the triaromatic retene (Otto et al., 2006). The highest concentration ratios for this compound were obtained in fine particles collected from the plumes of wildfires occurring at Nariz and Montemor-o-Velho (2.9 and 6.2 mg g<sup>-1</sup> OC, respectively). In coarse particles the highest concentrations were achieved in samples coming from wildfires at Montemor-o-Velho and Quinta da Póvoa, Sabugal (15 and 13 mg g<sup>-1</sup> OC, respectively). The concentration ratios are consistent with the dominant vegetation (pine trees) burned during these forest fires. Freshly emitted PAHs are associated mainly to fine aerosol and they can later become incorporated in coarse particles by volatilisation from fine particles followed by condensation onto coarse particles (Bi et al., 2005). Soil dust resuspension by convective updraft may also contribute to the persistence of PAHs in coarse fraction (Reid et al., 2005). The values obtained in this study were higher than those reported by Otto et al. (2006) for a wildfire in Canada, Hays et al. (2005) for the open burning of agricultural biomass and by Vicente et al. (2011) for smoke samples collected from a wildfire in Penedono, central Portugal. Besides retene, phenanthrene and naphthalene were the most abundant PAH in PM<sub>2.5-10</sub>, while phenanthrene, fluoranthene and pyrene dominate in PM<sub>2.5</sub>. Benzo[a]anthracene, benzo[a]pyrene and benzo[e]pyrene, components with high mutagenic and genotoxic potential (Kaden et al., 1979; White, 2002), were also present, but as minor constituents. The dominant oxy-PAH in fine and coarse particles was 9-fluorenone (0.13 and 0.19 mg g<sup>-1</sup> OC, respectively). The speciation

of a significant fraction of PAHs in both size ranges was not possible, representing, average estimated values of 2.9 and 5.4 mg g<sup>-1</sup> OC, respectively.

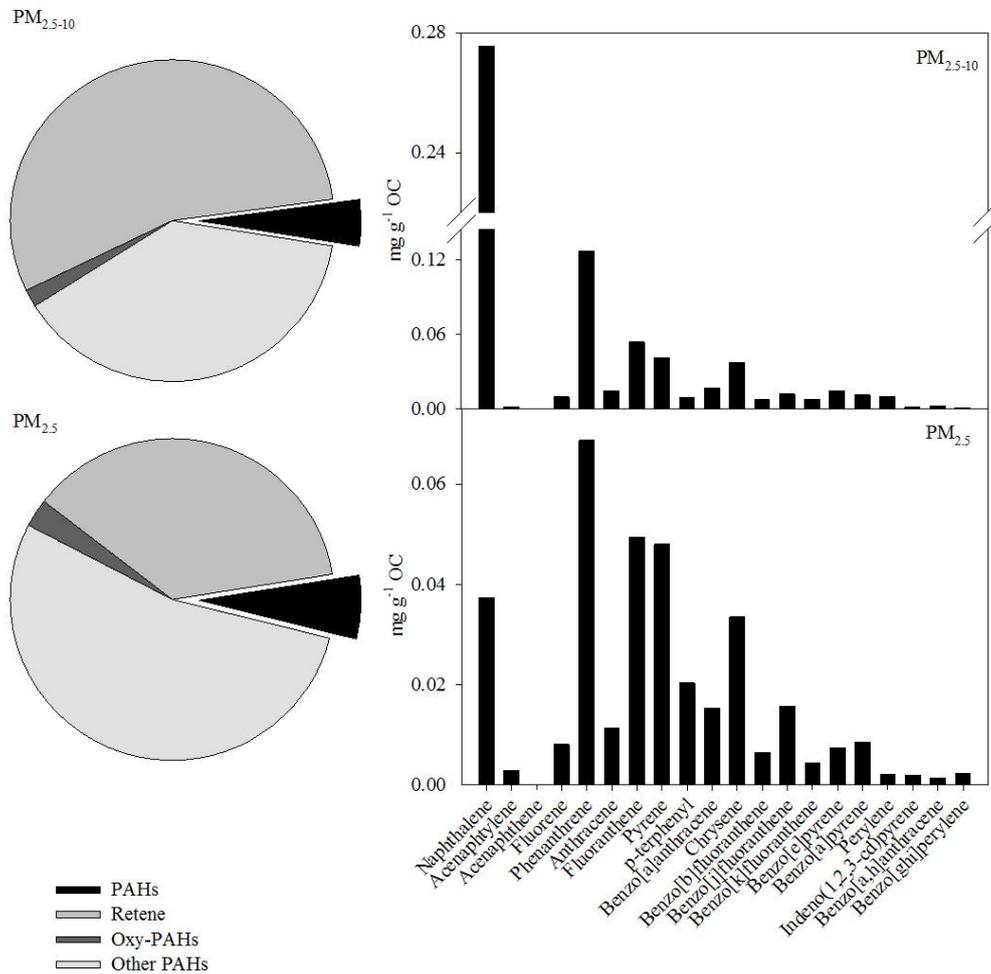


Figure 5.4 OC-normalised concentrations of all PAHs detected in coarse and fine particles.

PAHs in biomass burning emissions are generally of the same as from other anthropogenic combustion emissions. Diagnostic ratios are used as a tool for assessing the possible contribution of different sources (Alves, 2008). The Flu/(Flu+Pyr), IcdP/(BghiP+IcdP), BFs/BghiP, BeP/(BeP+BaP), BghiP/BaP and Phe/(Phe+Ant) ratios are listed and compared with those of other sources in Table 5.3. The Flu/(Flu+Pyr) ratios obtained in this study were in agreement with those reported in the literature for biomass burning sources (Alves et al., 2010a; Oros and Simoneit, 2001; Vicente et al., 2011). The BghiP/BaP ratio was in the ranges 0.33-0.58 and 0.18-0.57 for fine and coarse particles, respectively. These values are lower than those reported by Rogge et al. (1993) for

vehicular emissions or those obtained by Oliveira et al. (2011) in a road tunnel in Lisbon. The BF<sub>s</sub>/BghiP ratios varied from 2.7 to 33, i.e. were much higher than those reported by Rogge et al. (1993) or Oliveira et al. (2011) for traffic emissions. These values are also similar to those obtained by Vicente et al. (2011) for other fire in Portugal. Thus, the BghiP/BaP and BF<sub>s</sub>/BghiP ratios may also be used as a source assignment tool to separate vehicular and biomass burning emissions. The Phe/(Phe+Ant) ratio is in agreement with those reported for similar biomass burning sources (Vicente et al., 2011; Alves et al., 2011), but also falls in the range obtained for vehicular emissions (Rogge et al., 1993) and in a road tunnel in Lisbon, Portugal (Oliveira et al., 2011). Thus, while some isomeric or non-isomeric PAH ratios seem to be a reasonable source assignment tool to separate vehicular and biomass burning emissions, other ratios, however, show overlapping and cannot be used for apportionment purposes. The substantial intrasource variability and intersource similarity of PAH ratios contribute to the caveats associated with their use (Galarneau, 2008). Moreover, while isomers can be compared because their volatilities and resulting particle/gas distributions are supposed to be similar, this is not true for species of different volatilities. Thus, non-isomeric PAH ratios are expected to be more affected by temperature variations between the emission point and downwind ambient, rendering source identification more difficult.

Table 5.3 Comparison of PAH diagnostic ratios for different sources.

		Flu/(Flu+Pyr)	IcdP/(BghiP+IcdP)	BFs/BghiP	BeP/(BeP+BaP)	BghiP/BaP	Phe/(Phe+Ant)
This study	PM <sub>2.5</sub>	0.25-0.70	0.15-0.49	3.2-12	0.22-0.58	0.33-0.58	0.83-1.0
	PM <sub>2.5-10</sub>	0.51-0.68	0.24-0.57	2.7-33	0.32-0.82	0.18-0.57	0.84-0.96
Vicente et al. (2011)	PM <sub>2.5</sub>	0.53-0.86		3.5	0.10-0.50	0.64	0.74-0.89
	PM <sub>2.5-10</sub>	0.48-0.93		5.2-9.5	0.15-0.47	0.23-0.31	0.77-0.86
Alves et al. (2010a)	PM <sub>2.5</sub>	0.60±0.07	0.75 ± 0.06	4.0±2.2		0.86 ± 0.44	0.75±0.07
	PM <sub>2.5-10</sub>	0.56±0.25	0.74 ± 0.01	5.2±0.54		0.82 ± 0.13	0.85±0.02
Wang et al. (2009)	Broad-leaf trees	0.50-0.55					0.70-0.83
	Shrub	0.54-0.60					0.71-0.76
Hays et al. (2005)	Cereal straw	0.50-0.53	0.52-1.0				
Oros and Simoneit (2001)	Temperate climate conifer	0.16-0.88					0.67-0.99
Cheng et al. (2004)	Coal	0.48	0.43	1.9	0.91		
Rogge et al. (1993)	Noncatalyst-equipped vehicles	0.61		0.58		3.3	0.77
	Catalyst-equipped vehicles	0.44		1.2		2.5	0.89
	Heavy-duty diesel trucks	0.37		3.5		1.2	0.88
Oliveira et al. (2011)	Tunnel in Lisbon, Portugal	0.54	0.31	0.79	0.52	0.82	0.83

Flu – Fluoranthene; Pyr – Pyrene; IcdP – Indeno[1,2,3-cd]pyrene; BghiP – Benzo[ghi]perylene; BFs – Benzo[fluoranthenes]; BeP – Benzo[e]pyrene; BaP – Benzo[a]pyrene; Phe – Phenanthrene; Ant – Anthracene

### 5.3.2.3 Phenolic compounds

Methoxyphenols have been identified as major lignin thermal degradation products and as semi-volatile components of smoke particles (Hawthorne et al., 1988). These products can be classified, as regards to their origin, into three general groups: coumaryl, vanillyl (or guaiacyl) and syringyl compounds (Simoneit, 2002; Simoneit et al., 1993). In this study, many phenolic compounds were detected (Table 5.4). Vanillin was the most abundant in both size fractions with values ranging from 0.95 to 91 mg g<sup>-1</sup> OC. The lowest value of vanillin was obtained in samples collected for wildfires occurring in Ovar and Cinfães, where hardwood specie, mainly *Eucalyptus globulus*, has been combusted. This is in accordance with the fact that softwood smoke contains 4-hydroxy-3-methoxyphenyl (guaiacyl or vanillyl) compounds, whereas hardwood burning contributes mainly to the formation of 4-hydroxy-3,5-dimethoxyphenyl (syringyl) constituents because of a different lignin structure (Hawthorne et al., 1988). Other significant phenolic compounds in smoke samples were catechol, vanillic and benzoic acids. They were detected at mass concentrations in the ranges 0.037-14, 0.26-9.2 and 0.13-7.2 mg g<sup>-1</sup> OC, respectively. Vanillin, catechol, resorcinol, pyrogallol and hidroquinone showed an inverse relationship with MCE values, suggesting that their formation is promoted under smouldering conditions.

### 5.3.2.4 Other biomarkers

Steroids, terpenoids, including resin acids, and saccharides were the main biomarkers detected in the smoke samples. The most abundant sterol was  $\beta$ -Sitosterol, followed by stigmast-4-en-3-one, in fine particles, and stigmasta-3,5-dien-7-one, in coarse particles. The emission of these compounds decreased with increasing MCE values, indicating that they are preferentially formed during smouldering combustion. The concentration ratios of  $\beta$ -Sitosterol was very similar for wildfires with predominance of hardwood or softwood, so it cannot be regarded as a candidate to separate different types of biomass combustion emissions in source apportionment studies. Sitosterol is one of the most common steroids in the waxes of higher plants. Stigmasta-2,5-dien-7-one and stigmast-4-en-3-one are products from the thermal alteration of sterol precursors (Otto and Simpson, 2005).

Table 5.4 OC-normalised concentrations of the most abundant phenolic compounds in the wildfire emissions ( $\text{mg g}^{-1}\text{OC}$ ).

		Vanillin	Vanillic acid	3- Vanillylpropanol	Syringic acid	Catechol	Benzoic acid	4- methylcatechol	Resorcinol	Pyrogallol	Hydroquinone
Ovar	PM <sub>2.5</sub>	4.1	0.87	0.38	0.52	2.2	3.1	1.4	1.7	0.23	0.90
	PM <sub>2.5-10</sub>	1.3	2.8	0.076	0.25	2.2	4.6	0.64	0.47	+	0.097
Montemor-o-Velho	PM <sub>2.5</sub>	12	5.7	3.6	1.1	3.3	1.1	1.2	0.80	1.8	1.8
	PM <sub>2.5-10</sub>	41	1.4	1.4	0.92	6.7	2.34	3.4	1.2	0.75	0.67
Nariz (Aveiro)	PM <sub>2.5</sub>	5.1	2.0	0.61	0.20	1.2	0.78	0.30	0.18	0.20	0.83
	PM <sub>2.5-10</sub>	14	1.6	0.59	0.28	4.8	1.8	1.4	0.14	+	0.37
Cinfães (Viseu)	PM <sub>2.5</sub>	3.6	2.7	0.54	1.2	0.083	0.55	0.18	0.15	+	0.11
	PM <sub>2.5-10</sub> (a)										
Farejinha (Castro Daire)	PM <sub>2.5</sub>	1.1	0.93	0.14	0.76	0.12	0.23	0.19	0.12	0.14	0.12
	PM <sub>2.5-10</sub>	7.5	3.7	0.18	1.9	2.5	2.9	0.97	0.68	+	0.079
Quinta da Póvoa (Sabugal)	PM <sub>2.5</sub>	0.72	0.69	0.90	0.045	0.44	0.18	0.53	0.12	0.51	0.17
	PM <sub>2.5-10</sub>	12	1.4	2.7	0.096	4.5	1.7	2.9	+	+	+
Pendilhe (V. N. de Paiva)	PM <sub>2.5</sub>	5.0	1.5	0.20	0.61	1.4	0.82	1.0	0.37	0.55	0.35
	PM <sub>2.5-10</sub>	9.1	9.2	+	2.6	2.2	7.2	+	1.4	+	+

(a) damaged sample; (+) not detected

The triterpenoids with higher concentrations, in both size fractions, were urs-12-en-one ( $\alpha$ -amyrenone) and lupeol. These triterpenic compounds of the ursane and lupane type, respectively, only occur in angiosperms and are characteristic biomarkers of this vegetation (Otto and Simpson, 2005). Resin acids such as abietic, dehydroabietic, pimaric and isopimaric acids, were detected as significant components in smoke samples from wildfires with predominance of softwood (*Pinus pinaster*), whilst in the plumes of other wildfires (Ovar and Cinfães) for which the fuel was mainly hardwood, emissions were much lower. Abietic, isopimaric and pimaric acids are primary natural products occurring as such in resins, while dehydroabietic acid is an oxidative alteration product from other resin acids (Simoneit et al., 2000). Among resin acids, the major compound was dehydroabietic acid with values ranging between 0.619 and 120 mg g<sup>-1</sup> OC. As observed for other organic compounds, emissions of resin acids increased with decreasing MCE values.

The isoprenoid ketone 6,10,14-trimethylpentadecan-2-one was detected at concentrations of 0.0094-1.3 mg g<sup>-1</sup> OC and 0.030-1.2 mg g<sup>-1</sup> OC in fine and coarse particles, respectively. This ketone may be formed by both bacterial and photochemical oxidation of phytol, the isoprenoidyl side chain of chlorophyll (Oros et al., 2002). The utilisation of this isoprenoid branched ketone as biogenic tracer is questionable, due to the fact that it may be also a partially oxidised product derived from car exhausts (Simoneit, 1986).

The monosaccharide derivatives from the breakdown of cellulose and hemicelluloses, such as levoglucosan, mannosan and galactosan (Simoneit et al., 1999), were the major organic components of smoke particles from biomass burning. Levoglucosan was the most abundant anhydrosugar in both size fractions, followed by mannosan and galactosan (Table 5.5). The levoglucosan/OC ratios obtained in this study were higher than those reported by Vicente et al. (2011) and Alves et al. (2011a) in smoke samples from two other wildfires in central Portugal. It has been proposed that levoglucosan/OC ratios is probably more dependent on the fuel component burned (branches, leaves, wood, etc.) instead of the combustion efficiency (Sullivan et al., 2008). Although a weak inverse relationship between these compounds and MCE values was obtained, it is possible to observe a decreasing trend in anhydrosugar emissions with increasing combustion efficiency values. The levoglucosan/PM<sub>2.5</sub> ratios obtained in this

study varied between 0.8 and 11 mg g<sup>-1</sup>. Higher values, up to 31 mg g<sup>-1</sup>, were reported for residential wood combustion (Gonçalves et al., 2011).

Levoglucosan, mannosan, and galactosan were emitted in varying ratios, probably due to differences in the relative content of cellulose and hemicellulose in diverse biofuels (Engling et al., 2006). The levoglucosan-to-mannosan (L/M) and the levoglucosan-to-mannosan plus galactosan [L/(M+G)] ratios can be used to distinguish different biomass burning sources (Fabbri et al., 2009). In this study, the L/M and L/(M+G) ratios ranged from 1.5 to 6.0 and from 0.91 to 5.5, respectively (Table 5.5). The ratios were, on average, about two times higher than those obtained for other wildfires (Alves et al., 2011a; Vicente et al., 2011). The values agree more closely with those reported by Fine et al. (2004) and Engling et al. (2006) for softwood smoke.

Other saccharidic compounds identified in smoke samples include monosaccharides (ribose, erythrose, galactose and glucose), disaccharides (sucrose and maltose) and polyols (glycerol, erythritol, xylitol, arabitol, ribitol, mannitol, sorbitol and inositol) (Table A3, supplementary material A3). Medeiros and Simoneit (2008) identified some of these sugar compounds in smoke samples from controlled burnings of green vegetation from temperate climate forests. Alves et al. (2011a) and Vicente et al. (2011) also detected sugar compounds in smoke particles from wildfires in Portugal. Erythrose was the most abundant sugar compound with concentrations in the ranges 0.46-6.7 and 0.69-17 mg g<sup>-1</sup> OC, in fine and coarse particles, respectively. Ribose was the second most abundant compound, presenting concentrations between 0.041 and 1.2 mg g<sup>-1</sup> OC in fine particles. Values from 0.064 to 2.5 mg ribose g<sup>-1</sup> OC were quantified for coarse particles. Polyols and disaccharides were present in minor amounts in both size fractions. Graham et al. (2002) suggested that many of these sugars can be primary products of combustion, formed whether through direct volatilisation from plant matter or as products of the breakdown of polysaccharides. Some of the sugars may also be formed by hydrolysis of the corresponding anhydrosugars under the acidic atmospheric conditions created by biomass burning.

Table 5.5 OC-normalised concentrations and ratios between anhydrosugars in the emissions from the various wildfires, and comparison with values reported in the literature ( $\text{mg g}^{-1}\text{OC}$ ).

		Galactosan	Mannosan	Levoglucozan	L/M	L/(M+G)	
Ovar	PM <sub>2,5</sub>	0.89	1.2	3.7	3.2	1.8	
	PM <sub>2,5-10</sub>	0.52	0.69	3.2	4.6	2.7	
Montemor-o-Velho	PM <sub>2,5</sub>	9.3	15	22	1.5	0.91	
	PM <sub>2,5-10</sub>	8.0	15	28	1.8	1.2	
Nariz (Aveiro)	PM <sub>2,5</sub>	1.6	2.5	4.2	1.7	1.0	
	PM <sub>2,5-10</sub>	2.0	2.9	5.3	1.8	1.1	
This study Cinfães (Viseu)	PM <sub>2,5</sub>	1.8	2.4	7.2	3.0	1.7	
	PM <sub>2,5-10</sub> (a)						
Farejinha (Castro Daire)	PM <sub>2,5</sub>	0.69	0.39	2.3	6.0	2.2	
	PM <sub>2,5-10</sub>		2.8	16	5.5	5.5	
Quinta da Póvoa (Sabugal)	PM <sub>2,5</sub>	1.2	2.1	3.5	1.6	1.0	
	PM <sub>2,5-10</sub>	2.7	5.1	17	3.3	2.2	
Pendilhe (V. N. de Paiva)	PM <sub>2,5</sub>	1.6	2.4	9.4	4.0	2.4	
	PM <sub>2,5-10</sub>	5.9	8.1	32	4.0	2.3	
Vicente et al. (2011)	PM <sub>2,5</sub>	6.21±2.02	8.40±2.77	13.9±5.12	1.66	0.85	
	PM <sub>2,5-10</sub>	4.23±1.68	5.65±1.93	9.65±4.17			
Alves et al. (2011)	PM <sub>2,5</sub>	5.2	7.59	13.4	1.77	1.05	
	PM <sub>2,5-10</sub>	2.8	5.65	12.8			
Gonçalves et al. (2011)	fireplace	hot start	82.9	66.9	383	5.73	2.56
		cold start	80.5	206	289	1.40	1.01
	woodstove	hot start	58.5	60.9	236	3.88	1.98
		cold start	92.9	73.7	278	3.77	1.67
Puxbaum et al. (2007)	residential wood combustion			43-523			
Engling et al. (2006)	softwood				2.6-5	2.4-2.8	
	hardwood				13.8-52.3	4.5-39.3	
Fine et al. (2004)	fireplace	softwood			3.9-6.7	2.9-5.0	
		hardwood			13.24	10.4-14.2	

(a) damaged sample; (+) not detected

## 5.4 Conclusions

Trace gases and aerosol particle emissions from seven wildfires occurring in central Portugal in summer 2009 were determined. The most abundant oxygenated volatile organic compound was acetaldehyde with EFs between 1.03 and 1.87 g kg<sup>-1</sup> followed by formaldehyde with values in the range 0.090-0.96 g kg<sup>-1</sup>. Propionaldehyde was the scarcest, varying from 0.032 to 0.17 g kg<sup>-1</sup> (dry basis). The OC-normalised concentrations of all three aldehydes increased with decreasing MCE values. The OC concentrations were in the ranges 0.15-3.8 mg m<sup>-3</sup> for fine and 0.017-1.0 mg m<sup>-3</sup> for coarse particles. On average, the OC concentrations were 25 times higher in PM<sub>2.5</sub> than in PM<sub>2.5-10</sub>. The carbonaceous fraction of smoke samples from all wildfires was clearly dominated by organic carbon. The main organic components were phenolic compounds and their alteration products, especially guaiacyl type, acids, carbohydrates, in particular levoglucosan, diterpenoids, mostly dehydroabietic acid, and aliphatics. Some of the identified compounds can be used as tracer compounds for the presence of biomass burning smoke and to distinguish different biofuel types. Some overlap between PAH ratios obtained for wildfire smoke and those reported for vehicular emissions restrict the use of this tool in source assignment studies. Retene, a biomarker of softwood smoke, was the dominant aromatic hydrocarbon in samples. The levoglucosan-to-mannosan (L/M) and the levoglucosan-to-mannosan plus galactosan [L/(M+G)] ratios were in agreement with those obtained for emissions of softwood burning.

This study contributed to obtain detailed databases reflecting the distinct burning conditions and fuel types, thus helping to bridge the gap that exists concerning speciated emission profiles for wildfires. The database obtained is potentially useful to determine the contribution of wildfires to the atmospheric aerosol burden in the Mediterranean region, through source apportionment models.

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## **CHAPTER 6**



## Chapter 6. Emission factors and detailed chemical composition of smoke particles from the 2010 wildfire season in central Portugal

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### Abstract

This paper complements the information previously published (Atmospheric Environment 45, 641-649) on gaseous and particulate emissions from wildfires in Portugal for summer 2009, in an attempt at obtaining more extensive, complete and representative databases on emission factors and detailed chemical characterisation of smoke particles. Here, emission factors for carbon oxides (CO<sub>2</sub> and CO), total hydrocarbons (THC), fine (PM<sub>2.5</sub>) and coarse (PM<sub>2.5-10</sub>) particles obtained for fires occurring in Portugal in summer 2010 are presented. The carbonaceous content (OC and EC), water-soluble ions, elements and organic composition of smoke particles were, respectively, analysed by a thermal-optical transmission technique, ion chromatography, instrumental neutron activation analysis (INAA) and gas chromatography-mass spectrometry (GC-MS). The particle mass concentrations were in the ranges 0.69-25 mg m<sup>-3</sup> for PM<sub>2.5</sub> and 0.048-3.1 mg m<sup>-3</sup> for PM<sub>2.5-10</sub>. PM<sub>2.5</sub> particles represented 91±5.7% of the PM<sub>10</sub> mass. The OC/EC ratios in fine and coarse particles ranged from 2.5 to 205 and from 1.7 to 328, respectively. The water-soluble ions represented, on average, 3.9% and 2.8% of PM<sub>2.5</sub> and PM<sub>2.5-10</sub> mass, respectively. In general, the dominant ions in the water extracts were Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, Cl<sup>-</sup> and NO<sub>3</sub><sup>-</sup> for the PM<sub>2.5</sub> fraction, and K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup> for the PM<sub>2.5-10</sub> fraction. The K<sup>+</sup>/EC and K<sup>+</sup>/OC ratios obtained in this study were, on average, 0.22±0.23 and 0.011±0.014 for PM<sub>2.5</sub> and 0.83±1.0 and 0.024±0.023 for PM<sub>2.5-10</sub> particles, respectively.

The  $K^+$ /levoglucosan ratio was, on average, 2.0 for  $PM_{2.5}$  and 3.1 for  $PM_{2.5-10}$  particles. Levoglucosan was detected at mass fractions of 1.6-8.7  $mg\ g^{-1}$  OC in  $PM_{2.5}$  and 2.7-56  $mg\ g^{-1}$  OC in  $PM_{2.5-10}$ . The dominant elements detected in the smoke samples were Na, Br, Cr, Fe, K, Rb and Zn. The most representative organic constituents in the smoke samples were acids, alcohols, terpenoid-type compounds, sugars and phenols, in both size fractions.

Keywords: wildfires, trace gases, emission factors, organic compounds, water-soluble ions, trace elements.

## 6.1 Introduction

In Portugal and other southern European countries, the decline in population density in inland regions, due to ageing and emigration to coastal areas, coupled with the abandonment of farming practices have led to shrub encroachment and forest expansion. This, combined with the expected climatic trends of less rainfall and hotter weather, will increase the risk of ignition, resulting in larger and more prevalent fires in the near future (Moreira et al., 2010). The increase in the frequency and intensity of wildfires will result in far more intense emissions of trace gases and particles into the atmosphere. These emissions play an important role on atmospheric chemistry and biogeochemical cycles (Anttila et al., 2008; Crutzen and Andreae, 1990; Schimel and Baker, 2002; Yokelson et al., 2007), with a strong effect at the regional scale (Alves et al., 2011a,b; Balasubramanian and See, 2006; Jaffe et al., 2008; Liu et al., 2009) and also at sites thousands of kilometres far from the source (Duck et al., 2007; Jaffe et al., 2004; Lewis et al., 2007; Petzold et al., 2007; Witham and Manning, 2007).

The biomass burning particles degrade visibility, are efficient cloud condensation nuclei (CCN) and can influence the formation of precipitation (Petters et al., 2009; Reid et al., 2005; Reutter et al., 2009; Rose et al., 2010; Rosenfeld et al., 2008; Spracklen et al., 2007). The major fraction of smoke samples is organic matter, representing frequently more than 90% of the total mass (Alves et al., 2010b; Gonçalves et al., 2011; Yamasoe et al., 2000), whereas inorganic constituents constitute a small fraction of the smoke aerosol mass (Alves et al., 2010b; Alves et al., 2011b). However, the combustion-related trace elements and water-soluble ions are biogeochemically active species, being therefore important in global nutrient cycling (Baker, 2006; Furutani et al., 2010).

The study of wildfire emissions by our group in Portugal started in 2009. The main objective of this study is to further characterise the gas- and particulate-phase emissions for several wildfires occurring in central Portugal. These results provide important information to reduce the lack of detailed biomass burning emission profiles for Southern Europe and to lower uncertainty estimates of fire contribution to ambient aerosol levels when applying receptor models.

Emission factors of trace gases and particles for some wildland biomass burning events have been obtained (Alves et al., 2011b) and the detailed organic speciation has

been carried out for some particulate matter samples (Alves et al., 2011a; Vicente et al., 2011, 2012). In order to obtain more representative and extensive databases, the study was continued in 2010 with the collection of new smoke samples during large wildfire events affecting different forest types in districts of the central region of Portugal. In 2010, approximately 100 000 ha of burnt areas resulted from wildfires of large dimension ( $\geq 100$  ha) (DGRF, 2011). According to the National Forestry Authority, the districts most affected by wildfires were those situated in central Portugal. Although 2010 did not represent the year with the highest burnt area in the last decade, the hectares of Portuguese forest consumed by wildfires accounted for about 60% of the total area reported for Southern Europe (Schmuck et al., 2011).

## 6.2 Methodology

### 6.2.1 Sampling details

In summer 2010, smoke samples were collected from twelve wildfires occurring over central Portugal (Figure 6.1 and Table 6.1). New fire occurrences were followed through the National Authority for Civil Protection of Portugal web-site ([www.prociv.pt](http://www.prociv.pt)). When a wildfire broke out at a distance lower than 200 km from the University of Aveiro, the study team moved in a small four wheel drive truck with power generator and sampling/measuring equipment, to the vicinity of the fire. After arriving at a place near the wildfire front, the fire brigades were contacted asking for permission and advice on a safe place for sampling. Ground-level aerosol sampling, especially during the flaming phase of a wildfire, constitutes a very dangerous and daunting task, both because flames spread very easily and fast, and due to frequent vertical lifting of the plumes.

In order to collect sequentially coarse ( $PM_{2.5-10}$ ) and fine ( $PM_{2.5}$ ) smoke particles from the plumes, a tripod high volume sampler (TE-5200, Tisch Environmental Inc.) operating at a flow of  $1.13 \text{ m}^3 \text{ min}^{-1}$  was used. With the objective of eliminating organic contaminants, all the quartz fibre filters were previously pre-baked at  $500^\circ\text{C}$  for 6 hours. A total of twenty eight  $PM_{2.5}/PM_{2.5-10}$  sample pairs were obtained. Tedlar bags previously flushed with  $N_2$  were used to collect gas samples, in parallel and simultaneously with aerosol sampling. A detailed description of the sampling procedure can be found elsewhere (Alves et al., 2011a).

Background measurements, in air masses not impacted by the wildfire plume, were also carried out during the campaigns and the corresponding values were subtracted from those obtained in the smoke samples. Sampling was performed at 1.5 m above ground, downwind from the burning area, at distances of 10-100 m from the fires. Taking advantage of the uneven relief, the equipment was generally installed on the top of slopes, under a favourable wind direction, in order to obtain samples from the core of the smoke plume. Most samples contain a mixture of smouldering and flaming emissions. Considering the unpredictable behaviour of wildfires and the very tricky field conditions, the plumes cannot be sampled always at the same distance from the fire. Thus, smoke samples at different levels of dilution and ambient temperatures are obtained, likely contributing to different gas-particle interconversion processes, which affect short-lived compounds.

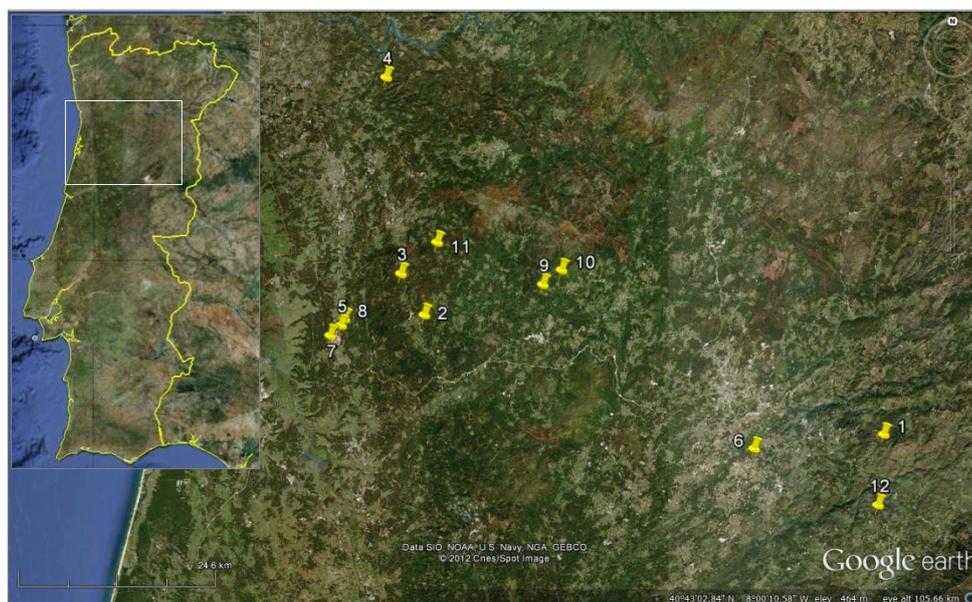


Figure 6.1 Location of wildfires during summer 2010 in central Portugal for which smoke samples were collected (numbers correspond to the location of wildfires indicated in table 6.1).

Table 6.1 Wildfire episodes over central Portugal in summer 2010, where smoke samples were obtained.

n°	Sampling locations	Latitude/Longitude	Altitude (a.s.l.)	Date	Major types of biomass	n° of samples (PM <sub>2.5</sub> +PM <sub>2.5-10</sub> )	MCE
1	Mangualde	40°35'42"N/7°41'17"W	384	25 Jul.	<i>Cytisus striatus</i> / <i>Pteridium aquilinum</i>	2	0.65
2	Sever do Vouga	40°43'45"N/8°21'45"W	231	26 Jul.	<i>Pteridium aquilinum</i> / <i>Agrostis</i> / <i>Grasses</i> /Mixed forest ( <i>Pinus pinaster</i> and <i>Eucalyptus globulus</i> )	4	0.78-0.79
3	Dornelas (Sever do Vouga)	40°46'31"N/8°23'49"W	227	26 Jul.	<i>Eucalyptus globulus</i> / <i>Furze</i> / <i>Grasses</i>	2	0.87
4	Rebordelo (Santa Maria da Feira)	40°59'47"N/8°25'14"W	244	27 Jul.	Vineyards/ <i>Castanea sativa</i> / <i>Grasses</i> / <i>Eucalyptus globulus</i> / <i>Pterospartum tridentatum</i> / <i>Gorse</i> / <i>Ericaceae</i>	6	0.83-0.94
5	Albergaria-a-Velha	40°43'01"N/8°29'07"W	173	3 Aug.	<i>Eucalyptus globulus</i> / <i>Acacia saligna</i> / <i>Pteridium aquilinum</i>	4	0.85
6	Fontanheiras (Nelas)	40°34'46"N/7°52'41"W	334	3 Aug.	<i>Pinus pinaster</i>	2	0.81
7	Albergaria-a-Velha	40°42'19"N/8°30'04"W	133	4 Aug.	Piles of Pine and Eucalyptus logs, sawdust, wood chips and giant roots	4	0.91-0.92
8	Albergaria-a-Velha	40°43'27"N/ 8°28'49"W	162	6 Aug.	<i>Pinus pinaster</i> / <i>Eucalyptus globulus</i> / <i>Bush</i> / <i>Ericaceae</i> and forest litter	2	0.89
9	Chão do Coto (Oliveira de Frades)	40°45'49"N/8°11'19"W	275	6 Aug.	<i>Eucalyptus globulus</i> and bush	2	0.79
10	Sobrosa (São Pedro do Sul)	40°46'48"N/8°09'40"W	282	7 Aug.	<i>Pinus pinaster</i> / <i>Pteridium aquilinum</i> / <i>Ericaceae</i> / <i>Cistus</i>	12	0.76-0.84
11	Junqueira (Vale de Cambra)	40°48'38"N/8°20'38"W	246	11 Aug.	<i>Pinus pinaster</i> / <i>Eucalyptus globulus</i> / <i>Cytisus striatus</i>	4	0.87-0.91
12	Vila Nova de Tazem (Gouveia)	40°30'56"N/7°41'48"W	374	13 Aug.	<i>Pinus pinaster</i> and pinea/ <i>Cytisus striatus</i> / <i>Acacia saligna</i> / <i>Quercus suber</i> / <i>Rubus fruticosus</i> / <i>Arbutus unedo</i> / <i>Olea europaea</i> L.	12	0.64-0.84

## 6.2.2 Analytical methodologies

The particulate matter mass concentrations were obtained by gravimetry on a microbalance. Filter weights were determined from the average of three measurements, with a precision of 0.1 mg, before and after sampling, after 24 h of stabilisation in a clean humidity-controlled box.

The total volatile hydrocarbons (THC) and carbon oxides (CO<sub>2</sub> and CO) in the Tedlar bags were measured using automatic analysers with flame ionisation (Dyna-FID, model SE-310) and non-dispersive infrared (Environment, MIR 9000) detectors, respectively. Each gas analyser was calibrated with appropriate gases, on zero and span points. The hydrocarbon concentrations were determined in methane-equivalents.

The carbonaceous content (OC and EC) of smoke particles was analysed by a thermal-optical transmission technique (Alves et al., 2011a). Two 9 mm diameter filter punches, in the case of the PM<sub>2.5</sub> samples, or strips representing 1/20 of the total area, in the case of PM<sub>2.5-10</sub> samples, were used in each analytical run. For each filter, two or three replicate analyses were done. The carbon carbonate analysis was also made in the aerosol samples through the release of CO<sub>2</sub>, and measurement by NDIR, when a punch of filter was acidified with orthophosphoric acid in a free CO<sub>2</sub> gas stream.

The analysis of major water soluble inorganic ions was carried out by ion chromatography in liquid phase. The contents of small parts of the filters were extracted ultrasonically with ultra-pure Milli-Q water. Cations (Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup> and Ca<sup>2+</sup>) were analysed using a CS12 (4 mm) column with a CG12 on guard. A Dionex CMMS III suppressor was used in these analyses. For anions (Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup>), an AS4 (4 mm) column with a AG4 guard column were used coupled to a Dionex AMMS II suppressor. For the final results blank values were taken into account.

The trace element speciation was performed by Instrumental Neutron Activation Analysis (INAA). Filter punches were rolled up, put into aluminium foils and irradiated in the Portuguese Research Reactor, at a thermal neutron flux of  $1.03 \times 10^{13} \text{ cm}^{-2} \text{ s}^{-1}$ , during 5 h. After the irradiation, filters were removed from the aluminium foils and transferred to polyethylene containers. For each irradiated sample, two gamma spectra were measured during 5-7 hours with a hyperpure germanium detector: one spectrum 2-3 days after irradiation and the other one after 4 weeks. A comparator – Al-0.1% Au alloy disk with a

thickness of 125  $\mu\text{m}$  and a diameter of 0.5 cm – was co-irradiated with the samples for the application of the  $k_0$ -INAA methodology (Almeida et al., 2012).

In earlier studies it has been demonstrated that the type of compound can change considerably due to the combustion regime and biofuel characteristics (Alves et al., 2011a; Engling et al., 2006; Vicente et al., 2011). Taking into account this and the fact that the organic speciation by gas chromatography-mass spectrometry (GC-MS) is very expensive and time consuming, a selection of some smoke samples was made, trying to represent different combustion efficiencies and types of ecosystems burned. From the total, six particulate matter samples were extracted and analysed for organic compounds.

Approximately  $\frac{3}{4}$  of each filter was extracted by refluxing 300 mL of dichloromethane (Fisher Scientific) for 24 h. After filtration, the pieces of filter were extracted 3 times with methanol (Fisher Scientific) (75 mL for 10 min, each extraction) in an ultrasonic bath. All the 4 extracts were then combined, vacuum concentrated and dried under a gentle nitrogen stream. The total organic extracts were subsequently separated into five different organic fractions by flash chromatography with silica gel (230-400 mesh, 60 Å Merck Grade 9385) and various solvents of increasing polarity (Alves et al., 2011a). After elution, the different fractions were vacuum concentrated and evaporated by ultra-pure nitrogen stream. Before injection, the compounds with hydroxylic and carboxylic groups were converted into the corresponding trimethylsilyl derivatives by addition of *N,O*-bis(trimethylsilyl)-trifluoroacetamide (BSTFA): trimethylchlorosilane (TMCS) 99:1 (Supelco). Finally, the extracts were analysed by GC-MS. The GC-MS calibration was based on a total of approximately 200 standards in different concentration ranges with relative response factors determined individually for the majority of compounds. Compound identification was made by comparison with authentic standards, matching against Wiley and NIST spectral libraries and analysis of fragmentation patterns. For those compounds with no authentic standards available, relative response factors were obtained as an average from the overall homologous series or from compounds of similar chemical structure and retention time. Standards and samples were both co-injected with two internal standards: tetracosane-d50 (Sigma-Aldrich), 1-chlorohexadecane or 1-chlorododecane (Merck). Taking into account that in previous studies (Alves et al., 2010a; Alves et al., 2011a; Vicente et al., 2012), oxygenated compounds were found to represent an overwhelming proportion of the chromatographic resolved organics, in this work only

alcohols, acids and saccharides were analysed and quantified. The internal standards were added to the vials in prescribed amounts to eliminate the error caused by variation in injection volume. The detailed description of the analytical procedure for the determination of organic compounds can be found in Alves et al. (2011a).

## 6.3 Results and Discussion

### 6.3.1 Emission factors of particulate matter and gaseous compounds

The smoke particle concentrations were in the ranges  $0.69\text{-}25\text{ mg m}^{-3}$  for  $\text{PM}_{2.5}$  and  $0.048\text{-}3.1\text{ mg m}^{-3}$  for  $\text{PM}_{2.5-10}$ . Fine particles represented  $91\pm 5.7\%$  of the  $\text{PM}_{10}$  mass. On average,  $51\pm 12\%$  of the  $\text{PM}_{2.5}$  emissions consisted of organic carbon, whilst the OC mass fraction obtained for coarse particles was  $32\pm 15\%$ . Carbonates represented between 0.0055 and 4.0% (on average,  $0.79\pm 0.82\%$ ) of  $\text{PM}_{2.5-10}$ , whereas its contribution to the mass of fine particles was negligible.

The calculation and detailed discussion of emission factors (EF) for the 2010 wildfires campaign, with an emphasis on volatile organic compounds can be found in Evtuygina et al. (2013). The modified combustion efficiency (MCE) ranged between 0.64 and 0.94. The  $\text{PM}_{2.5}$  and  $\text{PM}_{10}$  emission factors ranged between 4.3 and  $68\text{ g kg}^{-1}$  and from 4.6 to  $72\text{ g kg}^{-1}$  (dry basis), respectively. The OC/EC ratios in the fine (2.5-205) and coarse (1.7-328) particle fractions obtained in smoke samples reflect the much higher proportion of OC in relation to EC, typical of biomass burning emissions. Ratios of the same order were previously obtained for smoke samples from wildfires in Portugal during summer 2009 (Alves et al., 2010b; Vicente et al., 2012). The  $\text{EF}_{\text{OC}}$ , on average, were  $8.9\pm 8.2\text{ g kg}^{-1}$  and  $9.4\pm 8.4\text{ g kg}^{-1}$  (dry basis) for fine and coarse particles, respectively. The EC emission factors obtained for  $\text{PM}_{2.5}$  and  $\text{PM}_{10}$  ranged between 0.0087 and  $2.3\text{ g kg}^{-1}$  (dry basis). The CO emission factors varied from 67 to  $383\text{ g kg}^{-1}$  biomass (dry basis) burned. The  $\text{EF}_{\text{CO}}$  of this study are similar to those ( $231\pm 117\text{ g kg}^{-1}$ , dry basis) obtained for the 2009 wildfires in Portugal (Alves et al., 2011b). The  $\text{EF}_{\text{CO}_2}$  ranged between 1029 and  $1655\text{ g kg}^{-1}$  biomass (dry basis) burned. In 2009, the  $\text{CO}_2$  emission factors ranged from about 1000 to  $1700\text{ g kg}^{-1}$  (dry basis), depending on the combustion efficiency (Alves et al., 2011b). The carbon oxide emission values of this study are in accordance with those reported by Andreae and Merlet (2001) for savannah and grassland ( $65\pm 20$  for CO and  $1613\pm 95\text{ g kg}^{-1}$ , dry matter

burned, for CO<sub>2</sub>), tropical forest (65±95 for CO and 1580±90 g kg<sup>-1</sup>, dry matter burned, for CO<sub>2</sub>) and extratropical forest (107±37 for CO and 1569±131 g kg, dry matter burned, for CO<sub>2</sub>). The total hydrocarbon EFs in the gas phase reached a maximum of 28 g kg<sup>-1</sup> (dry basis), averaging 7.1±8.8 g kg<sup>-1</sup>. The CO and THC emission factors showed an inverse relationship with MCE values, while CO<sub>2</sub> emission factors were much higher for the flaming phase.

### 6.3.2 Mass balance

Taking into account the gravimetric data and all identified aerosol species, it is possible to reconstruct the particulate matter mass. Determination of organic matter (OM) from bulk OC measurements is needed for mass closure. A factor  $f$  is used to convert OC to OM to account for unmeasured elements, such as O, H, etc. (McMeeking et al., 2009). The  $f$  value used in this study was 1.5 (Reid et al., 2005). The water soluble ions accounted for in the mass balance were the NH<sub>4</sub><sup>+</sup>, Mg<sup>2+</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup>, for both size fractions. Carbonates were also added in the coarse fraction. Some trace elements were assumed to exist as oxides (e.g. Fe<sub>2</sub>O<sub>3</sub>, CaO, ZnO). Thus, the equation used to reconstruct the PM mass was as follows:

$$PM = \sum \text{ionic species} + \sum \text{metal oxides} + \sum \text{other elements} + EC + OC \times f$$

(1)

The calculated sum of analysed aerosol constituents corresponds, on average, to 87% of the weighted PM<sub>2.5</sub> mass. In the case of PM<sub>2.5-10</sub>, the reconstructed mass represents, on average, a fraction of 80% (Table 6.2). The unaccounted mass may be due to adsorbed water (Temesi et al., 2001; Harrison et al., 2003) and major elements (e.g. Al and Si) that have not been analysed.

Table 6.2 Ranges and averages (in brackets) for the various constituents for the mass balance calculation.

	<b>PM<sub>2.5</sub></b>	<b>PM<sub>2.5-10</sub></b>
<b>(mg m<sup>-3</sup>)</b>		
<b>PM</b>	0.69-25 (5.9)	0.10-3.1 (0.97)
<b>(mg g<sup>-1</sup> PM)</b>		
<b>OC</b>	234-656 (506)	115-612 (328)
<b>EC</b>	2.0-169 (24)	1.0-138 (16)
<b>NH<sub>4</sub><sup>+</sup></b>	0.79-36 (7.5)	0.34-2.4 (1.0)
<b>Mg<sup>2+</sup></b>	0.10-3.8 (1.4)	1.2-8.7 (2.6)
<b>Cl<sup>-</sup></b>	4.0-25 (8.5)	1.2-17 (3.6)
<b>NO<sub>3</sub><sup>-</sup></b>	0.46-13 (3.5)	0.12-3.6 (0.44)
<b>SO<sub>4</sub><sup>2-</sup></b>	0.97-8.0 (4.3)	2.8-15 (7.8)
<b>CO<sub>3</sub><sup>2-</sup></b>	-	0.055-40 (7.6)
<b>(mg g<sup>-1</sup> PM)</b>		
<b>CaO</b>	1.4-17 (6.5)	1.9-29 (11)
<b>Fe<sub>2</sub>O<sub>3</sub></b>	0.55-23 (6.2)	5.5-40 (15)
<b>ZnO</b>	0.12-1.8 (0.36)	0.069-112 (14)
<b>(mg g<sup>-1</sup> PM) (values multiplied by 100)</b>		
<b>As</b>	2.3 (0.084)	0.045-16 (4.1)
<b>Br</b>	1.3-15 (0.86)	0.94-18 (7.2)
<b>Ce</b>	0.082-2.8 (0.40)	2.2-20 (5.2)
<b>Co</b>	0.086-1.5 (0.32)	0.040-3.6 (0.78)
<b>Cr</b>	1.1-208 (30)	1.2-114 (22)
<b>Cs</b>	0.013-1.4 (0.18)	0.091-2.7 (0.60)
<b>Eu</b>	0.0014-0.25 (0.036)	0.042-0.064 (0.0039)
<b>Hf</b>	0.0039-2.8 (0.39)	0.0087-5.6 (1.1)
<b>K</b>	56-3345 (705)	216-15726 (3507)
<b>La</b>	0.051-1.1 (0.13)	0.033-6.9 (1.7)
<b>Na</b>	1.9-5666 (562)	30-29883-(6821)
<b>Nd</b>	0.94 (0.034)	4.5-31 (3.5)
<b>Rb</b>	0.34-16 (4.6)	1.2-108 (16)
<b>Sb</b>	0.080-2.2 (0.42)	1.5-16 (2.4)
<b>Sc</b>	0.058-0.70 (0.16)	0.15-0.84 (0.40)
<b>Sm</b>	0.010-0.31 (0.028)	0.29-0.50 (0.072)
<b>Ta</b>	0.031-0.25 (0.048)	0.012-0.86 (0.18)
<b>Tb</b>	0.028-0.18 (0.015)	0.065-0.74 (0.087)
<b>Th</b>	0.032-2.1 (0.34)	0.050-2.9 (0.46)
<b>U</b>	0.00027-0.40 (0.034)	0.040-11 (2.2)
<b>Yb</b>	0.014-0.067 (0.0069)	0.16-2.3 (0.39)
<b>% of PM</b>	62-103 (87)	61-99 (80)

(-) not analysed for fine fraction

### 6.3.3 Inorganic composition of smoke particles

#### 6.3.3.1 Water-soluble ions

The water-soluble inorganic ions represented, on average, 3.9% and 2.8% of  $PM_{2.5}$  and  $PM_{2.5-10}$  mass, respectively. In general, the highest mass concentration values were registered for  $Na^+$ ,  $NH_4^+$ ,  $Cl^-$  and  $NO_3^-$  for the fine fraction, and  $K^+$ ,  $Mg^{2+}$ ,  $Ca^{2+}$  and  $SO_4^{2-}$  for the coarse fraction (the concentration values can be found in appendix (Table A4.1, supplementary material A4). It should be noted, however, that the mass concentrations of fine particles are much higher than those of coarse particles, which means that the absolute masses of the latter ions are higher in  $PM_{2.5}$ . The relative abundances of inorganic species depend on fuel type, combustion conditions and soil characteristics (Chen et al., 2010). The highest levels of  $NH_4^+$ ,  $Ca^{2+}$  and  $Cl^-$  were registered in smoke particles from Vila Nova de Tazem, Chão do Coto and Albergaria-a-Velha. On average, the mass fractions were  $13 \mu g mg^{-1} PM_{2.5}$  and  $1.2 \mu g mg^{-1} PM_{2.5-10}$  for  $NH_4^+$ ,  $12 \mu g mg^{-1} PM_{2.5}$  and  $21 \mu g mg^{-1} PM_{2.5-10}$  for  $Ca^{2+}$  and  $19 \mu g mg^{-1} PM_{2.5}$  and  $15 \mu g mg^{-1} PM_{2.5-10}$  for  $Cl^-$ . A significant correlation between chloride and ammonium was obtained for fine particles ( $r=0.69$ ) (Table 6.3). The emission of  $NH_4Cl$  is enhanced during the flaming phase (Alves et al., 2010b; Liu et al., 2000). Since ammonium chloride is very soluble in water, it is expected to be active as cloud condensation nuclei (Alves et al., 2007), although due to its high volatility in summertime this effect should be minor.

Potassium concentrations reached values up to  $14 \mu g mg^{-1} PM_{2.5}$  and  $22 \mu g mg^{-1} PM_{2.5-10}$  with mean values of  $4.5 \pm 4.4 \mu g mg^{-1}$  and  $5.9 \pm 4.9 \mu g mg^{-1}$ , for the fine and coarse particles, respectively. These concentrations represent 0.6% of the total particle mass for both size fractions. However, taking into account that the mass of  $PM_{2.5}$  accounted for 91% of  $PM_{10}$ , on average, 89% of the total potassium ( $PM_{2.5}+PM_{2.5-10}$ ) is present in  $PM_{2.5}$  particles. Potassium in fine and coarse particles stand for, respectively, 0.46% and 0.04% of the  $PM_{10}$  mass. At temperatures  $> 760 \text{ }^\circ C$ , which are common in wildfires, potassium is volatilised (Neary et al., 1999) and subsequently condensed forming fine particles. Alves et al. (2011a,b) reported low potassium concentrations for wildfires in central Portugal during summer 2009 and in emissions from prescribed burnings. Chen et al. (2007) obtained, under laboratory conditions, potassium mass fractions less than 1% for some shrubs, grasses and softwood and higher than 20% for sagebrush. The  $K^+/EC$  and  $K^+/OC$  ratios

have been proposed to separate emission sources. Andreae (1983) reported  $K^+/EC$  ratio ranging between 0.21-0.46 for biomass burning and 0.025-0.09 for fossil fuel combustion. The potassium-to-elemental carbon and the potassium-to-organic carbon ratios obtained in this study were, on average,  $0.22\pm 0.23$  and  $0.011\pm 0.014$  for  $PM_{2.5}$  and  $0.83\pm 1.0$  and  $0.024\pm 0.023$  for  $PM_{2.5-10}$ , respectively. These values were in agreement with those obtained by Satsangi et al. (2012) for a suburban site with contribution of biomass burning ( $K^+/EC = 0.39\pm 0.25$  and  $K^+/OC = 0.08\pm 0.02$ ). Potassium showed a significant correlation with magnesium and chloride for fine particles ( $r=0.70$  and  $r=0.51$ , respectively) and with sulphates for coarse particles ( $r=0.46$ ).

$Mg^{2+}$  relative concentrations were higher in the coarse fraction (on average,  $2.6\pm 2.3 \mu g mg^{-1} PM_{2.5-10}$ ) than in fine fraction (on average,  $1.4\pm 1.0 \mu g mg^{-1} PM_{2.5}$ ), suggesting soil dust entrainment into the smoke aerosols. This ion showed a significant correlation with calcium and sulphates in fine ( $r=0.82$  for calcium and  $r=0.72$  for sulphates) and coarse ( $r=0.57$  for calcium and sulphates) particles. Also,  $Mg^{2+}$  and  $SO_4^{2-}$  presented a positive correlation with MCE, in both size fractions, indicating enhanced emissions during flaming combustion conditions. Sulphate presented mass fractions ranging from 0.97 to  $8.0 \mu g mg^{-1} PM_{2.5}$  and 0.75 to  $14 \mu g mg^{-1} PM_{2.5-10}$ . The presence of  $SO_4^{2-}$  in smoke aerosols can be related to the adsorption of  $SO_2$  on black carbon particles through a catalytic effect in the gas-to-particle conversion of  $SO_2$  to sulphate (Alves et al., 2011b; Novakov et al., 1974).

Chloride, with mass fractions up to  $25 \mu g mg^{-1}$  and  $17 \mu g mg^{-1}$  in fine and coarse particles, respectively, showed a positive correlation with MCE values. Particles from a more complete combustion (higher MCE values) are characterised by a higher content of inorganic constituents, such as potassium, sulphur and chlorine, and lower organic emissions. Chloride also presents a significant correlation with potassium, especially in fine particles ( $r=0.51$  for fine and  $r=0.30$  for coarse particles), suggesting the presence of this compound in the form of KCl. The mass ratio of chloride to elemental carbon was, on average,  $0.70\pm 0.83$  and  $0.60\pm 1.2$  for fine and coarse particles, respectively. Alves et al. (2010b) obtained an average  $Cl/EC$  ratio of 0.24 for smoke samples ( $PM_{2.5}$  and  $PM_{2.5-10}$ ) from prescribed fires in a Mediterranean shrubland, while Ferek et al. (1998) reported a ratio of 0.44 for forest, cerrado and pasture fires in Brazil. Andreae et al. (1998) obtained a much higher ratio (2.39) for savannah fires.

$Na^+$  was below the detection limit for the majority of the particulate matter samples

of the fine fraction and for all coarse fraction samples, this fact can be related to the high variability of  $\text{Na}^+$  concentrations in the blank filters. Nitrate showed average mass fractions of  $3.5 \pm 2.9 \mu\text{g mg}^{-1}$  for fine and  $0.39 \pm 0.99 \mu\text{g mg}^{-1}$  for coarse particles. This compound is produced in reactions involving the NO emitted during burning conditions.

Table 6.3 Pearson correlation coefficients obtained for ion particle mass concentrations.

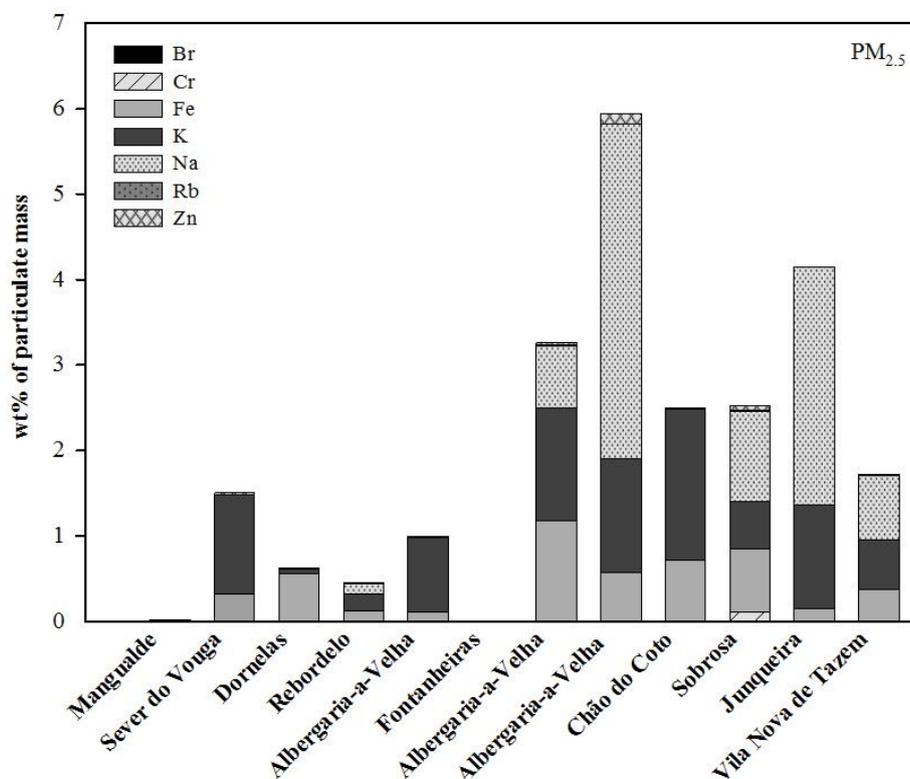
	$\text{Na}^+$	$\text{NH}_4^+$	$\text{K}^+$	$\text{Mg}^{2+}$	$\text{Ca}^{2+}$	$\text{Cl}^-$	$\text{NO}_3^-$	$\text{SO}_4^{2-}$
<b>PM<sub>2.5</sub></b>								
$\text{Na}^+$	1.00							
$\text{NH}_4^+$	-0.08	1.00						
$\text{K}^+$	0.26	-0.03	1.00					
$\text{Mg}^{2+}$	0.13	-0.30	<b>0.70</b>	1.00				
$\text{Ca}^{2+}$	-0.07	<b>-0.44</b>	0.46	<b>0.82</b>	1.00			
$\text{Cl}^-$	0.08	<b>0.69</b>	0.51	0.19	-0.10	1.00		
$\text{NO}_3^-$	-0.10	-0.36	0.11	0.41	0.48	-0.32	1.00	
$\text{SO}_4^{2-}$	0.07	-0.18	0.50	<b>0.72</b>	<b>0.57</b>	0.22	<b>0.63</b>	1.00
<b>PM<sub>2.5-10</sub></b>								
$\text{NH}_4^+$		1.00						
$\text{K}^+$		0.04	1.00					
$\text{Mg}^{2+}$		0.26	0.20	1.00				
$\text{Ca}^{2+}$		-0.13	0.34	<b>0.57</b>	1.00			
$\text{Cl}^-$		0.03	0.30	0.47	0.10	1.00		
$\text{NO}_3^-$		<b>-0.24</b>	-0.18	0.05	0.08	0.18	1.00	
$\text{SO}_4^{2-}$		0.13	0.46	<b>0.57</b>	0.41	0.31	0.26	1.00

### 6.3.3.2 Elements

More than 20 elements were detected in smoke samples from the wildfires of this study, representing, on average, 2.0% and 12% of the  $\text{PM}_{2.5}$  and  $\text{PM}_{2.5-10}$  mass, respectively (concentration values can be found in appendix, Table A4.2, supplementary material A4). These percentages are in accordance with those obtained for smoke samples from experimental fires in a Mediterranean shrubland (Alves et al., 2010b) and from wildfires in central Portugal in 2009 (Alves et al., 2011b).

The dominant elements were Na, K, Fe, Br, Cr, Rb and Zn (Figure 6.2). Alves et al. (2010b) reported high concentrations for iron in smoke samples from experimental fires in a Mediterranean shrubland. Gaudichet et al. (1995) also obtained higher concentrations for iron in savannah biomass burning aerosols, attributing its origin to soil remobilisation

processes during the fires and to terrigenous particles deposited on vegetation. The concentration of iron in coarse fraction was, on average, around 2 times higher than in fine fraction. Zinc is an essential vegetal constituent of various enzyme systems for energy production, protein synthesis, and growth regulation (Simoglou and Dordas, 2006). Andreae et al. (1998) also refers the presence of zinc in the cytoplasm of plants, which may be associated with the combustion of vegetation. Bromine is present in almost all plant tissues (Bisessar and McIlveen, 1992). Chromium is a natural component of earth crust. In this study, the concentration of Cr was, on average, about 2 times higher in  $PM_{2.5}$  than in  $PM_{2.5-10}$ , suggesting contributions of other sources besides a crustal origin. In trace amounts, chromium is essential for the growth processes in plants (Khan et al., 2010; and references therein). Potassium has an important role in the growth process and in the plant metabolism (Leigh and Wyn Jones, 1984). Rubidium is present in soil and contributes to the metabolism of plants, probably due to the similarities with K (Drobner and Tyler, 1998). The high Na mass fractions observed in  $PM_{2.5-10}$ , together with negligible  $Na^+$  concentrations, suggest a probable entrainment of soil dust with insoluble forms of sodium.



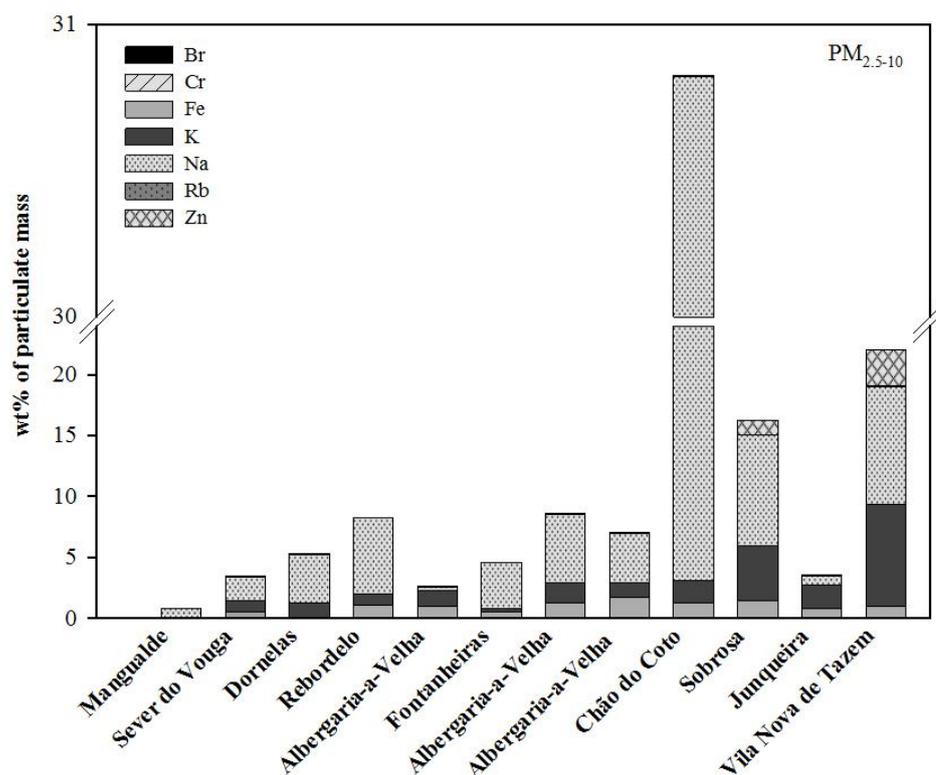


Figure 6.2 Major trace elements found in fine (PM<sub>2.5</sub>) and coarse (PM<sub>2.5-10</sub>) particles sampled in the plumes from various wildfires occurring in summer 2010.

### 6.3.4 Organic composition of smoke particles

In this study, the characterisation of dominant polar organic compounds in smoke particles was made. The OC-normalised concentrations of all these constituents can be found in appendix (Table A4.3, supplementary material A4). The chromatographically resolved organics were dominated by acids, phenols and their alteration products, diterpenoids and anhydrosugars, in both size fractions (Figure 6.3).

*n*-Alkanol homologous series from C<sub>10</sub> to C<sub>30</sub> were present in the smoke samples, showing an even to odd carbon predominance, with C<sub>max</sub> usually at C<sub>22</sub>, C<sub>24</sub>, C<sub>26</sub>, C<sub>28</sub> and C<sub>30</sub>, for both size fractions. The same distribution was observed by Vicente et al. (2011, 2012) in smoke samples (PM<sub>2.5</sub> and PM<sub>2.5-10</sub>) from wildfires in central Portugal in summer 2009. The OC-normalised mass concentrations in PM<sub>2.5</sub> and PM<sub>2.5-10</sub> were, on average, 1.9±0.93 and 3.8±2.4 mg g<sup>-1</sup> OC, respectively.

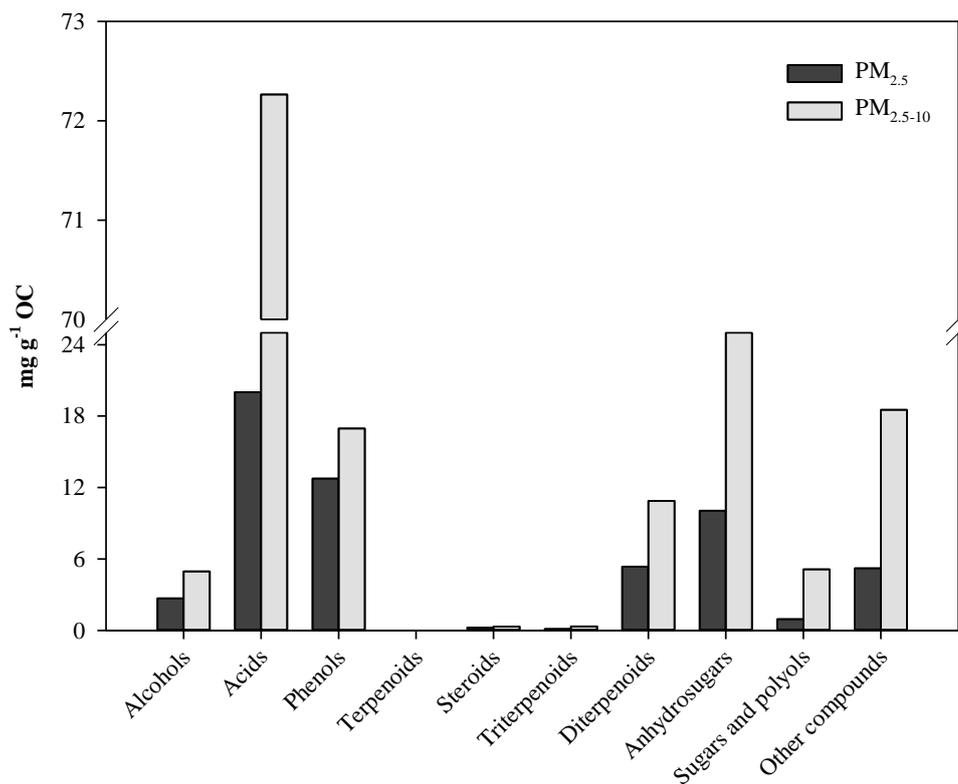


Figure 6.3 Average OC-normalised mass concentration of organic compounds detected in smoke samples collected from several wildfires in summer 2010.

*n*-Alkanoic acids ranging from C<sub>6</sub> to C<sub>30</sub> were also found in the smoke samples. In PM<sub>2.5</sub>, the carbon number peaked usually at C<sub>24</sub>, followed by C<sub>22</sub> and C<sub>16</sub>, whereas in coarse particles C<sub>16</sub>, followed by C<sub>18</sub> and C<sub>24</sub> were the most abundant. The OC-normalised mass concentrations in PM<sub>2.5</sub> and PM<sub>2.5-10</sub> were, on average, 12±8.8 and 50±41 mg g<sup>-1</sup> OC, respectively. The *n*-alkanoic acid OC-normalised content in coarse particles was, on average, more than 4 times higher than that in fine particles. The alkenoic acid with highest concentration in all smoke samples was *cis*-9-octadecenoic acid (oleic acid), though at different amounts, depending on wildfires. The second most abundant was 9,12-octadecadienoic acid (linoleic acid), followed by *cis*-9-hexadecenoic acid (palmitoleic acid), which was only detected in the fine particle fraction. These constituents are important components of plant oils (Lísa et al., 2009). The OC-normalised concentration of unsaturated fatty acids in coarse particles was, on average, more than 3 times higher than that in fine particles. Alkanedioic acids, ranging from C<sub>3</sub> to C<sub>16</sub>, were also detected in smoke samples. Among them, butanedioic acid (succinic acid) was the most representative

constituent in coarse particles ranging, on average, from 0.20 to 1.9 mg g<sup>-1</sup> OC, whereas in fine particles nonanedioic (azelic acid) was the most abundant, ranging from 0.088 to 1.7 mg g<sup>-1</sup> OC. Heptanedioic (pimelic acid) and octanedioic (suberic acid) were also frequent diacids in the smoke extracts. A series of *n*-alkanedioic acids have also been detected in fine particle emissions from domestic biomass burning (Fine et al., 2004), combustion of foliar fuels (Hays et al., 2002), prescribed fires in pine forests (Lee et al., 2005) and in smoke samples (PM<sub>10</sub>) from woodstove combustion of common woods in Portugal (Gonçalves et al., 2010). In this study, hydroxy-acids (e.g. malic acid) and oxo-acids (e.g. levulinic acid) were also detected.

Methoxyphenols have been identified as major lignin thermal degradation products and as semi-volatile components of smoke particles (Hawthorne et al., 1988). Softwood smoke contains 4-hydroxy-3-methoxyphenyl (guaiacyl or vanillyl) compounds, whereas hardwood burning contributes mainly to the formation of 4-hydroxy-3,5-dimethoxyphenyl (syringyl) constituents because of a different lignin structure (Hawthorne et al., 1988). In the coarse fraction, vanillin was the most abundant compound with values ranging from 0.48 to 8.2 mg g<sup>-1</sup> OC. The lowest value of vanillin was obtained in samples collected from wildfires with predominance of hardwood species. The alteration products, benzoic acid and vanillic acid, showed OC-normalised concentrations ranging from 0.23 to 14 mg g<sup>-1</sup> OC and 0.25 to 12 mg g<sup>-1</sup> OC, respectively. Other representative phenolics were catechol and syringic acid, with OC-normalised mass concentrations, on average, in the ranges 0.080-2.9 mg g<sup>-1</sup> OC and 0.44-3.8 mg g<sup>-1</sup> OC, respectively. Resorcinol was also identified with similar mass concentrations in fine fraction (0.13-4.7 mg g<sup>-1</sup> OC).

Steroids and terpenoids, including resin acids, have been detected in the smoke samples.  $\beta$ -Sitosterol was the most abundant phytosterol found in both size fractions, followed by stigmast-4-en-3-one in fine fraction and by stigmasterol in coarse fraction. These compounds showed an inverse relationship with MCE values, suggesting that their formation is favoured by smouldering conditions. As obtained by Vicente et al. (2012) in smoke samples from other wildfires in Portugal, the  $\beta$ -sitosterol concentration was similar in samples from wildfires with predominance of softwood or hardwood. Thus, it cannot be used as a tracer to differentiate between softwood and hardwood smoke in source apportionment studies. Sitosterol is one of the most common steroids in the waxes of higher plants. Stigmast-4-en-3-one is a product from the thermal alteration of sterol

precursors (Otto and Simpson, 2005). The triterpenoid with highest concentrations, in both size fractions, was lupeol. It was detected at average mass concentrations of  $0.064 \pm 0.093$  mg g<sup>-1</sup> OC in fine particles and  $0.26 \pm 0.59$  mg g<sup>-1</sup> OC in coarse particles. The lupeol only occurred in samples from fires where hardwood was the predominant type of biomass combusted, suggesting its ability as a tracer to apportion angiosperm wood smoke particle emissions. The most abundant resin acid in all smoke samples was dehydroabietic acid. The mass concentrations of this diterpenoid varied from 0.065 to 12 mg g<sup>-1</sup> OC and from 0.76 to 24 mg g<sup>-1</sup> OC in fine and coarse particles, respectively. Pimaric acid was the second most representative in both size fractions, followed by isopimaric and abietic acids in fine fraction and by abietic and isopimaric in coarse fraction. The samples with the highest mass concentrations of diterpenoids were from smoke emissions of wildfires whose fuel was mainly softwood. Slightly less abundant, but also representative, other diterpenoid resin constituents, such as abietic, isopimaric and pimaric acids, were also present. They are primary natural products occurring as such in resins, while dehydroabietic acid is an oxidative alteration product from other resin acids (Simoneit et al., 2000). As observed for other organic compounds, emissions of resin acids increased with decreasing MCE values. This observation corroborates the findings of Vicente et al. (2012).

The monosaccharide derivatives from the breakdown of cellulose and hemicelluloses, such as levoglucosan, mannosan and galactosan (Simoneit et al., 1999), were the major organic components of smoke particles from biomass burning. Levoglucosan was the most abundant anhydrosugar in both size fractions, followed by mannosan and galactosan, with values for fine and coarse particles in the ranges of 1.6-8.7 mg g<sup>-1</sup> OC and 2.7-56 mg g<sup>-1</sup> OC, respectively. The levoglucosan/OC ratios obtained in this study were lower than those reported by Vicente et al. (2012) in smoke samples from wildfires in central Portugal in summer 2009. This can be related to the fact that the smoke samples of this study benefited from a greater proportion of flaming phase samples. Sullivan et al. (2008) proposed that levoglucosan/OC ratios are probably more dependent on the fuel component burned (branches, leaves, wood, etc.) instead of the combustion efficiency. On the other hand, Engling et al. (2006) concluded, from laboratory studies, that levoglucosan is essentially formed in the smouldering phase, which is in agreement with the results obtained in the present study. Levoglucosan also showed a positive

correlation with potassium. The potassium-to-levoglucosan ratio can be normally used as a tracer for biomass combustion. The values obtained in this study were, on average, 2.0 and 3.1 for fine and coarse particles, respectively. Puxbaum et al. (2007) argued that ratios  $<0.2$  can be associated with domestic combustion emissions, while ratios around 0.5 are typical of open fires. The ratios obtained for rural sites influenced by domestic biomass burning in wintertime were 0.2-2.1 for the cold season and 3.3-9.0 for summertime (Puxbaum et al., 2007). The higher ratios observed in summer were attributed to strong contribution of aerosols from wildfires. These results are in agreement with those obtained in this study.

Levoglucosan, mannosan, and galactosan were emitted in varying ratios, probably due to differences in the relative content of cellulose and hemicellulose in diverse biofuels (Engling et al., 2006). The levoglucosan-to-mannosan (L/M) and the levoglucosan-to-mannosan plus galactosan [L/(M+G)] ratios were calculated in this study. They can be used to distinguish different biomass burning sources (Fabbri et al., 2009). The L/M and L/(M+G) ratios ranged from 1.3 to 5.2 and from 0.91 to 2.8, respectively. The ratios obtained in this study agree with those reported by Vicente et al. (2012).

Other saccharidic compounds identified in smoke samples include monosaccharides (ribose, lyxose, erythrose, galactose and glucose), disaccharides (sucrose and maltose) and polyols (glycerol, erythritol, xylitol, arabitol, ribitol, mannitol, sorbitol and inositol). Medeiros and Simoneit (2008) identified some of these sugar compounds in smoke samples (fine particles  $PM_{>1.0}$ ) from controlled burnings of green vegetation from temperate climate forests. Graham et al. (2002) detected these compounds in aerosols (fine and coarse particles) from biomass burning in Amazonia. Alves et al. (2011a) and Vicente et al. (2011, 2012) also identified sugar compounds in smoke particles ( $PM_{2.5}$  and  $PM_{2.5-10}$ ) from wildfires in Portugal. In the fine particle fraction, ribitol was the most abundant sugar compound ( $0.47 \pm 0.27 \text{ mg g}^{-1} \text{ OC}$ ), followed by erythritol ( $0.096 \pm 0.15 \text{ mg g}^{-1} \text{ OC}$ ) and maltose ( $0.096 \pm 0.048 \text{ mg g}^{-1} \text{ OC}$ ). Lyxose was the most abundant constituent in the coarse fraction with mass concentrations, on average  $2.4 \pm 5.6 \text{ mg g}^{-1} \text{ OC}$ . The second most representative saccharidic compound was glycerol ( $0.99 \pm 1.2 \text{ mg g}^{-1} \text{ OC}$ ), followed by erythrose (on average,  $0.40 \pm 0.65 \text{ mg g}^{-1} \text{ OC}$ ). Graham et al. (2002) suggested that many of these sugars can be primary products of combustion, formed whether through direct volatilisation from plant matter or as products of the breakdown of polysaccharides. Some of the sugars may also be formed by hydrolysis of the corresponding anhydrosugars under

the acidic atmospheric conditions created by biomass burning. Galactose and sucrose showed a positive correlation with  $K^+$  values, in both size fractions. Inositol presented a positive correlation, although weak, with OC, EC and K in fine fraction. Ribose, arabitol, ribitol and galactose showed a positive correlation with levoglucosan in fine and coarse fraction. These correlations suggest a dominant biomass combustion source for these compounds. Graham et al. (2002) likewise obtained the same correlation for some sugar and sugar polyols in aerosols from biomass burning in Amazonia. Zhang et al. (2010) argued that microbial and other biological species (including fungal spores) in contact with the plant material may be incorporated unaltered into the smoke particles during the burning process. Fungal spores were found in a previous study to be present in smoke from biomass burning, despite the high temperatures encountered in the fire (Mims and Mims, 2004). According to Martin et al. (2010), it is also possible that actively wet spore discharging fungi also emit organic substances like sugar alcohols (e.g. mannitol) in aqueous jets, and these jets break up to form droplets that can rapidly dry as fine particles.

## 6.4 Conclusions

In this study, the characterisation of smoke samples collected from several wildfires in central Portugal in summer 2010 was performed. As expected, it was found that the smouldering phase promotes the emission of CO, OC and THC, whereas the CO<sub>2</sub> emissions are much higher for the flaming phase.

An overwhelming proportion of PM<sub>10</sub> emissions (around 90%) was composed of fine particles. On average, about 50% of the PM<sub>2.5</sub> emissions consisted of organic carbon, whilst the OC mass fraction obtained for PM<sub>2.5-10</sub> particles was around 30%. The OC concentrations always remained much higher than EC, with OC/EC ratios in fine and coarse particles from 2.5 to 205 and from 1.7 to 328, respectively.

The most abundant water-soluble ions were Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, Cl<sup>-</sup> and NO<sub>3</sub><sup>-</sup> for the fine grain size, and K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup> for the coarse particle fraction. The potassium-to-elemental carbon and potassium-to-organic carbon ratios obtained in this study were, on average, 0.22±0.23 and 0.011±0.014 for PM<sub>2.5</sub> and 0.83±1.0 and 0.024±0.023 for PM<sub>2.5-10</sub> particles, respectively. These values were in agreement with those reported in the literature for biomass burning sources.

The dominant elements were Na, Br, Cr, Fe, K, Rb and Zn. Additional studies are necessary to evaluate the potential use of these elements, or ratios between them, as potential tracers of biomass burning.

The main organic components were phenolic compounds and their alteration products, acids, carbohydrates, in particular levoglucosan and diterpenoids, such as dehydroabietic acid. Some of the identified compounds can be used as tracers for the presence of biomass burning smoke and to distinguish different biofuel types. The  $K^+$ /levoglucosan ratio obtained in this study was, on average, 2.0 for fine and 3.1 for coarse particles.

The comprehensive chemical characterisation data set obtained in this study contribute to complement the information already published about wildfires in Portugal and in this way to reduce the lack of detailed emission profiles for wildfires in Southern Europe.

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## **CHAPTER 7**



## Chapter 7. General Conclusions

In Portugal, during summer, the occurrence of wildfires is very common due to the high temperatures and the low air humidity, with some of these wildfires lasting for several days and burning significant forest, shrubland and plantation areas. Another consequence of this fact is that every year tons of gaseous pollutants and aerosols are emitted into the atmosphere, with important impacts at different levels.

In this study, gaseous and particulate compounds (inorganic and organic constituents) were identified and quantified in smoke samples from several wildfires that broke out in summers of 2009 and 2010 in central Portugal. Special attention has been focused on two of the nine wildfires whose smoke plumes were sampled in 2009: Sever do Vouga and Penedono. In the first case, the collection of different samples representing the two most important combustion phases (flaming versus smouldering) was possible. The high number of samples, under different conditions, collected in the second case also deserved special treatment and a more detailed characterisation. The main conclusions of the present work can be summarised as follows:

Regarding gaseous compounds:

- The CO and CO<sub>2</sub> emission factors obtained in the smoke samples collected from all the wildfires were in the ranges 52-488 and 822-1690 g kg<sup>-1</sup> (dry basis), respectively. The THC emission factors were between 0.33 and 334 g kg<sup>-1</sup> (dry basis). PM<sub>2.5</sub> and PM<sub>10</sub> emissions factors showed values in the ranges 0.50 to 68 and 0.86 to 72 g kg<sup>-1</sup>(dry basis), respectively. The MCE values ranged from 0.52 to 0.97 for the smoke samples collected during the wildfires in both seasons. While, as expected, the CO<sub>2</sub> emissions increased with increasing MCE values, the opposite was observed for CO, THC and particulate matter. The results obtained in this study consolidate previous arguments that the smouldering phase may contribute to significant amounts of atmospheric pollutants into the atmosphere. Keeping in mind that this phase may last for several hours to days, the corresponding emission factors should be taken into consideration when calculating the global wildfire emissions.

Three oxygenated volatile organic compounds were measured in samples collected during the 2009 wildfire season: formaldehyde, acetaldehyde and propionaldehyde. The most abundant was acetaldehyde with EFs (dry basis) between 1.03 and 1.87 g kg<sup>-1</sup>, followed by formaldehyde with values in the range 0.09-0.96 g kg<sup>-1</sup>. Propionaldehyde was the scarcest, varying from 0.03 to 0.17 g kg<sup>-1</sup>. The acetaldehyde EFs obtained in samples from the wildfire that took place in Penedono, one of the largest since 2005, were between 1.22 and 3.17 g kg<sup>-1</sup>, while values in the range 0.012-0.17 g kg<sup>-1</sup> were achieved for formaldehyde. The aldehyde EFs obtained in this study were in accordance with those reported in the literature for residential wood burning experiments. The emission factors of all three aldehydes increased with decreasing MCE values. The inverse relationship between acetaldehyde and MCE values was more significant compared to those of formaldehyde and propionaldehyde. The same relationship was reported by some authors for laboratory measurements of biomass burning emissions from different fuel types and for smoke samples from African savannah fires.

Concerning particulate matter and its carbonaceous content:

- The gravimetric data showed that PM<sub>10</sub> mass was dominated by the PM<sub>2.5</sub> fraction in all smoke samples collected in both wildfire seasons. Around 90% of the PM<sub>10</sub> aerosol mass was represented by PM<sub>2.5</sub>. The percentage of OC mass in fine and coarse particles were similar in smoke samples collected in the 2009 and 2010 campaigns, reaching values up to 55 % of the PM<sub>2.5</sub> mass and around 40% of PM<sub>2.5-10</sub> mass. The OC-to-EC ratios obtained for all the smoke samples were very high. The lowest ratios were measured in samples collected during the flaming phase (4.4 for the 2009 season and 1.7 for smoke samples of the 2010 wildfire season), whereas the highest values, of several hundreds or thousands, were measured in particle samples emitted during the smouldering stage. It was observed that the particulate matter and OC emissions enhanced considerably under smouldering conditions. In contrast, the EC emissions increased with increasing MCE values.

About the water-soluble ions and trace elements in smoke particles:

- In the smoke samples collected from the wildfires in both seasons, the water-soluble ions, on average, contributed up to 3.9% and 2.8% of the  $PM_{2.5}$  and  $PM_{2.5-10}$  particle mass, respectively. The low potassium mass fractions obtained in samples from these wildfires could be due to the prevailing smouldering conditions. The highest levels of  $Cl^-$  and  $Mg^{2+}$  were observed in smoke particles collected during a wildfire that consumed a seaside forest, reflecting the influence on emissions of previous wet deposition of marine aerosol on the fuels. However, the important role of the temperature on the efficiency of the volatilisation of the fuel water-soluble ions was pointed out in one of the samples collected under smouldering conditions (MCE=0.66 vs. MCE>0.86 for the other samples). In this case, the  $Cl^-$  and  $Mg^{2+}$  content were below the detection limit. Trace elements were detected in the smoke samples obtained during the wildfires in both seasons, representing, on average, values up to 2.0% and 12% the  $PM_{2.5}$  and  $PM_{2.5-10}$  mass, respectively. Additional studies are necessary to evaluate the potential use of trace elements, or ratios between them, as potential tracers of biomass burning. For almost all water-soluble ionic components and trace elements, the relative concentrations increased with increasing values of MCE, which is in accordance with the observation of lower OC levels during the flaming phase compared to the smouldering stage.

Concerning the organic speciation of the smoke particles:

- The chromatographically resolved organics was mainly composed of phenolic compounds and their alteration products, especially guaiacyl type, acids, aliphatics, sugar constituents, such as anhydrosugar in particular levoglucosan, diterpenoids and PAHs. Some of the identified constituents can be used as biomarkers for the presence of biomass burning emissions and also to distinguish different biofuel types. The most abundant aromatic hydrocarbon found in all smoke samples collected during the 2009 wildfire season was retene, identified as a biomarker of softwood smoke. The polycyclic aromatic hydrocarbon diagnostic ratios gotten can be taken as indicative of vegetation burning in source apportionment studies. The BghiP/BaP values obtained for the smoke particles from the wildfire plumes in 2009 support the fact that this ratio may be used as a tool to differentiate vehicular and biomass burning emissions in source assignment attempts. The ratio of

benzo[e]pyrene to benzo[a]pyrene plus benzo[a]pyrene [BeP/(BeP+BaP)] has been identified as a source assignment tool and as an indicator of the particle ageing, due to the relative short lifetime of BaP (decomposed very easily by light and oxidants). The increasing of the ratio can be considered as an index of the aging of the particles. The ratios obtained for the smoke samples of the 2009 wildfires were in accordance with the values proposed in the literature for freshly emitted plumes. As expected, levoglucosan was the most abundant anhydrosugar in all smoke samples, followed by mannosan and galactosan. The levoglucosan/OC ratio is especially useful in assessment approaches of the contribution of biomass burning emissions to the ambient aerosols. The values obtained in this study ( $15 \pm 9.6$  and  $14 \pm 15 \text{ mg g}^{-1} \text{ OC}$  for  $\text{PM}_{2.5}$  and  $\text{PM}_{2.5-10}$ , respectively) were similar to those registered for prescribed forest fires and for the dry season in Amazonia, but deviate significantly from the ratios reported in the literature for other biomass types and burning regimes. Since levoglucosan/OC ratios for wildfires were low compared with those obtained in domestic wood burning, different values should be taken into account in source apportionment studies. The levoglucosan-to-mannosan (L/M) and the levoglucosan-to-mannosan plus galactosan [L/(M+G)] ratios are reported in the literature as tools to distinguish different biomass burning sources. The ratios obtained in the smoke particles from the 2009 and 2010 wildfires were in agreement with those obtained for emissions of softwood burning in residential appliances, and in accordance with the predominance of softwood combustion in the wildfires where smoke samples were collected.

Smoke particles obtained from the plume of the wildfire that took place in 2009 in Sever do Vouga showed the presence of monoglycerides, which, up to now, have been used as tracers for assigning meat cooking. For most of the organic constituents in smoke particles, a dependence on the fire regime was observed. In the smoke particles from Penedono, it was possible to verify that emissions of di-, oxo-, and hydroxy-acids, monosugars, polyols and some phenolics like vanillic acid are promoted during the flaming phase, while aldehydes, aliphatic compounds and resin acids are predominantly formed during the smouldering combustion phase. Thus, the combustion conditions exert a great influence on the formation pathways and emission rates of organic compounds.

Since biomass burning is a global problem due to the high amount of gases and particulate matter emitted into the atmosphere, the study of wildfire emissions is of utmost importance. Due to the high number and, in many cases, the severity of events, especially during the increasingly frequent heat waves, emissions from wildfires in Mediterranean countries may have a significant impact at a regional or even global scale. The databases obtained in this thesis contribute with new data to model atmospheric processes, improve emission inventories, and apply source apportionment methodologies and thus help fulfilling the gap that exists in what concerns emission factors and chemical emission profiles for wildfires in Mediterranean countries. This study is a valuable contribution, since databases were obtained under real field conditions. In spite of the considerable progress that has been made with regard to the determination of emission factors from wildfires, future research is needed to answer several still open questions.

There remain some gaps for important species, including ones that could be valuable atmospheric tracers, such as nitrogen-containing compounds (e.g. hydrogen cyanide and acetonitrile), and methyl halides. Some poorly characterised biofuel and fire types also need further study. The global emission estimates from biomass burning have been refined but require further validation. This applies particularly to the estimates of biomass burned as a function of space, time, and type of combustion. A particularly important question is related to the calculation of weighted emission factors taking into account the proportion between flaming and smouldering combustion.

A significant step in evaluating smoke particle impacts on climate is to model the relationship of data from individual fires to the evolved plumes that affect the chemistry and radiative balance of the atmosphere. In addition to the determination of accurate emission factors, global emission estimates need proper information about the amount of area burned and fuel load, which are sources of high uncertainties. Until such extensive parameters are better defined, through a combination of better government documentation, satellite burn scar analysis, or active remote sensing fire detection, forward derivations of smoke particle emissions will remain highly uncertain.

It has yet to be identified and quantified most of the higher molecular weight non-methane organic compounds, which tend to be semi-volatile and thus move between the gas-phase and condensed phase in poorly understood way, profoundly affecting the chemical evolution of both phases. Another point is that measurements are seldom done in

the immediate vicinity of a fire, but more often in the plumes at certain distances from the fire. Concentrations of several constituents (e.g. volatile organic compounds) and patterns change with the age of a plume due to mixing with ambient air and photochemical processing. Thus, the post-emission processing, photochemistry and formation of secondary aerosols should be the focus of additional studies. It is a challenge considering the significant variability in both space and time scales that characterise smoke emissions, along with the evolution of optical properties as smoke ages, and interactions with atmospheric dynamics and cloud microphysics. Smoke plume height and vertical profiles are important properties for smoke particles impacts on the atmosphere, including locations of warming layers, stability structure, clouds, and smoke transport. New techniques for measurement, analysis, and modelling are required to help investigate the different optical properties and climate effects of EC and OC.

Studies to estimate the trajectory/transport of the smoke plume generated by forest fires, and their possible influence on surrounding areas, especially for PM<sub>2.5</sub> particles should be undertaken, because they are the most dangerous to the human health. Because woodsmoke is made up of such a large mixture of different chemicals, it is impossible at present to attempt to accurately assess its health impacts by simply summing the potential effects of individual constituents. Particularly in high-exposure situations with fresh woodsmoke, as with wildfire episodes, there may be a need to derive indices of exposure that take into account a range of toxic endpoints, such as acute-acting as well as chronic toxicants, so that appropriate protective actions can be adequately taken. Use of fine particles or any other single metric by itself may not be sufficient in these circumstances. In addition, given the weight of toxicologic evidence, further epidemiologic studies are needed.

# Supplementary Material

## Supplementary Material A1

The average concentrations for some inorganic compounds from Chapter 2.

**Table A1.** Average concentrations ( $\mu\text{g g}^{-1}$  PM) of minor trace elements in the smoke plume from several wildfires recorded in summer 2009 in Portugal.

	SEVER		OVAR		PENEDONO		MONTEMOR		NARIZ		CINFÃES		FAREJINHA		PENDILHE		SABUGAL	
	PM <sub>2.5</sub>	PM <sub>2.5-10</sub>																
<b>Li</b>	20.2	9.58	31.9	7.51	6.95	19.9	11.8	14.8	38.2	49.2	547	51.2	39.5	81.5	98.6	71.5	10.9	48.9
<b>Be</b>	1.35	0.00	2.69	1.34	0.61	1.75	0.00	0.00	1.88	1.21	21.7	0.00	1.65	1.87	6.84	5.35	1.27	0.00
<b>Sc</b>	0.00	0.00	3.10	0.00	0.63	0.29	0.00	0.00	1.43	0.63	28.2	0.00	1.40	0.00	4.78	0.00	0.06	0.00
<b>V</b>	31.2	11.9	86.3	58.5	8.58	16.8	2.50	13.1	69.7	57.1	271	15.9	22.5	41.6	36.3	37.4	8.76	5.84
<b>Cr</b>	20.7	0.00	41.8	31.0	25.4	6.23	19.8	3.30	41.2	0.28	230	0.00	0.00	165	49.1	0.00	0.00	0.00
<b>Co</b>	1.55	0.10	6.61	1.24	1.17	1.44	2.02	0.54	18.1	3.31	29.4	2.22	2.39	19.7	17.8	2.77	2.07	1.30
<b>Ni</b>	10.9	10.2	44.2	61.6	38.4	23.0	3.10	7.18	18.6	64.2	121	68.0	13.2	359	7.55	3.58	0.00	0.00
<b>Ga</b>	7.65	4.05	13.1	13.9	2.66	4.28	0.00	2.15	0.00	8.27	176	1.10	13.0	22.7	30.2	14.9	2.02	4.18
<b>Ge</b>	13.7	0.00	5.55	0.15	0.00	0.37	0.00	2.45	17.2	10.0	50.4	0.00	0.00	16.2	8.55	1.87	0.00	4.71
<b>As</b>	27.8	5.34	740	149	28.0	13.8	13.8	20.3	170	36.7	209	7.62	23.4	22.2	61.8	34.3	5.66	4.04
<b>Se</b>	20.7	2.37	18.7	17.5	4.66	5.51	4.05	8.50	12.2	33.1	62.3	6.98	5.56	20.8	11.5	26.0	5.52	3.92
<b>Rb</b>	84.5	22.5	87.1	57.5	29.9	60.1	0.00	16.1	29.8	69.2	1258	9.78	98.0	114	267	101	96.3	37.3
<b>Sr</b>	180	120	250	206	60.3	158	0.00	69.1	54.7	200	931	68.2	93.8	197	135	66.0	133	223
<b>Y</b>	14.2	8.24	17.0	25.9	4.17	5.11	0.00	2.26	0.00	9.09	95.7	0.00	6.11	10.7	28.0	5.93	4.10	1.62
<b>Nb</b>	15.7	0.23	25.4	3.56	5.56	6.22	5.27	0.09	38.5	10.8	192	0.00	13.6	44.6	21.7	0.00	9.14	0.00
<b>Mo</b>	240	0.00	164	135	26.9	6.52	0.00	12.7	0.00	1.86	822	0.00	0.00	37.4	170	0.00	0.00	0.00
<b>Cd</b>	5.67	0.03	5.00	0.90	2.15	0.36	0.02	0.82	5.54	2.69	3.59	2.34	0.00	6.76	1.02	0.00	3.15	1.07
<b>Sn</b>	10.6	1.61	59.1	5.82	4.67	5.68	20.0	3.43	24.4	6.38	146	0.00	21.2	16.5	40.7	0.00	13.1	5.09
<b>Sb</b>	5.33	6.54	16.1	0.00	1.52	0.04	23.4	11.8	34.7	33.2	125	53.2	28.7	50.5	70.1	38.4	30.2	40.1

## Supplementary Material

<b>Cs</b>	4.93	2.41	6.26	7.73	2.65	6.72	2.33	1.59	9.84	5.44	69.8	0.49	0.00	11.7	0.00	6.12	0.00	1.94
<b>La</b>	8.66	2.55	16.2	12.2	4.07	7.84	0.00	1.07	8.08	9.75	185	0.00	13.6	18.4	49.5	21.7	5.45	0.00
<b>Ce</b>	23.0	5.94	39.0	27.7	8.73	15.6	0.00	4.24	19.8	28.0	488	0.00	34.1	50.9	134	64.1	10.8	2.88
<b>Pr</b>	2.23	0.70	3.45	3.12	0.85	1.43	0.00	0.33	1.68	2.51	42.0	0.00	3.11	4.39	12.2	5.90	1.24	0.21
<b>Nd</b>	11.6	3.95	16.7	16.9	4.14	6.72	0.00	1.94	6.59	12.8	195	0.00	14.5	21.8	58.1	29.2	5.98	2.58
<b>Sm</b>	3.61	1.48	4.37	5.22	1.05	1.48	0.00	0.64	0.11	3.10	44.7	0.00	3.49	5.10	13.1	6.73	1.31	1.02
<b>Eu</b>	1.28	0.00	1.22	3.20	0.32	0.00	0.00	0.00	0.00	0.45	5.07	0.00	0.39	0.00	1.33	0.00	0.08	0.00
<b>Gd</b>	4.41	2.17	4.57	5.09	1.07	1.48	0.00	0.71	0.00	3.49	39.3	0.00	3.10	5.18	10.7	5.45	1.28	1.34
<b>Tb</b>	0.65	0.00	0.62	0.00	0.14	0.09	0.00	0.00	0.00	0.51	5.10	0.00	0.45	0.00	1.43	0.00	0.21	0.00
<b>Dy</b>	3.71	2.00	3.34	3.50	0.83	0.94	0.00	0.63	0.00	2.37	23.4	0.00	2.19	3.36	6.82	2.91	1.03	0.93
<b>Ho</b>	0.56	0.00	0.51	0.00	0.13	0.09	0.00	0.00	0.00	0.49	3.48	0.00	0.31	0.00	0.98	0.00	0.14	0.00
<b>Er</b>	1.35	0.12	1.30	1.36	0.36	0.37	0.46	0.83	1.36	2.78	9.67	1.87	0.82	2.80	2.66	2.65	0.31	2.40
<b>Tm</b>	1.44	0.00	0.74	0.00	0.19	0.00	0.00	0.00	0.65	0.00	3.97	0.00	0.91	0.00	2.62	0.00	1.10	0.00
<b>Yb</b>	1.71	0.02	1.56	2.02	0.44	0.41	0.00	0.12	0.00	0.68	7.97	0.00	0.66	0.76	1.97	0.31	0.25	0.05
<b>Lu</b>	1.46	0.00	0.76	0.00	0.14	0.00	0.00	0.00	0.57	0.00	3.60	0.00	0.82	0.00	2.31	0.00	0.97	0.00
<b>Hf</b>	58.7	2.63	44.5	1.37	15.6	1.90	13.5	0.37	150	0.70	20.0	0.00	0.00	7.16	0.00	0.00	4.62	0.00
<b>Ta</b>	0.00	0.00	1.22	0.00	0.51	0.00	0.52	0.00	6.23	0.78	8.43	0.00	0.00	0.00	0.00	0.00	0.20	0.00
<b>W</b>	0.00	0.00	33.7	0.00	0.74	0.00	0.15	0.00	3.06	0.00	66.6	0.00	2.05	0.00	14.1	0.00	0.00	0.00
<b>Tl</b>	1.23	0.00	0.89	0.00	0.61	0.09	0.30	0.00	5.81	0.00	9.97	0.00	0.94	0.00	2.05	0.00	2.86	0.00
<b>Pb</b>	108	2.56	263	120	19.3	17.9	35.7	17.3	95.5	88.0	476	4.42	37.0	57.3	84.2	26.8	39.5	29.3
<b>Bi</b>	0.64	2.26	19.5	5.41	0.85	0.33	1.57	0.38	10.2	2.46	15.3	0.00	1.28	1.62	5.85	0.76	2.83	0.70
<b>Th</b>	7.82	0.00	10.6	2.12	2.14	2.15	0.00	0.00	2.57	5.09	125	0.00	9.91	7.89	29.4	8.17	2.40	0.00
<b>U</b>	10.1	0.49	10.6	4.48	1.92	2.96	0.22	1.57	2.17	5.57	107	0.00	8.85	12.0	25.0	11.3	3.29	3.04

## Supplementary Material A2

## Supplementary Information from Chapter 4.

The concentration range (and average) for some organic compounds from Chapter 4.

Table A2. Detailed speciation of organic compounds in smoke samples.

Compound	Formula	PM <sub>2.5</sub>	PM <sub>2.5-10</sub>
<b><i>n</i>-Alkanes (µg g<sup>-1</sup> OC)</b>			
Decane	C <sub>10</sub> H <sub>22</sub>	4.961-8.758 (6.400)	nd-31.46 (16.97)
Tridecane	C <sub>13</sub> H <sub>28</sub>	nd-1.105 (0.4454)	nd
Tetradecane	C <sub>14</sub> H <sub>30</sub>	0.5471-3.407 (1.510)	nd
Pentadecane	C <sub>15</sub> H <sub>32</sub>	2.386-7.778 (5.820)	nd
Hexadecane	C <sub>16</sub> H <sub>34</sub>	5.405-32.19 (22.54)	nd
Heptadecane	C <sub>17</sub> H <sub>36</sub>	19.71-127.4 (75.56)	3.189-26.06 (16.93)
Octadecane	C <sub>18</sub> H <sub>38</sub>	56.17-187.3 (126.6)	41.37-56.67 (49.30)
Nonadecane	C <sub>19</sub> H <sub>40</sub>	33.77-459.9 (246.4)	88.41-137.3 (114.6)
Eicosane	C <sub>20</sub> H <sub>42</sub>	200.9-614.7 (367.2)	101.0-160.4 (127.7)
Heneicosane	C <sub>21</sub> H <sub>44</sub>	nd-1348 (317.9)	nd-189.4 (114.1)
Docosane	C <sub>22</sub> H <sub>46</sub>	150.2-832.2 (488.8)	109.3-157.5 (141.1)
Tricosane	C <sub>23</sub> H <sub>48</sub>	292.3-873.7 (531.5)	106.8-139.2 (124.1)
Tetracosane	C <sub>24</sub> H <sub>50</sub>	223.0-653.4 (386.0)	45.53-122.1 (86.73)
Pentacosane	C <sub>25</sub> H <sub>52</sub>	212.0-636.6 (404.1)	23.58-97.28 (50.73)
Hexacosane	C <sub>26</sub> H <sub>54</sub>	147.4-472.2 (276.8)	20.76-51.69 (33.30)
Heptacosane	C <sub>27</sub> H <sub>56</sub>	245.0-727.9 (429.4)	nd-28.97 (4.139)
Octacosane	C <sub>28</sub> H <sub>58</sub>	142.2-355.8 (214.3)	19.16-50.81 (32.42)
Nonacosane	C <sub>29</sub> H <sub>60</sub>	375.2-916.6 (603.7)	55.23-241.0 (124.0)
Hentriacontane	C <sub>31</sub> H <sub>64</sub>	382.8-815.2 (532.9)	33.06-440.1 (249.3)
Dotriacontane	C <sub>32</sub> H <sub>66</sub>	nd-69.04 (15.58)	nd
Tritriacontane	C <sub>33</sub> H <sub>68</sub>	61.47-288.2 (182.0)	nd-109.6 (40.02)
<i>Other Alkanes</i>		95.17-1309 (484.6)	31.08-538.9 (150.0)
<i>Branched Alkanes</i>		21.46-631.4 (128.7)	84.13-319.7 (196.4)
<b><i>n</i>-Alkenes (µg g<sup>-1</sup> OC)</b>			
Tetradecene	C <sub>14</sub> H <sub>28</sub>	1.083-3.400 (2.181)	0.4088-7.897 (2.846)
Pentadecene	C <sub>15</sub> H <sub>30</sub>	2.351-12.60 (8.172)	nd-2.480 (0.6273)
Hexadecene	C <sub>16</sub> H <sub>32</sub>	2.601-35.63 (22.00)	5.608-22.55 (12.13)
Heptadecene	C <sub>17</sub> H <sub>34</sub>	19.22-102.1 (80.87)	31.32-56.39 (43.78)
Octadecene	C <sub>18</sub> H <sub>36</sub>	28.28-314.3 (166.3)	60.71-102.1 (78.36)
Nonadecene	C <sub>19</sub> H <sub>38</sub>	245.3-575.0 (430.8)	129.5-244.7 (177.8)

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Eicosene	C <sub>20</sub> H <sub>40</sub>	207.2-1240 (781.5)	222.9-427.6 (286.2)
Docosene	C <sub>22</sub> H <sub>44</sub>	nd-1330 (649.1)	nd-377.2 (260.5)
Tricosene	C <sub>23</sub> H <sub>46</sub>	416.1-1033 (664.8)	147.9-211.5 (168.8)
Tetracosene	C <sub>24</sub> H <sub>48</sub>	464.6-1641 (979.2)	250.1-427.5 (349.0)
Pentacosene	C <sub>25</sub> H <sub>50</sub>	293.4-470.6 (376.3)	nd-79.85 (55.31)
Hexacosene	C <sub>26</sub> H <sub>52</sub>	358.6-1142 (720.0)	198.7-307.6 (240.3)
Heptacosene	C <sub>27</sub> H <sub>54</sub>	207.0-320.3 (248.3)	50.65-112.3 (89.34)
Octacosene	C <sub>28</sub> H <sub>56</sub>	317.9-543.9 (442.4)	163.5-264.4 (192.6)
Squalene	C <sub>30</sub> H <sub>50</sub>	nd-163.7 (40.38)	nd-56.12 (21.56)
<i>Other Alkenes</i>		492.9-1056 (740.6)	26.96-378.7 (234.0)
<i>Branched Alkenes</i>		60.24-388.5 (228.6)	68.60-164.9 (122.1)
<b>PAHs (µg g<sup>-1</sup> OC)</b>			
Naphthalene	C <sub>10</sub> H <sub>8</sub>	nd-40.69 (14.15)	13.86-137.0 (61.55)
Acenaphthylene	C <sub>12</sub> H <sub>8</sub>	nd	nd-101.6 (14.60)
Acenaphthene	C <sub>12</sub> H <sub>10</sub>	nd	nd-7.102 (1.014)
Fluorene	C <sub>13</sub> H <sub>10</sub>	nd-99.16 (17.10)	4.795-80.67 (20.75)
Phenanthrene	C <sub>14</sub> H <sub>10</sub>	nd-232.5 (49.10)	14.37-196.3 (78.68)
Anthracene	C <sub>14</sub> H <sub>10</sub>	nd-57.39 (10.81)	2.864-41.89 (15.49)
Fluoranthene	C <sub>16</sub> H <sub>10</sub>	nd-262.0 (43.60)	5.575-160.1 (61.23)
Pyrene	C <sub>16</sub> H <sub>10</sub>	nd-44.42 (10.60)	2.439-54.06 (16.52)
p-terphenyl	C <sub>18</sub> H <sub>14</sub>	nd	nd-0.9235 (0.1319)
Retene	C <sub>18</sub> H <sub>18</sub>	23.89-7661 (1690)	395.1-6056 (2404)
Benzo[a]anthracene	C <sub>18</sub> H <sub>12</sub>	2.367-22.69 (8.865)	3.334-11.49 (5.453)
Chrysene	C <sub>18</sub> H <sub>12</sub>	5.092-38.67 (17.89)	4.734-19.35 (8.846)
Benzo[b]fluoranthene	C <sub>20</sub> H <sub>12</sub>	nd-6.980 (3.733)	1.303-3.683 (1.967)
Benzo[k]fluoranthene	C <sub>20</sub> H <sub>12</sub>	nd-4.530 (2.172)	0.6245-1.976 (0.9665)
Benzo[a]pyrene	C <sub>20</sub> H <sub>12</sub>	nd-14.28 (5.480)	1.928-6.606 (3.189)
Perylene	C <sub>20</sub> H <sub>12</sub>	0.6965-3.725 (2.135)	0.5414-1.454 (0.8487)
Dibenzo[a,h]anthracene	C <sub>24</sub> H <sub>14</sub>	nd	nd-53.23 (7.605)
Benzo[ghi]perylene	C <sub>22</sub> H <sub>12</sub>	nd-2.811 (0.4016)	nd-2.016 (0.6671)
Benzo[e]pyrene	C <sub>20</sub> H <sub>12</sub>	nd-3.406 (1.682)	0.5529-1.686 (1.193)
Benzo[j]fluoranthene	C <sub>20</sub> H <sub>12</sub>	nd-5.618 (2.949)	1.300-4.769 (2.304)
<b>Other PAHs (mg g<sup>-1</sup> OC)</b>		15-31	3.8-12
<b>Oxy-PAHs (µg g<sup>-1</sup> OC)</b>			
9-Fluorenone	C <sub>13</sub> H <sub>8</sub> O	nd-5.28 (2.09)	110-169 (127)
9,10-Anthraquinone	C <sub>14</sub> H <sub>8</sub> O <sub>2</sub>	nd-19.2 (2.79)	nd-289 (49.7)
2,6-Di-tert-butyl-1,4-Benzoquinone	C <sub>14</sub> H <sub>20</sub> O <sub>2</sub>	nd-0.768 (0.110)	nd-110 (41.2)
<b>n-Alcohols (µg g<sup>-1</sup> OC)</b>			
n-Decanol	C <sub>10</sub> H <sub>22</sub> O	nd	nd-622.5 (88.92)
n-Pentadecanol	C <sub>15</sub> H <sub>32</sub> O	nd-23.99 (5.271)	47.02-123.4 (81.09)

<i>n</i> -Hexadecanol	C <sub>16</sub> H <sub>34</sub> O	nd	nd-357.1 (189.5)
<i>n</i> -Octadecanol	C <sub>18</sub> H <sub>38</sub> O	74.91-307.2 (176.5)	125.0-374.2 (269.7)
<i>n</i> -Docosanol	C <sub>22</sub> H <sub>42</sub> O	nd-65.79 (52.36)	nd-1523 (977.0)
<i>n</i> -Tricosanol	C <sub>23</sub> H <sub>48</sub> O	66.05-8373.1 (2288)	nd-2678 (1173)
<i>n</i> -Tetracosanol	C <sub>24</sub> H <sub>50</sub> O	nd-40.20 (5.742)	nd-1765 (443.8)
<i>n</i> -Pentacosanol	C <sub>25</sub> H <sub>52</sub> O	21.30-287.5 (119.3)	nd-2798 (1989)
<i>n</i> -Hexacosanol	C <sub>26</sub> H <sub>54</sub> O	nd-34.70 (4.958)	nd-1538 (474.6)
<i>n</i> -Heptacosanol	C <sub>27</sub> H <sub>56</sub> O	10.81-79.68 (38.50)	53.81-908.6 (431.8)
<i>n</i> -Octacosanol	C <sub>28</sub> H <sub>58</sub> O	10.20-115.3 (38.50)	992.2-2888 (1760)
<i>n</i> -Tricontanol	C <sub>30</sub> H <sub>62</sub> O	7.163-75.84 (30.27)	550.6-1797 (1201.8)

**Other alcohols (µg g<sup>-1</sup> OC)**

Myrtenol	C <sub>10</sub> H <sub>16</sub> O	nd-179 (77.1)	nd-75.3 (19.6)
Benzyl alcohol	C <sub>7</sub> H <sub>8</sub> O	75.4-288 (152)	4.71-19.7 (11.4)
2-ethylhexanol	C <sub>8</sub> H <sub>18</sub> O	nd-36.7 (16.4)	nd-842 (135)

**Ethyl ester of fatty acids (µg g<sup>-1</sup> OC)**

Methyl tetradecanoate	C <sub>15</sub> H <sub>30</sub> O <sub>2</sub>	nd-170 (71.8)	18.3-85.3 (54.3)
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***n*-alkanoic acids (mg g<sup>-1</sup> OC)**

Hexanoic acid	C <sub>6</sub> H <sub>12</sub> O <sub>2</sub>	nd-0.021 (0.0056)	0.020-0.074 (0.041)
Heptanoic acid	C <sub>7</sub> H <sub>14</sub> O <sub>2</sub>	nd-0.053 (0.014)	0.081-0.23 (0.16)
Octanoic acid	C <sub>8</sub> H <sub>16</sub> O <sub>2</sub>	0.003-0.18 (0.044)	0.30-0.92 (0.509)
Nonanoic acid	C <sub>9</sub> H <sub>18</sub> O <sub>2</sub>	0.003-0.19 (0.030)	0.027-0.75 (0.36)
Decanoic acid	C <sub>10</sub> H <sub>20</sub> O <sub>2</sub>	0.0035-0.37 (0.058)	0.55-0.99 (0.76)
Undecanoic acid	C <sub>11</sub> H <sub>22</sub> O <sub>2</sub>	nd-0.011 (0.0039)	0.0034-0.015 (0.0091)
Dodecanoic Acid	C <sub>12</sub> H <sub>24</sub> O <sub>2</sub>	0.072-1.3 (0.27)	1.5-2.6 (2.1)
Tridecanoic acid	C <sub>13</sub> H <sub>26</sub> O <sub>2</sub>	0.0066-0.012 (0.0094)	0.0019-0.026 (0.012)
Tetradecanoic acid	C <sub>14</sub> H <sub>28</sub> O <sub>2</sub>	nd-0.96 (0.18)	2.0-2.9 (2.4)
Pentadecanoic acid	C <sub>15</sub> H <sub>30</sub> O <sub>2</sub>	0.0041-0.012 (0.0085)	0.0069-0.11 (0.048)
Hexadecanoic acid	C <sub>16</sub> H <sub>32</sub> O <sub>2</sub>	0.22-1.4 (0.45)	3.7-5.7 (4.5)
Heptadecanoic acid	C <sub>17</sub> H <sub>34</sub> O <sub>2</sub>	0.0026-0.088 (0.016)	0.31-0.57 (0.47)
Octadecanoic acid	C <sub>18</sub> H <sub>36</sub> O <sub>2</sub>	0.13-0.44 (0.27)	1.6-2.5 (2.1)
Nonadecanoic acid	C <sub>19</sub> H <sub>38</sub> O <sub>2</sub>	0.0038-0.35 (0.084)	0.013-0.43 (0.21)
Eicosanoic acid	C <sub>20</sub> H <sub>40</sub> O <sub>2</sub>	0.0073-0.24 (0.10)	2.3-3.8 (3.0)
Docosanoic acid	C <sub>22</sub> H <sub>44</sub> O <sub>2</sub>	0.012-0.59 (0.24)	5.5-6.9 (6.3)
Tetracosanoic acid	C <sub>24</sub> H <sub>48</sub> O <sub>2</sub>	0.021-0.92 (0.32)	5.8-8.2 (7.5)
<i>Other n-alkanoic acids</i>		nd-0.74 (0.11)	0.85-1.7 (1.4)

**Unsaturated fatty acids (µg g<sup>-1</sup> OC)**

Oleic acid (C <sub>18:1</sub> )	C <sub>18</sub> H <sub>34</sub> O <sub>2</sub>	nd-512 (73.1)	2412-3875 (3154)
Linoleic acid (C <sub>18:2</sub> )	C <sub>18</sub> H <sub>32</sub> O <sub>2</sub>	9.71-16.5 (13.9)	7.835-27.81 (17.36)
Palmitoleic acid (C <sub>16:1</sub> )	C <sub>16</sub> H <sub>30</sub> O <sub>2</sub>	nd-264 (37.8)	nd-867 (447)

**Ketones (mg g<sup>-1</sup> OC)**

2-Tridecanone	C <sub>13</sub> H <sub>26</sub> O	nd-0.0055 (0.00078)	nd-0.083 (0.023)
2-Pentadecanone	C <sub>15</sub> H <sub>30</sub> O	nd-0.015 (0.0022)	nd-0.22 (0.083)
3-Hexadecanone	C <sub>16</sub> H <sub>32</sub> O	nd	nd-0.10 (0.049)
2-Octadecanone	C <sub>18</sub> H <sub>36</sub> O	nd-0.0085 (0.0022)	nd-0.18 (0.051)
6,10,14-trimethyl-pentadecan-2-one	C <sub>18</sub> H <sub>38</sub> O	nd-0.47 (0.18)	0.14-0.28 (0.20)
Benzophenone	C <sub>13</sub> H <sub>10</sub> O	nd	0.012-0.044 (0.030)
<i>Other Ketones</i>		nd-0.033 (0.0091)	0.70-3.6 (1.3)

**n-Alkanals (µg g<sup>-1</sup> OC)**

Decanal	C <sub>10</sub> H <sub>20</sub> O	nd	nd-55 (14)
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**Terpenoids (µg g<sup>-1</sup> OC)**

Isopulegol	C <sub>10</sub> H <sub>18</sub> O	nd	12-32 (21)
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**Steroids and alteration products (mg g<sup>-1</sup> OC)**

Campesterol	C <sub>28</sub> H <sub>48</sub> O	nd	nd-0.39 (0.18)
β-Sitosterol	C <sub>29</sub> H <sub>50</sub> O	nd-0.44 (0.065)	0.62-1.4 (0.95)
Stigmasterol	C <sub>29</sub> H <sub>48</sub> O	nd-0.12 (0.025)	0.18-0.39 (0.27)
Stigmastan-3,5-diene	C <sub>29</sub> H <sub>48</sub>	0.53-1.01 (0.78)	nd-0.55 (80.27)
Stigmasta-3,5-dien-7-one	C <sub>29</sub> H <sub>46</sub> O	nd-1.1 (0.35)	0.54-1.7 (1.00)
Stigmast-4-en-3-one	C <sub>29</sub> H <sub>48</sub> O	nd-0.40 (0.12)	0.30-0.71 (0.51)
Trendione	C <sub>18</sub> H <sub>20</sub> O <sub>2</sub>	nd-1.6 (0.96)	nd-0.36 (0.097)

**Diterpenoids and alteration products (mg g<sup>-1</sup> OC)**

Isopimaric acid	C <sub>20</sub> H <sub>30</sub> O <sub>2</sub>	nd-0.024 (0.012)	0.71-1.4 (0.88)
Pimaric acid	C <sub>20</sub> H <sub>30</sub> O <sub>2</sub>	nd-0.18 (0.053)	1.5-3.3 (2.1)
Abietic acid	C <sub>20</sub> H <sub>30</sub> O <sub>2</sub>	0.013-0.19 (0.042)	1.5-4.5 (2.4)
Methyl dehydroabietate	C <sub>21</sub> H <sub>30</sub> O <sub>2</sub>	0.30-3.6 (2.3)	0.34-1.2 (0.61)
Dehydroabietic acid	C <sub>20</sub> H <sub>28</sub> O <sub>2</sub>	0.11-3.1 (1.2)	8.7-19 (14)
7-Oxodehydroabietic acid	C <sub>20</sub> H <sub>26</sub> O <sub>3</sub>	nd-1.3 (0.73)	nd

**Triterpenoids and alteration products (µg g<sup>-1</sup> OC)**

Lupeol	C <sub>30</sub> H <sub>50</sub> O	nd-4.83 (0.690)	30.5-118 (66.0)
Cholesterol	C <sub>27</sub> H <sub>46</sub> O	nd-44.6 (7.02)	nd-299 (154)
4-Cholesten-3-one	C <sub>27</sub> H <sub>44</sub> O	nd-48.2 (6.91)	nd-726 (104)
Urs-12-en-one (α-amyrenone)	C <sub>30</sub> H <sub>48</sub> O	nd-6.53 (0.949)	nd-311 (126)

**Phenols and alteration products (mg g<sup>-1</sup> OC)**

Vanillin	C <sub>8</sub> H <sub>8</sub> O	3.9-19 (12)	31-142 (93)
Vanillic acid	C <sub>8</sub> H <sub>8</sub> O <sub>4</sub>	2.4-5.8 (4.0)	2.2-5.7 (3.9)
Homovanillic acid	C <sub>9</sub> H <sub>10</sub> O <sub>4</sub>	0.49-1.3 (1.0)	0.25-0.74 (0.42)

Vanillyl acetic acid	C <sub>9</sub> H <sub>10</sub> O <sub>5</sub>	0.19-1.5 (0.64)	nd-1.1 (0.28)
Homovanillyl alcohol	C <sub>10</sub> H <sub>14</sub> O <sub>3</sub>	nd-0.96 (0.48)	nd-0.39 (0.097)
Methyl homovanillate	C <sub>10</sub> H <sub>12</sub> O <sub>4</sub>	nd-0.073 (0.010)	nd-0.14 (0.054)
3-Vanillylpropanol	C <sub>10</sub> H <sub>14</sub> O <sub>3</sub>	0.63-2.8 (2.3)	0.89-1.2 (1.1)
Coniferyl aldehyde	C <sub>10</sub> H <sub>10</sub> O <sub>3</sub>	nd-0.16 (0.023)	0.067-0.39 (0.18)
Coniferyl alcohol	C <sub>10</sub> H <sub>12</sub> O <sub>3</sub>	0.14-2.1 (0.77)	nd-0.019 (0.0076)
Syringaldehyde	C <sub>9</sub> H <sub>10</sub> O <sub>4</sub>	nd-0.75 (0.38)	0.00096-14 (5.1)
Syringic acid	C <sub>9</sub> H <sub>10</sub> O <sub>5</sub>	0.39-2.1 (0.98)	0.56-1.6 (1.1)
Sinapyl alcohol	C <sub>11</sub> H <sub>14</sub> O <sub>4</sub>	0.017-0.20 (0.090)	nd-0.27 (0.089)
Sinapic acid	C <sub>11</sub> H <sub>12</sub> O <sub>5</sub>	0.0057-0.0088 (0.0073)	0.0036-0.010 (0.0063)
<i>p</i> -Ethylguaiaicol	C <sub>9</sub> H <sub>12</sub> O <sub>2</sub>	nd-0.11 (0.036)	nd-0.16 (0.033)
<i>m</i> -Guaiacol	C <sub>7</sub> H <sub>8</sub> O <sub>2</sub>	nd-0.096 (0.016)	nd-0.20 (0.084)
Guaiacyl acetone	C <sub>10</sub> H <sub>12</sub> O <sub>3</sub>	nd-1.1 (0.61)	nd
<i>p</i> -Coumaric acid	C <sub>9</sub> H <sub>8</sub> O <sub>3</sub>	0.25-1.0 (0.61)	nd-0.38 (0.13)
(±)- $\alpha$ -Tocopherol (Vitamin E)	C <sub>29</sub> H <sub>50</sub> O <sub>2</sub>	nd-0.30 (0.062)	0.23-1.1 (0.79)
3-Hydroxybenzoic acid	C <sub>7</sub> H <sub>6</sub> O <sub>3</sub>	nd-0.59 (0.30)	nd-0.53 (0.34)
4-Hydroxybenzoic acid	C <sub>7</sub> H <sub>6</sub> O <sub>3</sub>	0.11-1.2 (0.39)	0.37-0.98 (0.71)
Benzoic acid	C <sub>7</sub> H <sub>6</sub> O <sub>2</sub>	0.009-0.19 (0.053)	0.035-1.3 (0.56)
Resorcinol	C <sub>6</sub> H <sub>6</sub> O <sub>2</sub>	1.1-3.0 (2.3)	0.30-1.4 (0.77)
2-Methoxyresorcinol	C <sub>7</sub> H <sub>8</sub> O <sub>3</sub>	nd-0.11 (0.016)	nd
5-Methylresorcinol	C <sub>7</sub> H <sub>8</sub> O <sub>2</sub>	nd-2.7 (0.39)	nd
Catechol	C <sub>6</sub> H <sub>6</sub> O <sub>2</sub>	4.9-6.8 (5.7)	2.4-9.8 (5.4)
4-Methylcatechol	C <sub>7</sub> H <sub>8</sub> O <sub>2</sub>	1.1-6.1 (3.7)	0.54-6.1 (3.2)
3-Methylcatechol	C <sub>7</sub> H <sub>8</sub> O <sub>2</sub>	nd-3.4 (1.1)	nd-4.6 (2.1)
4-Ethylcatechol	C <sub>8</sub> H <sub>10</sub> O <sub>2</sub>	nd-0.23 (0.042)	nd
Pyrogallol	C <sub>9</sub> H <sub>14</sub> O <sub>3</sub>	1.1-6.1 (4.0)	nd-2.1 (0.77)
Isoeugenol	C <sub>10</sub> H <sub>12</sub> O <sub>2</sub>	nd	nd-2.0 (0.86)
Hydroquinone	C <sub>6</sub> H <sub>4</sub> (OH) <sub>2</sub>	0.96-4.2 (2.7)	nd-3.0 (1.4)
<i>trans</i> -Cinnamic acid	C <sub>9</sub> H <sub>8</sub> O <sub>2</sub>	0.27-0.49 (0.38)	0.16-0.37 (0.25)
<i>Other phenols</i>		0.052-1.7 (1.3)	0.15-1.6 (0.61)

#### Carbohydrates and polyols (mg g<sup>-1</sup> OC)

Galactosan	C <sub>6</sub> H <sub>10</sub> O <sub>5</sub>	3.8-9.1 (6.2)	2.1-7.2 (4.2)
Mannosan	C <sub>6</sub> H <sub>10</sub> O <sub>5</sub>	5.1-13 (8.4)	3.6-9.1 (5.6)
Levoglucozan	C <sub>6</sub> H <sub>10</sub> O <sub>5</sub>	8.8-22 (14)	5.2-18 (9.7)
l-Lyxose	C <sub>5</sub> H <sub>10</sub> O <sub>5</sub>	nd-	nd-3.9 (0.55)
D-(-)-Ribose	C <sub>5</sub> H <sub>10</sub> O <sub>5</sub>	nd-0.46 (0.30)	nd-0.61 (0.20)
D-Galactose	C <sub>6</sub> H <sub>12</sub> O <sub>6</sub>	nd-0.027 (0.0039)	nd-0.016 (0.0022)
Glucose	C <sub>6</sub> H <sub>12</sub> O <sub>6</sub>	nd-0.091 (0.044)	nd-0.057 (0.014)
Inositol	C <sub>6</sub> H <sub>12</sub> O <sub>6</sub>	0.033-0.081 (0.049)	nd-0.032 (0.012)
D-(+)-Arabitol	C <sub>5</sub> H <sub>12</sub> O <sub>5</sub>	nd-0.22 (0.14)	nd-0.14 (0.077)
D-Mannitol	C <sub>6</sub> H <sub>14</sub> O <sub>6</sub>	0.043-0.10 (0.060)	0.0074-0.065 (0.031)
Xylitol	C <sub>5</sub> H <sub>12</sub> O <sub>5</sub>	nd	nd-0.24 (0.034)
Ribitol	C <sub>5</sub> H <sub>12</sub> O <sub>5</sub>	nd	nd-0.044 (0.0062)

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Sucrose	C <sub>12</sub> H <sub>22</sub> O <sub>11</sub>	nd	nd-0.015 (0.0038)
Maltose	C <sub>12</sub> H <sub>22</sub> O <sub>11</sub>	0.10-0.65 (0.25)	nd-0.25 (0.072)
<i>Other sugars</i>		1.6-8.4 (5.0)	nd-2.5 (1.0)
<b>Phthalates (µg g<sup>-1</sup> OC)</b>			
Dibutyl phthalate	C <sub>16</sub> H <sub>22</sub> O <sub>4</sub>	1.99-13.5 (4.97)	2.12-13.9 (5.33)
Isooctyl phthalate	C <sub>24</sub> H <sub>38</sub> O <sub>4</sub>	nd-231 (33.0)	nd-779 (286)
Diocetyl phthalate	C <sub>24</sub> H <sub>38</sub> O <sub>4</sub>	4.32-28.0 (10.4)	1.85-8.32 (3.59)
<b>Other compounds (mg g<sup>-1</sup> OC)</b>			
<i>cis</i> -Pinonic acid	C <sub>10</sub> H <sub>16</sub> O <sub>3</sub>	0.024-0.041 (0.034)	0.025-0.066 (0.036)
Pinic acid	C <sub>11</sub> H <sub>18</sub> O <sub>4</sub>	0.54-1.5 (1.0)	0.28-0.98 (0.62)
D-Glucuronic acid lactone	C <sub>6</sub> H <sub>8</sub> O <sub>6</sub>	0.0092-0.022 (0.015)	0.0046-0.14 (0.027)
D-Glucuronic acid	C <sub>6</sub> H <sub>10</sub> O <sub>7</sub>	0.0027-0.020 (0.0083)	0.0078-0.021 (0.011)
2-Pentenoic acid	C <sub>5</sub> H <sub>8</sub> O <sub>2</sub>	nd-0.0072 (0.0018)	nd-0.020 (0.0068)
2-Furoic acid	C <sub>5</sub> H <sub>4</sub> O <sub>3</sub>	0.66-1.4 (1.1)	0.35-0.83 (0.58)
Benzeneacetic acid	C <sub>8</sub> H <sub>8</sub> O <sub>2</sub>	nd-0.36 (0.23)	0.031-0.27 (0.13)
Benzenepropanoic acid	C <sub>9</sub> H <sub>10</sub> O <sub>2</sub>	nd-0.52 (0.24)	nd-0.51 (0.31)
Hydrocinnamic acid	C <sub>6</sub> H <sub>10</sub> O <sub>2</sub>	nd-0.34 (0.079)	nd-0.64 (0.14)
Ferulic acid	C <sub>10</sub> H <sub>10</sub> O <sub>4</sub>	0.065-0.35 (0.24)	nd-0.12 (0.052)
Laevulic acid	C <sub>5</sub> H <sub>8</sub> O <sub>3</sub>	nd-0.53 (0.22)	nd
Furan-3-carboxylic acid	C <sub>26</sub> H <sub>20</sub> N <sub>2</sub> O <sub>3</sub>	nd-0.034 (0.016)	nd
3-Hydroxypyridine	C <sub>5</sub> H <sub>4</sub> O <sub>3</sub>	nd-8.4 (5.9)	nd-4.5 (3.0)
<i>p</i> -Hydroxyacetophenone	C <sub>8</sub> H <sub>8</sub> O <sub>2</sub>	nd	nd-0.91 (0.55)
Benzaldehyde	C <sub>7</sub> H <sub>6</sub> O	0.35-0.93 (0.48)	0.022-0.19 (0.091)
Nitriles		nd-0.53 (0.30)	0.082-0.57 (0.27)
Methyl esters of acids		1.2-3.1 (2.4)	1.1-3.4 (1.8)

nd - not detected

## Supplementary Material A3

### Supplementary Information from Chapter 5.

#### Meteorological analysis

Synoptic analysis ([www.wetterzentrale.de](http://www.wetterzentrale.de)) showed the presence of high pressures affecting the Iberian Peninsula over the period during which sampling of wildfire plumes was carried out. A clear influence of an Atlantic high pressure centre was observed during the sampling days, generating high temperatures, a great stability and no rain. This situation hinders the dispersive capacity of the atmosphere. Because of the isobars configuration and their duration, these atmospheric conditions are typical of Iberian Peninsula summers.

During wildfire events, at 850 hPa, a ridge from Africa entered warm air to the north, affecting the whole Peninsula. For several days during the period of study, at 700 hPa, there was wetter air in some areas of the Peninsula than around, but not affecting the Portuguese territory (only barely on 31<sup>th</sup> August).

At surface level, the isobars configuration, frequently not very well defined and separated, suggests that there were calm or weak winds. At height level, winds are also weak, except for 17<sup>th</sup> July, 31<sup>th</sup> August and 1<sup>st</sup> of September. For these three days, closely spaced contours indicate stronger winds (Figure A3.1).

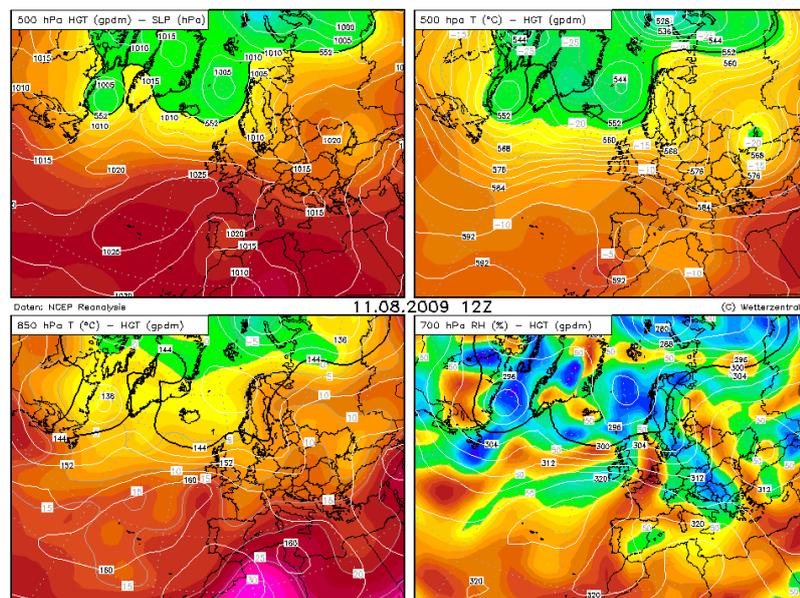


Figure A3.1 Synoptic situation on 11<sup>th</sup> August 2009 at 12Z at 500 hPa, 700 hPa and 850 hPa.

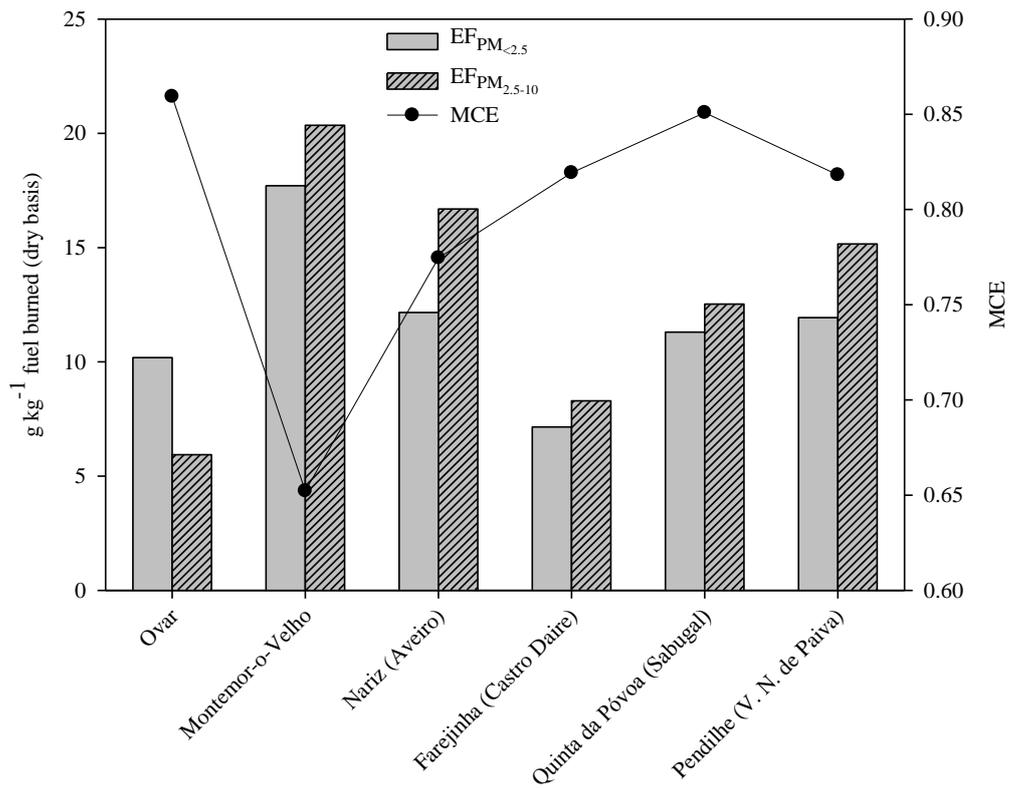


Figure A3.2 PM<sub>2.5</sub> and PM<sub>2.5-10</sub> emission factors as a function of modified combustion efficiency.

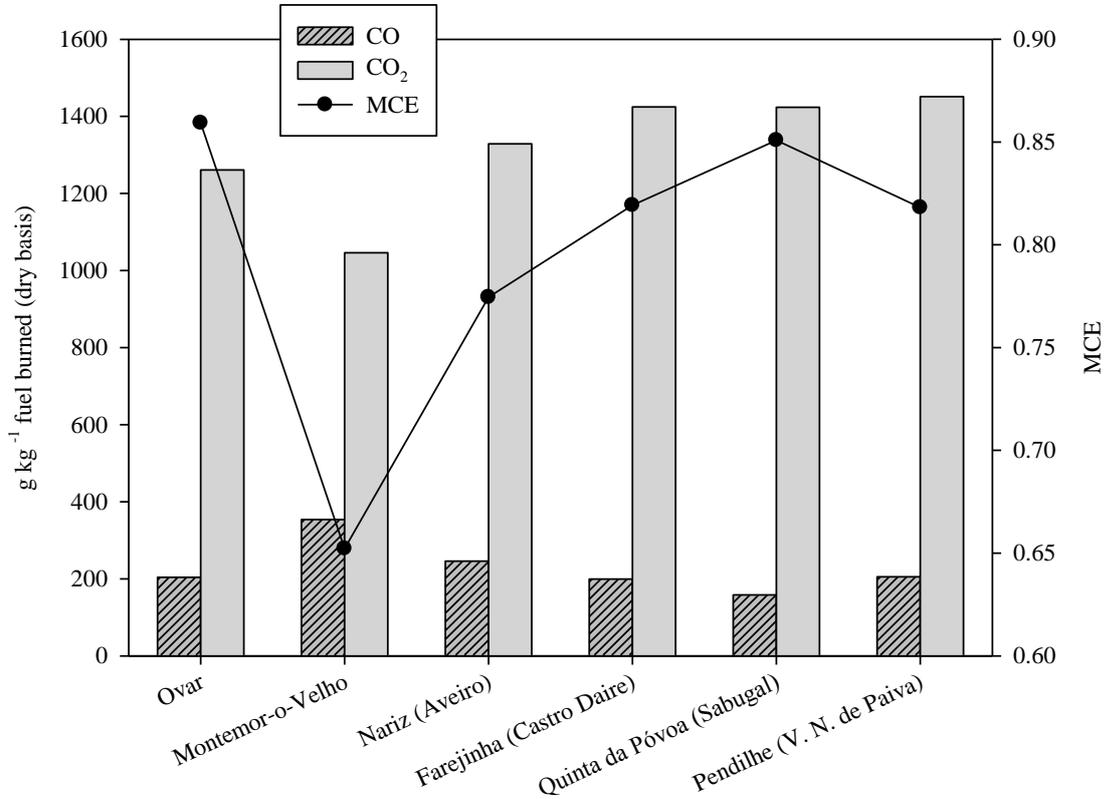


Figure A3.3 Carbon oxides emission factors as a function of modified combustion efficiency.

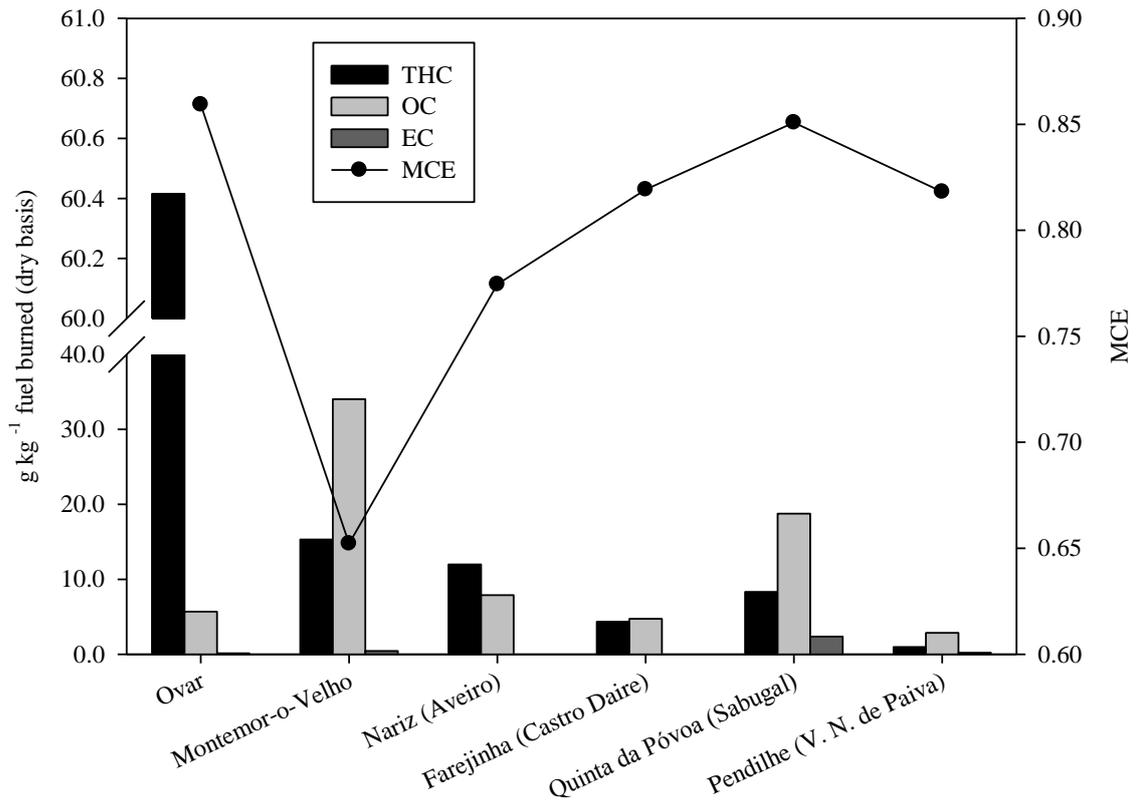


Figure A3.4 Total hydrocarbons, OC and EC emission factors as a function of modified combustion efficiency.

The concentrations of all organic compounds from Chapter 5.

Table A3. Detailed speciation of organic compounds in smoke particles (mg g<sup>-1</sup> OC).

Wildfires	PM <sub>2.5</sub>							Pendilhe (V. N. de Paiva)
	Ovar	Montemor-o- Velho	Nariz (Aveiro)	Cinfães (Viseu)	Farejinha (Castro Daire)	Quinta da Póvoa (Sabugal)		
Compounds	Formula							
<b>Alkanes</b>								
Pentadecane	C <sub>15</sub> H <sub>32</sub>	--- -0.0049	0.00048	---	---	---	---	---
Hexadecane	C <sub>16</sub> H <sub>34</sub>	0.061-.087	0.0033-0.011	---	---	---	---	---
Heptadecane	C <sub>17</sub> H <sub>36</sub>	0.082-0.58	0.018-0.031	---	---	0.015-0.029	---	---
Octadecane	C <sub>18</sub> H <sub>38</sub>	0.31-0.62	0.035-0.046	--- -0.018	---	---	---	---
Nonadecane	C <sub>19</sub> H <sub>40</sub>	0.73-1.3	0.11-0.14	0.0018-0.061	---	0.0030-0.0046	---	0.028
Eicosane	C <sub>20</sub> H <sub>42</sub>	1.2-1.8	0.26-0.32	0.033-0.11	---	0.020-0.024	---	0.10
Heneicosane	C <sub>21</sub> H <sub>44</sub>	1.5-2.0	0.59	0.054-0.11	0.031	0.058-0.078	---	0.17
Docosane	C <sub>22</sub> H <sub>46</sub>	1.4-2.0	0.44-0.66	0.030-0.12	0.0094	0.063-0.090	---	0.12
Tricosane	C <sub>23</sub> H <sub>48</sub>	1.3-2.0	0.42-0.58	--- -0.087	---	0.057-0.087	---	0.071
Tetracosane	C <sub>24</sub> H <sub>50</sub>	1.1-1.9	0.31-0.42	--- 0.037	---	0.014-0.060	---	---
Pentacosane	C <sub>25</sub> H <sub>52</sub>	1.4-2.0	0.26-0.38	--- -0.0048	---	0.0033-0.049	---	---
Hexacosane	C <sub>26</sub> H <sub>54</sub>	1.1-1.6	0.18-0.29	---	---	---	---	---
Heptacosane	C <sub>27</sub> H <sub>56</sub>	1.4-2.0	0.24-0.34	---	---	0.0046	---	---
Octacosane	C <sub>28</sub> H <sub>58</sub>	0.84-1.6	0.14-0.20	---	---	---	---	---
Nonacosane	C <sub>29</sub> H <sub>60</sub>	1.5-2.4	0.49-0.62	---	---	0.10-0.22	---	---
Hentriacontane	C <sub>31</sub> H <sub>64</sub>	0.54-0.87	0.63-1.0	---	---	0.13-0.20	---	---
Dotriacontane	C <sub>32</sub> H <sub>66</sub>	0.27-0.54	0.078-0.29	---	0.0062	0.015	---	---
Tritriacontane	C <sub>33</sub> H <sub>68</sub>	0.36-0.59	0.30-0.42	---	---	0.0024-0.012	0.0037-0.0043	---
Tetratriacontane	C <sub>34</sub> H <sub>70</sub>	0.16-0.36	+	0.0046	+	0.020	0.0011	0.035
<i>Other alkanes</i>		0.64-0.88	0.12-0.19	0.018-0.12	0.42	0.063-0.23	0.0051-0.010	0.16

<i>Branched alkanes</i>		0.070-0.36	0.053-0.062	0.19-0.25	1.9	0.33-0.78	0.20-0.34	0.30		
<b>Alkenes</b>										
Tetradecene	C <sub>14</sub> H <sub>28</sub>	0.0035-0.012	0.00025-0.0016	---	---	---	---	---		
Pentadecene	C <sub>15</sub> H <sub>30</sub>	0.0044-0.022	0.0022-0.0042	---	+	0.018	+	---		
Hexadecene	C <sub>16</sub> H <sub>32</sub>	0.034-0.063	0.0048-0.0081	---	---	---	---	---		
Heptadecene	C <sub>17</sub> H <sub>34</sub>	0.13-0.33	0.022-0.026	---	-0.0037	---	---	---		
Octadecene	C <sub>18</sub> H <sub>36</sub>	0.34-0.67	0.061-0.073	---	-0.050	---	---	---		
Nonadecene	C <sub>19</sub> H <sub>38</sub>	0.93-1.5	0.14-0.16	0.036-0.086	0.031	0.014-0.018	0.00054-0.0016	0.079		
Eicosene	C <sub>20</sub> H <sub>40</sub>	1.9-3.0	0.47-0.60	0.12-0.33	0.14	0.055-0.086	0.0026-0.0057	0.30		
Heneicosene	C <sub>21</sub> H <sub>42</sub>	1.5-1.9	0.82	0.18	0.12	0.072-0.085	0.0039-0.0069	0.24		
Tricosene	C <sub>23</sub> H <sub>46</sub>	1.2-1.7	0.42-0.62	0.094-0.16	0.095	0.076-0.11	0.0016-0.0051	0.24		
Tetracosene	C <sub>24</sub> H <sub>48</sub>	1.5-2.2	0.72-0.80	0.11-0.20	0.18	0.15-0.20	0.0035-0.0097	0.47		
Hexacosene	C <sub>26</sub> H <sub>52</sub>	1.4-2.3	0.24-0.41	0.041-0.12	0.21	0.13-0.17	0.0016-0.0031	0.44		
Octacosene	C <sub>28</sub> H <sub>56</sub>	+	+	0.026	0.035	0.0061-0.013	+	0.023		
Squalene	C <sub>30</sub> H <sub>50</sub>	+	+	---	+	0.010-0.013	---	0.014		
<i>Other alkenes</i>		6.5-10	1.8-2.6	0.31-0.54	0.70	0.37-0.54	0.0065-0.013	1.3		
<i>Branched alkenes</i>		1.6-1.9	0.054-0.058	0.0015-0.14	0.042	0.021-0.041	---	-0.00051	0.033	
<b>PAHs</b>										
Naphthalene	C <sub>10</sub> H <sub>8</sub>	0.055-0.10	---	-0.030	0.0038-0.034	0.027	0.017-0.032	0.011-0.012	0.092	
Acenaphthylene	C <sub>12</sub> H <sub>8</sub>	0.0010-0.019	0.0039	0.00	0.0008	0.00034-0.00039	0.00091-0.0087	0.00067		
Acenaphthene	C <sub>12</sub> H <sub>10</sub>	+	+	+	0.00045	0.000086-0.000087	---	+		
Fluorene	C <sub>13</sub> H <sub>10</sub>	0.0090-0.077	---	-0.0046	0.00059-0.0049	0.00046	0.00028-0.00039	0.00033-0.0016	0.00090	
Phenanthrene	C <sub>14</sub> H <sub>10</sub>	0.15-0.56	---	-0.11	0.0039-0.041	0.0048	0.0028-0.0040	0.0093-0.013	0.012	
Anthracene	C <sub>14</sub> H <sub>10</sub>	0.026-0.10	---	-0.0061	0.00043-0.0083	0.0007	0.00036-0.00063	0.0018-0.0021	0.0019	
Fluoranthene	C <sub>16</sub> H <sub>10</sub>	0.14-0.27	0.024	0.0064-0.019	0.023	0.0072-0.021	0.016-0.017	0.041		
Pyrene	C <sub>16</sub> H <sub>10</sub>	0.20-0.22	0.012	0.0028-0.057	0.042	0.0071-0.012	0.0094-0.010	0.028		
<i>p</i> -terphenyl	C <sub>18</sub> H <sub>14</sub>	0.065-0.25	---	-0.0028	0.00036-0.0014	---	0.000042-0.00029	---	-0.000027	0.000061
Retene	C <sub>18</sub> H <sub>18</sub>	0.38-1.0	3.4-8.9	1.7-4.1	0.77	0.49-0.59	0.76-0.80	2.1		
Benzo[a]anthracene	C <sub>18</sub> H <sub>12</sub>	0.048-0.071	0.012	0.0022-0.0045	0.014	0.0074-0.017	0.0034-0.0039	0.0069		

## Supplementary Material

Chrysene	C <sub>18</sub> H <sub>12</sub>	0.12-0.17	--- -0.023	0.0064-0.012	0.027	0.014-0.029	0.0049-0.0078	0.014
Benzo[b]fluoranthene	C <sub>20</sub> H <sub>12</sub>	0.019-0.024	--- -0.0023	0.00048-0.00060	0.0048	0.0073-0.018	0.0015-0.0018	0.0039
Benzo[j]fluoranthene	C <sub>20</sub> H <sub>12</sub>	0.044-0.12	--- -0.0072	0.0014-0.0025	0.016	0.0060-0.014	0.0016-0.0018	0.0026
Benzo[k]fluoranthene	C <sub>20</sub> H <sub>12</sub>	0.0044-0.0062	--- -0.0017	0.00058-0.00066	0.013	0.0065-0.0084	0.0016-0.0017	0.0016
Benzo[e]pyrene	C <sub>20</sub> H <sub>12</sub>	0.025-0.034	--- -0.0021	0.00048-0.0024	0.0045	0.0078-0.015	0.0011-0.0014	0.0038
Benzo[a]pyrene	C <sub>20</sub> H <sub>12</sub>	0.022-0.034	--- -0.0075	0.0013-0.0021	0.0085	0.0057-0.013	0.0025-0.0028	0.0051
Perylene	C <sub>20</sub> H <sub>12</sub>	0.0040-0.0085	--- -0.0034	0.00043-0.00062	0.0017	0.0018-0.0039	0.00045	0.00092
Indeno(1,2,3-cd)pyrene	C <sub>22</sub> H <sub>12</sub>	0.0037-0.0086	0.0025	0.00037-0.00048	---	0.00085-0.0023	0.0011-0.0013	0.0030
Benzo[a,h]anthracene	C <sub>22</sub> H <sub>14</sub>	0.0050-0.0063	0.00090	+	0.00083	0.0010-0.0024	0.00020-0.00026	0.00056
Benzo[ghi]perylene	C <sub>22</sub> H <sub>12</sub>	0.010-0.013	+	+	0.0029	0.0024-0.0050	0.0013-0.0016	+
<i>Other PAHs</i>		1.6-2.4	11-18	1.4-1.6	0.39	0.17-0.44	0.37-0.38	1.0
<b>Oxy-PAH</b>								
9-Fluorenone	C <sub>13</sub> H <sub>8</sub> O	0.33-1.2	0.041-0.18	0.011-0.080	0.0023	0.0034-0.0049	0.00088-0.0027	0.0037
9,10-Anthraquinone	C <sub>14</sub> H <sub>8</sub> O <sub>2</sub>	0.12-0.18	0.029	0.0082-0.017	0.0029	0.0012-0.0018	0.00078-0.0017	0.0033
2,6-Di-tert-butyl-1,4-Benzoquinone	C <sub>14</sub> H <sub>20</sub> O <sub>2</sub>	0.0040	--- -0.00007	---	---	---	---	---
<b>n-Alcohols</b>								
<i>n</i> -Decanol	C <sub>10</sub> H <sub>22</sub> O	0.41-2.8	0.14	0.067-0.13	+	+	+	0.039
<i>n</i> -Dodecanol	C <sub>12</sub> H <sub>26</sub> O	+	+	+	+	+	+	+
<i>n</i> -Tetradecanol	C <sub>14</sub> H <sub>30</sub> O	+	+	+	+	+	+	+
<i>n</i> -Pentadecanol	C <sub>15</sub> H <sub>32</sub> O	--- -0.61	--- -0.0023	0.033-0.070	---	0.014-0.064	0.0018-0.0022	0.17
<i>n</i> -Hexadecanol	C <sub>16</sub> H <sub>34</sub> O	0.27	0.43	--- -0.37	+	---	---	---
<i>n</i> -Heptadecanol	C <sub>17</sub> H <sub>36</sub> O	+	+	0.21-0.39	+	+	+	+
<i>n</i> -Octadecanol	C <sub>18</sub> H <sub>38</sub> O	0.0067-1.4	0.12-0.36	--- -1.4	---	--- -0.0030	--- -0.0020	---
<i>n</i> -Eicosanol	C <sub>20</sub> H <sub>42</sub> O	+	+	2.0	+	+	+	0.56
<i>n</i> -Heneicosanol	C <sub>21</sub> H <sub>44</sub> O	+	+	+	+	0.045	+	+
<i>n</i> -Docosanol	C <sub>22</sub> H <sub>46</sub> O	--- -2.8	0.042-0.70	0.29-0.95	0.39	0.27-0.38	0.040-0.041	1.3
<i>n</i> -Tricosanol	C <sub>23</sub> H <sub>48</sub> O	0.20	+	0.014-0.19	0.013	0.25	0.012-0.013	0.090
<i>n</i> -Tetracosanol	C <sub>24</sub> H <sub>50</sub> O	1.7	0.38	0.51-1.5	0.47	0.32-0.47	0.099	1.4
<i>n</i> -Pentacosanol	C <sub>25</sub> H <sub>52</sub> O	0.16	+	0.0047-0.066	0.031	0.0072-0.0083	0.00045-0.0015	0.070

<i>n</i> -Hexacosanol	C <sub>26</sub> H <sub>54</sub> O	0.049-1.7	+	0.18	0.47	0.20-0.28	0.043-0.045	0.96
<i>n</i> -Heptacosanol	C <sub>27</sub> H <sub>56</sub> O	0.0019-0.094	--- -0.0016	0.011-0.039	0.032	0.0050-0.0061	0.0022-0.0025	0.055
<i>n</i> -Octacosanol	C <sub>28</sub> H <sub>58</sub> O	0.044-1.4	0.0096-0.047	0.14-0.22	0.38	0.070-0.10	0.011-0.012	0.60
<i>n</i> -Nonacosanol	C <sub>29</sub> H <sub>60</sub> O	---	---	---	---	+	---	---
<i>n</i> -Triacontanol	C <sub>30</sub> H <sub>62</sub> O	0.066-0.69	0.013-0.32	0.12-0.54	0.89	0.047-0.076	0.015-0.028	0.44
<b>Other alcohols</b>								
(-)-Myrtenol	C <sub>10</sub> H <sub>16</sub> O	+	0.087-0.098	0.0030	+	+	+	+
Benzyl alcohol	C <sub>7</sub> H <sub>8</sub> O	0.0086-0.13	0.019-0.068	0.047-0.13	0.10	0.024-0.062	0.015-0.044	0.16
<i>cis</i> -2-Methylcyclohexanol	C <sub>7</sub> H <sub>14</sub> O	+	+	+	+	+	+	+
(1S,2S,3R,5S) -(+)-2,3-Pinandediol	C <sub>10</sub> H <sub>18</sub> O <sub>2</sub>	0.024	+	+	+	+	+	+
<b>Fatty alcohol</b>								
2-ethylhexanol	C <sub>8</sub> H <sub>18</sub> O	0.030-0.10	0.026-0.043	0.20-0.48	1.3	0.17-0.44	0.54-0.71	0.51
<b>Fatty acids</b>								
Methyl tetradecanoate	C <sub>15</sub> H <sub>30</sub> O <sub>2</sub>	+	+	+	+	+	+	+
Isopropyl Myristate	C <sub>17</sub> H <sub>34</sub> O <sub>2</sub>	+	+	0.035	+	+	+	+
<b><i>n</i>-Alkanoic acids</b>								
Hexanoic acid	C <sub>6</sub> H <sub>12</sub> O <sub>2</sub>	0.0062-0.020	+	+	+	+	+	+
Heptanoic acid	C <sub>7</sub> H <sub>14</sub> O <sub>2</sub>	0.015-0.033	0.020	0.0052-0.0091	+	0.0017	+	+
Octanoic acid	C <sub>8</sub> H <sub>16</sub> O <sub>2</sub>	0.11-0.36	0.00039-0.090	0.067-0.12	0.032	0.0054-0.010	0.0017-0.0041	0.12
Nonanoic acid	C <sub>9</sub> H <sub>18</sub> O <sub>2</sub>	0.17-0.45	0.00023-0.13	0.11-0.25	0.053	0.011-0.024	0.0018-0.0060	0.37
Decanoic acid	C <sub>10</sub> H <sub>20</sub> O <sub>2</sub>	0.26-0.63	0.00049-0.41	0.62-0.68	0.099	0.022-0.054	0.0020-0.0076	0.36
Undecanoic acid	C <sub>11</sub> H <sub>22</sub> O <sub>2</sub>	0.0047-0.044	0.75-0.90	0.0076-0.39	0.053	0.016-0.045	0.0023-0.0092	0.14
Dodecanoic Acid	C <sub>12</sub> H <sub>24</sub> O <sub>2</sub>	0.40-1.04	--- -3.5	0.87-1.8	---	0.23-0.44	---	0.82
Tridecanoic acid	C <sub>13</sub> H <sub>26</sub> O <sub>2</sub>	0.11-0.30	0.46	0.16-0.18	0.057	0.054-0.080	0.0037-0.0088	0.11
Tetradecanoic acid	C <sub>14</sub> H <sub>28</sub> O <sub>2</sub>	0.95-3.2	0.0030-3.6	0.96-1.7	2.4	0.40-0.75	0.090-0.091	1.6
Pentadecanoic acid	C <sub>15</sub> H <sub>30</sub> O <sub>2</sub>	0.36-1.1	0.00094-1.4	0.52-0.52	0.16	0.29-0.40	0.0061-0.026	0.69
Hexadecanoic acid	C <sub>16</sub> H <sub>32</sub> O <sub>2</sub>	1.5-4.8	0.26-6.4	2.0-2.0	2.3	1.0-1.7	0.21-0.26	3.6

## Supplementary Material

Heptadecanoic acid	C <sub>17</sub> H <sub>34</sub> O <sub>2</sub>	0.27-0.94	0.00048-0.96	0.22-0.38	0.15	0.21-0.22	0.0041-0.017	0.51
Octadecanoic acid	C <sub>18</sub> H <sub>36</sub> O <sub>2</sub>	0.53-2.4	0.17-2.2	0.45-0.78	0.36	0.31-0.48	0.11-0.12	0.99
Nonadecanoic acid	C <sub>19</sub> H <sub>38</sub> O <sub>2</sub>	0.011-0.20	0.00035-0.50	0.0088-0.093	0.11	0.13-0.16	0.0015-0.0065	0.064
Eicosanoic acid	C <sub>20</sub> H <sub>40</sub> O <sub>2</sub>	0.24-1.6	0.0019-2.9	1.2-1.4	0.49	0.38-0.61	0.0074-0.12	1.5
Heneicosanoic acid	C <sub>21</sub> H <sub>42</sub> O <sub>2</sub>	0.072-0.40	+	0.28	0.074	0.094-0.12	+	0.17
Docosanoic acid	C <sub>22</sub> H <sub>44</sub> O <sub>2</sub>	0.056-2.8	0.0032-0.050	0.17-1.8	0.72	0.40-0.58	0.017-0.17	1.0
Tricosanoic acid	C <sub>23</sub> H <sub>46</sub> O <sub>2</sub>	0.060-0.58	0.50	0.11-0.40	0.095	0.19-0.20	0.063	0.26
Tetracosanoic acid	C <sub>24</sub> H <sub>48</sub> O <sub>2</sub>	0.33-3.5	0.13-3.0	2.3-3.1	1.1	0.69-0.94	0.20-0.23	1.9
Pentacosanoic acid	C <sub>25</sub> H <sub>50</sub> O <sub>2</sub>	0.18-0.23	+	0.034-0.13	0.052	0.050-0.053	+	0.098
Hexacosanoic acid	C <sub>26</sub> H <sub>52</sub> O <sub>2</sub>	0.11-1.0	0.34	0.11-0.41	0.12	0.11-0.12	+	0.27
Heptacosanoic acid	C <sub>27</sub> H <sub>54</sub> O <sub>2</sub>	0.024-0.097	+	0.081	+	0.014-0.016	+	0.053
Octacosanoic acid	C <sub>28</sub> H <sub>56</sub> O <sub>2</sub>	0.039-0.51	0.16	0.068-0.32	0.10	0.083-0.087	+	0.28
Nonacosanoic acid	C <sub>29</sub> H <sub>58</sub> O <sub>2</sub>	0.016-0.022	0.085	0.12	+	0.016	+	0.062
Triacosanoic acid	C <sub>30</sub> H <sub>60</sub> O <sub>2</sub>	0.032-0.26	+	0.18	0.10	0.035-0.040	+	---
<b><i>n</i>-di-Acids</b>								
Propanedioic acid	C <sub>3</sub> H <sub>4</sub> O <sub>4</sub>	---	0.0013	---	---	---	---	0.0068
Butanedioic acid	C <sub>4</sub> H <sub>6</sub> O <sub>4</sub>	0.10-0.23	0.53-0.54	0.18-0.25	0.51	0.038-0.12	0.11-0.16	0.31
Pentanedioic acid	C <sub>5</sub> H <sub>8</sub> O <sub>4</sub>	0.028-0.28	0.15-0.45	0.14-0.24	0.19	0.016-0.037	0.11-0.12	0.12
Hexanedioic acid	C <sub>6</sub> H <sub>10</sub> O <sub>4</sub>	0.025-0.11	0.011-0.10	0.013-0.015	0.016	0.0056-0.012	0.0018-0.0054	0.024
Heptanedioic acid	C <sub>7</sub> H <sub>12</sub> O <sub>4</sub>	0.11-0.12	0.17-1.2	0.10-0.22	0.13	0.17	0.077-0.089	0.15
Octanedioic acid	C <sub>8</sub> H <sub>14</sub> O <sub>4</sub>	0.077-0.12	0.0081-0.13	+	0.28	0.049-0.056	0.036-0.047	0.21
Nonanedioic acid	C <sub>9</sub> H <sub>16</sub> O <sub>4</sub>	0.073-0.15	0.014-1.0	0.10-0.12	0.55	0.046-0.10	0.021-0.023	0.25
Decanedioic acid	C <sub>10</sub> H <sub>18</sub> O <sub>4</sub>	0.012-0.16	0.0017-0.13	0.020-0.022	0.060	0.011-0.021	0.0033-0.0049	0.050
Hexadecanedioic acid	C <sub>16</sub> H <sub>30</sub> O <sub>4</sub>	0.0097-0.066	0.00084-0.021	0.033-0.073	0.13	0.030-0.032	0.014-0.016	0.15
<b><i>n</i>-Alkenoic acids</b>								
Oleic acid(C <sub>18:1</sub> )	C <sub>18</sub> H <sub>34</sub> O <sub>2</sub>	0.62-2.5	--- -4.4	0.78-1.5	0.20	0.30-0.31	0.15-0.27	0.56
Linoleic acid (C <sub>18:2</sub> )	C <sub>18</sub> H <sub>32</sub> O <sub>2</sub>	0.18-0.72	0.0022-1.6	0.27-0.71	0.38	0.14-0.17	0.12-0.25	0.34
Palmitoleic acid (C <sub>16:1</sub> )	C <sub>16</sub> H <sub>30</sub> O <sub>2</sub>	0.099	+	+	+	0.030-0.047	+	+

**Dicarboxylic acids**

Methylmalonic acid	C <sub>4</sub> H <sub>6</sub> O <sub>4</sub>	0.008-0.026	0.00054-0.0049	0.0025-0.0038	0.011	--- -0.0010	0.00052	0.019
Pinic acid	C <sub>11</sub> H <sub>18</sub> O <sub>4</sub>	0.17-0.32	0.095-0.75	0.32-0.34	0.55	0.14-0.19	0.22-0.27	0.49

**Oxo-acids**

Levulinic acid	C <sub>5</sub> H <sub>8</sub> O <sub>3</sub>	0.15-0.42	0.048-0.15	0.24-0.27	0.15	0.015-0.016	0.030-0.045	0.38
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**Hydroxy-acids**

Glycolic acid	C <sub>2</sub> H <sub>4</sub> O <sub>3</sub>	0.094-0.60	0.92-1.2	0.57-1.4	0.28	0.083-0.12	0.12-0.19	0.39
L-(-)-Malic acid	C <sub>4</sub> H <sub>6</sub> O <sub>5</sub>	0.00044-0.0037	0.00090-0.0084	0.0012	0.0032	0.0020	0.00013-0.00045	0.017
2-Hydroxybutyric acid	C <sub>4</sub> H <sub>8</sub> O <sub>3</sub>	0.048-0.049	+	0.032	+	0.00008-0.0043	0.0038	0.0086
4-Hydroxybutyric acid	C <sub>4</sub> H <sub>8</sub> O <sub>3</sub>	+	+	+	+	+	+	+
Propanoic acid	C <sub>3</sub> H <sub>6</sub> O <sub>2</sub>	0.10	0.12-0.26	+	-	---	---	---

**Ketones**

$\gamma$ -Heptalactone	C <sub>7</sub> H <sub>12</sub> O <sub>2</sub>	0.00029	+	+	+	---	+	+
2-Decanone	C <sub>10</sub> H <sub>20</sub> O	0.028	+	+	+	+	+	+
2-Tridecanone	C <sub>13</sub> H <sub>26</sub> O	0.018-0.039	0.0066	0.0026-0.0029	0.0022	0.00047-0.00071	--- -0.000020	0.016
2-Pentadecanone	C <sub>15</sub> H <sub>30</sub> O	0.11-0.26	0.00076-0.036	0.035-0.041	0.012	0.0058-0.010	0.00015-0.00022	0.018
3-Hexadecanone	C <sub>16</sub> H <sub>32</sub> O	0.89-1.2	0.24	0.13-0.27	0.034	0.045-0.059	0.0024-0.0035	0.066
2-Octadecanone	C <sub>18</sub> H <sub>36</sub> O	0.13-0.20	0.00026-0.098	0.027-0.070	0.0065	0.012-0.019	+	0.011
2-Pentadecanone, 6,10,14-trimethyl-	C <sub>18</sub> H <sub>38</sub> O	0.86-1.3	0.38	0.10-0.12	0.084	0.074-0.082	0.0094	0.12
Benzophenone	C <sub>13</sub> H <sub>10</sub> O	+	+	+	+	+	+	+
1-(10-Methylanthracen-9-yl)ethanone	C <sub>17</sub> H <sub>14</sub> O	+	1.60	0.17	+	0.022-0.024	+	+
<i>Other Ketones</i>		1.8-3.4	--- -1.9	0.40-0.52	0.26	0.20-0.24	---	0.44

***n*-Alkanals**

Decanal	C <sub>10</sub> H <sub>20</sub> O	+	+	+	+	0.0010	0.0044	+
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**Terpenoids**

Isopulegol	C <sub>10</sub> H <sub>18</sub> O	0.0024	+	0.00026-0.00085	0.00083	0.00053	+	0.0023
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Supplementary Material

$\beta$ -Amyrin	C <sub>30</sub> H <sub>50</sub> O	+	0.18	+	+	0.0057	+	+
Eucalyptol	C <sub>10</sub> H <sub>18</sub> O	0.00069	0.0038	0.00033-0.0010	+	+	+	0.0017
<b>Steroids and alteration products</b>								
Stigmasterol	C <sub>29</sub> H <sub>48</sub> O	0.038	0.11	0.030-0.042	0.026	0.016-0.017	0.0026-0.0033	0.061
$\beta$ -Sitosterol	C <sub>29</sub> H <sub>50</sub> O	0.00081-0.18	0.69	0.18-0.20	0.20	0.043-0.060	0.32-0.041	0.24
Stigmasta-3,5-dien-7-one	C <sub>29</sub> H <sub>46</sub> O	--- -0.072	--- -0.48	--- -0.11	0.24	0.023-0.16	--- -0.035	0.21
Stigmast-4-en-3-one	C <sub>29</sub> H <sub>48</sub> O	0.21	0.51	0.21-0.26	0.15	0.028	+	+
Stigmastan-3,5-diene	C <sub>29</sub> H <sub>48</sub>	+	+	+	+	0.088-0.11	0.0069	+
<b>Triterpenoids and alteration products</b>								
4-Cholesten-3-one	C <sub>27</sub> H <sub>44</sub> O	0.013-0.048	0.037	0.0089	+	0.0014-0.0028	+	+
Urs-12-en-one ( $\alpha$ -amyrenone)	C <sub>30</sub> H <sub>48</sub> O	0.034-0.18	0.10	0.0019-0.0030	0.0045	0.0028-0.010	0.00022-0.0057	0.0028
Lupeol	C <sub>30</sub> H <sub>50</sub> O	0.089	0.091	0.031-0.043	0.019	0.0044-0.0063	0.0054-0.0094	0.036
Cholesterol	C <sub>27</sub> H <sub>46</sub> O	0.089	+	+	+	0.0030	+	0.010
<b>Diterpenoids and alteration products</b>								
Isopimaric	C <sub>20</sub> H <sub>30</sub> O <sub>2</sub>	0.43	1.4	0.70-0.74	0.096	0.23-0.25	1.3-1.8	0.49
Pimaric acid	C <sub>20</sub> H <sub>30</sub> O <sub>2</sub>	+	1.0	0.56-0.81	0.069	0.18-0.28	--- -0.58	0.60
Abietic acid	C <sub>20</sub> H <sub>30</sub> O <sub>2</sub>	+	0.0032-3.8	0.46-0.66	0.037	0.10-0.16	0.59-1.7	0.29
Methyl dehydroabietate	C <sub>21</sub> H <sub>30</sub> O <sub>2</sub>	--- -0.25	4.8-4.9	0.017-0.50	0.10	0.17-0.26	0.34-0.70	0.30
Dehydroabietic acid	C <sub>20</sub> H <sub>28</sub> O <sub>2</sub>	--- -2.0	1.7-25	5.0-5.0	1.1	1.2-2.3	4.0-4.5	6.3
7-Oxodehydroabietic acid	C <sub>20</sub> H <sub>26</sub> O <sub>3</sub>	+	1.8	+	+	+	+	+
<b>Phenols and alteration products</b>								
Vanillin	C <sub>8</sub> H <sub>8</sub> O	--- -9.2	2.9-21	5.1-5.1	3.6	0.95-1.2	0.000010-1.4	5.0
Vanillic acid	C <sub>8</sub> H <sub>8</sub> O <sub>4</sub>	0.66-1.3	4.6-6.7	1.6-2.3	2.7	0.70-1.1	0.60-0.78	1.5
Homovanillic acid	C <sub>9</sub> H <sub>10</sub> O <sub>4</sub>	0.16-0.26	1.4-2.0	0.29-0.34	0.38	0.13-0.23	0.15-0.20	0.43
Vanillyl acetic acid	-	--- -0.079	--- -1.7	0.56-0.32	---	---	0.32-0.33	---
Homovanillyl alcohol	C <sub>10</sub> H <sub>14</sub> O <sub>3</sub>	+	+	0.12	+	+	0.11-0.12	+

Methyl homovanillate	C <sub>10</sub> H <sub>12</sub> O <sub>4</sub>	+	+	+	+	+	+	+
3-Vanillylpropanol	C <sub>10</sub> H <sub>14</sub> O <sub>3</sub>	0.26-0.58	2.8-4.4	0.59-0.64	0.54	0.13-0.14	0.81-0.98	0.20
Coniferyl aldehyde	C <sub>10</sub> H <sub>10</sub> O <sub>3</sub>	1.50	+	0.010-0.037	+	0.0012	0.00048-0.00055	+
Coniferyl alcohol	C <sub>10</sub> H <sub>12</sub> O <sub>3</sub>	0.015-0.020	0.18-0.24	0.029-0.036	0.012	0.0046-0.0049	0.022-0.031	0.023
Syringaldehyde	C <sub>9</sub> H <sub>10</sub> O <sub>4</sub>	0.25	1.90	0.0015	0.0012	0.00023-0.00047	0.00045	+
Syringic acid	C <sub>9</sub> H <sub>10</sub> O <sub>5</sub>	0.43-0.64	0.081-2.2	0.094-0.31	1.2	0.51-1.0	0.038-0.052	0.61
Sinapyl alcohol	C <sub>11</sub> H <sub>14</sub> O <sub>4</sub>	0.0036-0.0052	0.0061-0.0091	--- -0.00052	0.0024	--- -0.00012	0.000036- 0.00083	---
Sinapic acid	C <sub>11</sub> H <sub>12</sub> O <sub>5</sub>	0.0013-0.0042	0.00081-0.0096	0.0011-0.0014	0.012	0.0032-0.0054	0.00072-0.00076	0.0050
<i>p</i> -Ethylguaiacol	C <sub>9</sub> H <sub>12</sub> O <sub>2</sub>	+	+	+	+	+	+	+
(±)- $\alpha$ -Tocopherol = Vitamin E	C <sub>29</sub> H <sub>50</sub> O <sub>2</sub>	0.19-0.21	0.0025-0.19	0.0099-0.052	0.087	0.0041-0.018	0.0026	0.046
3-Hydroxybenzoic acid	C <sub>7</sub> H <sub>6</sub> O <sub>3</sub>	0.27-0.34	0.43	0.22-0.28	+	0.10-0.16	0.064-0.072	0.22
4-Hydroxybenzoic acid	C <sub>7</sub> H <sub>6</sub> O <sub>3</sub>	0.024-0.62	0.0099-0.46	0.27-0.52	1.1	0.16-0.34	0.14-0.21	0.58
Benzoic acid	C <sub>7</sub> H <sub>6</sub> O <sub>2</sub>	2.8-3.3	0.64-1.5	0.75-0.81	0.55	0.15-0.30	0.13-0.22	0.82
Resorcinol	C <sub>6</sub> H <sub>6</sub> O <sub>2</sub>	1.5-1.9	0.71-0.89	0.12-0.25	0.15	0.095-0.14	0.11-0.12	0.37
5-methylresorcinol	C <sub>7</sub> H <sub>8</sub> O <sub>2</sub>	1.3-3.6	2.1-4.5	0.78-1.5	0.083	0.037-0.20	0.42-0.46	1.4
Catechol	C <sub>6</sub> H <sub>6</sub> O <sub>2</sub>	0.35-0.69	0.61-1.0	0.46	+	+	0.13-0.14	+
3-Methylcatechol	C <sub>7</sub> H <sub>8</sub> O <sub>2</sub>	0.97-1.8	0.54-1.8	0.14-0.45	0.18	0.17-0.20	0.52-0.54	1.0
4-methylcatechol	C <sub>7</sub> H <sub>8</sub> O <sub>2</sub>	+	+	+	+	+	+	+
Pyrogallol	C <sub>9</sub> H <sub>14</sub> O <sub>3</sub>	0.083-0.62	1.6-2.1	0.41	+	0.079-0.20	0.49-0.53	0.55
<i>trans</i> -Cinnamic acid	C <sub>9</sub> H <sub>8</sub> O <sub>2</sub>	+	+	0.16	+	+	0.074	+
Isoeugenol	C <sub>10</sub> H <sub>12</sub> O <sub>2</sub>	0.057-0.12	0.0061-0.067	0.090-0.12	0.034	0.011-0.025	0.016-0.023	0.078
Hydroquinone	C <sub>6</sub> H <sub>4</sub> (OH) <sub>2</sub>	0.82-0.95	1.6-2.0	0.26-1.4	0.11	0.10-0.13	0.16-0.18	0.35
<b>Carbohydrates</b>								
Galactosan	C <sub>6</sub> H <sub>10</sub> O <sub>5</sub>	0.46-1.1	8.0-11	1.3-1.8	1.8	0.59-0.78	1.1-1.4	1.6
Mannosan	C <sub>6</sub> H <sub>10</sub> O <sub>5</sub>	0.70-1.4	12-16	2.0-3.0	2.4	--- -0.77	1.7-2.6	2.4
Levoglucosan	C <sub>6</sub> H <sub>10</sub> O <sub>5</sub>	3.2-4.3	20-30	3.0-5.3	7.2	2.3-2.4	2.6-4.4	9.4
Glycerol	C <sub>3</sub> H <sub>8</sub> O <sub>3</sub>	0.067	0.054-0.090	---	-	---	---	---
Erythrose	C <sub>4</sub> H <sub>8</sub> O <sub>4</sub>	0.98-1.2	6.7	1.2-1.6	+	+	0.46-0.65	1.3
Erythritol	C <sub>4</sub> H <sub>10</sub> O <sub>4</sub>	+	+	+	+	+	0.32	+

## Supplementary Material

Arabinose	C <sub>5</sub> H <sub>10</sub> O <sub>5</sub>	+	+	+	+	+	+	+
l-Lyxose	C <sub>5</sub> H <sub>10</sub> O <sub>5</sub>	+	+	+	+	+	+	+
D-(-)-Ribose	C <sub>5</sub> H <sub>10</sub> O <sub>5</sub>	--- -0.62	0.99-1.2	0.11-0.15	---	0.041-0.073	--- -0.087	0.12
Xylitol	C <sub>5</sub> H <sub>12</sub> O <sub>5</sub>	0.091-0.16	+	---	+	+	+	+
D-(+)-Arabitol	C <sub>5</sub> H <sub>12</sub> O <sub>5</sub>	0.032-0.043	0.20-0.29	0.035-0.052	0.044	0.018-0.023	0.045-0.053	0.071
Ribitol	C <sub>5</sub> H <sub>12</sub> O <sub>5</sub>	+	0.13	+	+	+	+	+
D-Mannitol	C <sub>6</sub> H <sub>14</sub> O <sub>6</sub>	+	+	+	+	+	+	0.030
Sorbitol	C <sub>6</sub> H <sub>14</sub> O <sub>6</sub>	+	+	+	+	+	+	+
D-Galactose	C <sub>6</sub> H <sub>12</sub> O <sub>6</sub>	--- -0.015	0.071-0.076	---	---	0.0069-0.015	--- -0.014	0.034
Glucose	C <sub>6</sub> H <sub>12</sub> O <sub>6</sub>	+	+	+	+	+	0.0055	+
Inositol	C <sub>6</sub> H <sub>12</sub> O <sub>6</sub>	+	0.021-0.026	+	+	+	+	0.018
Sucrose	C <sub>12</sub> H <sub>22</sub> O <sub>11</sub>	0.020-0.027	+	+	+	+	+	+
Maltose	C <sub>12</sub> H <sub>22</sub> O <sub>11</sub>	+	0.15	0.029	+	+	0.040-0.054	+
D-Erythronic acid $\gamma$ -lactone	C <sub>4</sub> H <sub>6</sub> O <sub>4</sub>	+	0.41-0.64	0.15-0.16	+	0.047	0.056-0.095	+
<b>Other Aldehydes</b>		--- -6.2	+	0.64-1.0	1.9	0.87-1.5	---	3.5
<b>Methyl esters</b>		2.3-4.2	1.5-2.2	0.71-1.1	0.35	0.30-0.51	0.033-0.038	0.83
<b>Other Phenols</b>								
Phenol, 2,4-di-ter-butyl	C <sub>14</sub> H <sub>22</sub> O	0.43	+	---	---	---	---	---
4-Octylphenol	C <sub>14</sub> H <sub>22</sub> O	+	+	+	+	+	+	+
<i>Other Phenols</i>		0.098-0.30	--- -0.14	--- -0.0013	---	--- -0.0022	---	---
<b>Other compounds</b>								
5 $\alpha$ -Cholestan-3 $\beta$ -ol	C <sub>27</sub> H <sub>48</sub> O	+	0.05	0.025	0.086	---	+	0.027
Lactic acid	C <sub>3</sub> H <sub>6</sub> O <sub>3</sub>	0.013-0.76	0.20-0.26	0.0010-0.0038	---	---	---	---
Hydracrylic acid	C <sub>3</sub> H <sub>6</sub> O <sub>3</sub>	+	+	0.33	+	0.073		0.58
(R)-3-hydroxybutyric acid	C <sub>4</sub> H <sub>8</sub> O <sub>3</sub>	0.013-0.095	0.0015-0.018	0.033-0.069	0.0063	0.00077	---	0.10
Benzaldehyde	C <sub>7</sub> H <sub>6</sub> O	0.30-0.48	0.48-1.6	0.15-0.24	0.078	0.032-0.033	0.036	0.31
<i>cis</i> -Pinonic acid	C <sub>10</sub> H <sub>16</sub> O <sub>3</sub>	0.0084-0.026	+	+	0.051	0.0059-0.0078	0.0067-0.0075	0.034

D-Glucuronic acid lactone	C <sub>6</sub> H <sub>8</sub> O <sub>6</sub>	0.0040-0.0072	0.013-0.82	0.0029-0.081	0.25	0.00032-0.00046	0.00078-0.0011	0.0036
D-Glucuronic acid	C <sub>6</sub> H <sub>10</sub> O <sub>7</sub>	0.0041-0.010	0.0030-0.022	0.0037-0.0046	---	0.0013-0.0021	0.0035-0.0048	0.0069
2-Furoic acid	C <sub>5</sub> H <sub>4</sub> O <sub>3</sub>	0.18-0.24	--- -0.38	0.26-0.28	+	0.035-0.044	0.010	0.21
Benzeneacetic acid	C <sub>8</sub> H <sub>8</sub> O <sub>2</sub>	0.065-0.64	0.20-0.21	0.34-0.90	+	+	+	+
Benzenepropanoic acid	C <sub>9</sub> H <sub>10</sub> O <sub>2</sub>	0.14	+	+	+	+	+	+
Hydrocinnamic acid	C <sub>6</sub> H <sub>10</sub> O <sub>2</sub>	0.17-0.28	+	0.089	+	+	+	+
Butanoic acid	C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>	0.070	0.46-0.85	0.062-0.14	0.25	0.040-0.057	0.070-0.10	0.078
3-Hydroxypyridine	C <sub>5</sub> H <sub>4</sub> O <sub>3</sub>	3.8-6.0	2.6-3.4	0.38-1.4	+	0.0035-0.21	+	0.56
<i>p</i> -hydroxyacetophenone	C <sub>8</sub> H <sub>8</sub> O <sub>2</sub>	0.15-0.20	0.45-0.46	0.15-0.18	0.16	0.062	0.027-0.039	0.21
Methylmaleic acid	C <sub>5</sub> H <sub>6</sub> O <sub>4</sub>	+	+	+	+	+	+	+
Isocitric acid	C <sub>6</sub> H <sub>8</sub> O <sub>7</sub>	+	+	0.13	+	+	+	+
Diethylene glycol	C <sub>4</sub> H <sub>10</sub> O <sub>3</sub>	+	+	+	+	+	+	+
<i>m</i> -Anisic acid	C <sub>8</sub> H <sub>8</sub> O <sub>3</sub>	0.69	0.69	0.33-0.45	+	+	+	0.49
Ferulic acid	C <sub>10</sub> H <sub>10</sub> O <sub>4</sub>	+	0.084-0.12	+	+	0.018	+	+
Phosphoric acid	H <sub>3</sub> PO <sub>4</sub>	+	1.4-1.8	0.062-0.10	0.74	0.089-0.44	---	2.5
Nitriles	-	---	+	0.076-0.093	0.024	0.058-0.068	---	0.089
1,4-Anhydro-3-deoxypentitol-2-carboxylic acid, TMS	C <sub>12</sub> H <sub>26</sub> O <sub>4</sub> Si <sub>2</sub>	+	+	+	+	+	0.25-0.37	+
2,3-Dihydroxypropyl octadecanoate (Monoglyceride)	C <sub>21</sub> H <sub>42</sub> O <sub>4</sub>	0.058-1.3	+	0.19	---	---	+	0.20
D-arabino-Hexonic acid, 3-deoxy-2,5,6-tris-O-(TMS)-, lactone		+	4.0-5.7	0.67-1.1	+	0.26	0.91-1.0	2.0

PM<sub>2.5-10</sub>

Wildfires		Ovar	Montemor-o-Velho	Nariz (Aveiro)	Cinfães (Viseu)	Farejinha (Castro Daire)	Quinta da Póvoa (Sabugal)	Pendilhe (V. N. de Paiva)
Compounds	Formula							
<b>Alkanes</b>								
Pentadecane	C <sub>15</sub> H <sub>32</sub>	---	---	---	(a)	---	---	+
Hexadecane	C <sub>16</sub> H <sub>34</sub>	---	--- -0.0037	---		---	---	---

## Supplementary Material

Heptadecane	C <sub>17</sub> H <sub>36</sub>	0.0093-0.26	0.0047-0.034	0.05	0.91-1.3	---	---
Octadecane	C <sub>18</sub> H <sub>38</sub>	0.25-0.34	0.026-0.14	0.12	--- -0.0016	---	---
Nonadecane	C <sub>19</sub> H <sub>40</sub>	0.41-0.54	0.058-0.30	0.15	0.069-0.12	---	---
Eicosane	C <sub>20</sub> H <sub>42</sub>	0.48-0.80	0.040-0.52	0.21	0.17-0.36	---	0.03
Heneicosane	C <sub>21</sub> H <sub>44</sub>	0.49-0.70	0.14-1.1	0.23	0.10-0.42	---	0.15
Docosane	C <sub>22</sub> H <sub>46</sub>	0.45-0.71	0.11-0.87	0.23	0.15-0.58	---	0.33
Tricosane	C <sub>23</sub> H <sub>48</sub>	0.39-0.57	0.098-0.62	0.20	--- -0.29	---	---
Tetracosane	C <sub>24</sub> H <sub>50</sub>	0.36-0.52	0.17-0.53	0.17	0.084-0.40	0.042-0.57	0.67
Pentacosane	C <sub>25</sub> H <sub>52</sub>	0.35-0.44	0.13-0.72	0.17	0.084-0.16	0.046-0.56	0.67
Hexacosane	C <sub>26</sub> H <sub>54</sub>	0.18-0.25	0.11-0.53	0.041	0.082-0.11	0.048-0.61	0.64
Heptacosane	C <sub>27</sub> H <sub>56</sub>	0.092-0.23	0.13-0.61	0.081	0.084-0.11	0.050-0.72	0.66
Octacosane	C <sub>28</sub> H <sub>58</sub>	0.14-0.24	0.14-0.53	0.11	0.080-0.17	0.048-0.61	0.63
Nonacosane	C <sub>29</sub> H <sub>60</sub>	--- -0.012	0.034-0.82	---	--- -1.1	---	---
Hentriacontane	C <sub>31</sub> H <sub>64</sub>	0.10-0.25	0.14-1.5	0.092	0.012-1.5	0.039-0.53	0.48
Dotriacontane	C <sub>32</sub> H <sub>66</sub>	0.12-0.17	0.22-0.60	---	---	--- -0.035	---
Tritriacontane	C <sub>33</sub> H <sub>68</sub>	0.097-0.27	0.50-0.99	---	--- -0.11	0.028-0.38	---
Tetratriacontane	C <sub>34</sub> H <sub>70</sub>	0.39-0.70	0.29	0.0083	0.230	0.076-1.0	0.68
<i>Other alkanes</i>		0.15-0.84	0.25-0.47	0.17	2.6-3.3	0.23-2.6	2.7
<i>Branched alkanes</i>		1.0-2.7	0.16-2.8	0.69	13-17	0.87-7.1	8.8
<b>Alkenes</b>							
Tetradecene	C <sub>14</sub> H <sub>28</sub>	--- -0.0030	0.0006-0.0026	---	---	---	---
Pentadecene	C <sub>15</sub> H <sub>30</sub>	---	--- -0.0054	0.0027	+	---	+
Hexadecene	C <sub>16</sub> H <sub>32</sub>	0.030-0.074	0.036-0.027	0.023	--- -0.0042	---	---
Heptadecene	C <sub>17</sub> H <sub>34</sub>	0.15-0.24	0.015-0.078	0.070	0.031-0.55	0.0074-0.023	0.045
Octadecene	C <sub>18</sub> H <sub>36</sub>	0.32-0.36	0.037-0.19	0.27	---	---	---
Nonadecene	C <sub>19</sub> H <sub>38</sub>	0.69-0.89	0.071-0.49	0.21	0.16-0.27	0.047-0.10	0.27
Eicosene	C <sub>20</sub> H <sub>40</sub>	0.93-1.5	0.15-1.0	0.58	0.42-0.79	--- -0.022	0.24
Heneicosene	C <sub>21</sub> H <sub>42</sub>	0.64-0.86	0.25-1.1	0.38	0.58	0.16-0.44	1.2
Tricosene	C <sub>23</sub> H <sub>46</sub>	0.51-0.60	0.028-0.63	0.23	--- -0.31	---	---
Tetracosene	C <sub>24</sub> H <sub>48</sub>	0.37-0.58	0.16-0.80	0.33	0.023-0.74	---	---

Hexacosene	C <sub>26</sub> H <sub>52</sub>	0.012-0.40	0.19-0.24	0.050	--- -0.014	---	---
Octacosene	C <sub>28</sub> H <sub>56</sub>	+	0.092-0.12	0.048	+	+	+
Squalene	C <sub>30</sub> H <sub>50</sub>	0.085-0.19	0.11	0.12	0.26-0.32	0.071-1.1	0.65
<i>Other alkenes</i>		3.7-4.6	0.80-2.5	---	0.57-2.8	0.051-0.82	3.9
<i>Branched alkenes</i>		0.93-1.3	0.064-0.43	0.12	0.010-0.25	0.0066-0.64	0.060
<b>PAHs</b>							
Naphthalene	C <sub>10</sub> H <sub>8</sub>	0.0060-1.2	0.021-0.23	0.17	0.0012-0.32	0.30-1.1	0.11
Acenaphthylene	C <sub>12</sub> H <sub>8</sub>	+	+	0.0059	+	0.0025	0.0024
Acenaphthene	C <sub>12</sub> H <sub>10</sub>	+	+	0.0019	+	+	+
Fluorene	C <sub>13</sub> H <sub>10</sub>	0.0024-0.014	0.0023-0.039	0.025	0.0016-0.0020	0.0018-0.0031	0.00479
Phenanthrene	C <sub>14</sub> H <sub>10</sub>	0.14-0.42	0.080-0.17	0.18	0.014-0.086	0.063-0.064	0.038
Anthracene	C <sub>14</sub> H <sub>10</sub>	0.018-0.063	0.0039-0.014	0.033	0.0013-0.0044	0.0061-0.010	0.0026
Fluoranthene	C <sub>16</sub> H <sub>10</sub>	0.083-0.096	0.0085-0.020	0.027	0.024-0.11	0.033-0.11	0.051
Pyrene	C <sub>16</sub> H <sub>10</sub>	0.040-0.086	0.0055-0.014	0.020	0.023-0.085	0.026-0.088	0.041
<i>p</i> -terphenyl	C <sub>18</sub> H <sub>14</sub>	0.036-0.064	---	0.0023	--- -0.0024	---	-
Retene	C <sub>18</sub> H <sub>18</sub>	0.63-0.86	5.2-22	5.2	3.6-6.5	4.8-21	7.8
Benzo[a]anthracene	C <sub>18</sub> H <sub>12</sub>	0.020-0.053	0.0030-0.0063	0.0054	0.0072-0.053	0.0065-0.018	0.012
Chrysene	C <sub>18</sub> H <sub>12</sub>	0.056-0.12	0.0058-0.017	0.013	0.017-0.096	0.0090-0.031	0.031
Benzo[b]fluoranthene	C <sub>20</sub> H <sub>12</sub>	0.0082-0.013	0.0011-0.0042	0.00088	0.0054-0.045	0.0032-0.0084	0.0036
Benzo[j]fluoranthene	C <sub>20</sub> H <sub>12</sub>	0.0037-0.12	0.0017-0.0038	0.0036	0.0038-0.025	0.0026-0.0054	0.0052
Benzo[k]fluoranthene	C <sub>20</sub> H <sub>12</sub>	0.0017-0.070	--- -0.00065	0.00078	0.0043-0.024	0.0019-0.0046	0.0021
Benzo[e]pyrene	C <sub>20</sub> H <sub>12</sub>	0.013-0.041	0.0010-0.0032	0.0030	0.0092-0.086	0.0023-0.0061	0.0071
Benzo[a]pyrene	C <sub>20</sub> H <sub>12</sub>	0.0089-0.023	0.0019-0.0047	0.0024	0.0055-0.063	0.0047-0.011	0.0055
Perylene	C <sub>20</sub> H <sub>12</sub>	0.0019-0.0033	0.0010-0.0033	0.00071	0.065	0.00026-0.010	0.016
Indeno(1,2,3-cd)pyrene	C <sub>22</sub> H <sub>12</sub>	0.0016-0.0040	--- -0.00069	0.00089	+	0.0029-0.0063	+
Benzo[a,h]anthracene	C <sub>22</sub> H <sub>14</sub>	0.0025-0.0075	+	+	0.020	0.001	+
Benzo[ghi]perylene	C <sub>22</sub> H <sub>12</sub>	0.0040-0.0061	+	0.00067	+	+	+
<i>Other PAHs</i>		0.15-1.6	4.6-22	1.4	2.2-3.1	1.9-4.9	11

**Oxy-PAH**

## Supplementary Material

9-Fluorenone	C <sub>13</sub> H <sub>8</sub> O	0.47-0.96	0.010-0.73	0.056	0.033-0.052	0.011-0.055	+
9,10-Anthraquinone	C <sub>14</sub> H <sub>8</sub> O <sub>2</sub>	0.050-0.081	0.0019-0.045	0.0065	0.0053-0.0090	+	0.0078
2,6-Di-tert-butyl-1,4-Benzoquinone	C <sub>14</sub> H <sub>20</sub> O <sub>2</sub>	0.14-0.27	--- -0.040	0.00073	0.0040-0.017	---	-
<b><i>n</i>-Alcohols</b>							
<i>n</i> -Decanol	C <sub>10</sub> H <sub>22</sub> O	0.059	0.23-2.0	0.30	+	+	+
<i>n</i> -Dodecanol	C <sub>12</sub> H <sub>26</sub> O	0.22-0.64	+	+	+	0.96	0.64
<i>n</i> -Tetradecanol	C <sub>14</sub> H <sub>30</sub> O	0.44-0.56	0.550	0.26	0.240	0.69	0.79
<i>n</i> -Pentadecanol	C <sub>15</sub> H <sub>32</sub> O	0.27-0.37	0.00067-0.042	0.0051	0.18-0.21	0.0093-0.20	0.77
<i>n</i> -Hexadecanol	C <sub>16</sub> H <sub>34</sub> O	0.086-0.26	0.18-0.31	0.19	--- -0.014	---	-
<i>n</i> -Heptadecanol	C <sub>17</sub> H <sub>36</sub> O	+	+	+	+	+	+
<i>n</i> -Octadecanol	C <sub>18</sub> H <sub>38</sub> O	0.20-0.49	0.045-0.45	0.96	--- -0,21	---	0.15
<i>n</i> -Eicosanol	C <sub>20</sub> H <sub>42</sub> O	0.34-0.49	+	+	0.250	+	1.9
<i>n</i> -Heneicosanol	C <sub>21</sub> H <sub>44</sub> O	0.21-0.23	+	+	0.090-0.27	+	0.43
<i>n</i> -Docosanol	C <sub>22</sub> H <sub>46</sub> O	1.1-2.9	0.24-1.3	0.47	0.47-1.8	--- -0.085	2.7
<i>n</i> -Tricosanol	C <sub>23</sub> H <sub>48</sub> O	0.13-0.15	0.022	0.0091	0.063-0.17	---	0.45
<i>n</i> -Tetracosanol	C <sub>24</sub> H <sub>50</sub> O	0.97-1.1	0.64-1.8	0.54	0.69-2.4	0.13	5.6
<i>n</i> -Pentacosanol	C <sub>25</sub> H <sub>52</sub> O	0.11-0.19	0.012-0.026	0.0013	0.049-0.15	0.003	0.15
<i>n</i> -Hexacosanol	C <sub>26</sub> H <sub>54</sub> O	0.89-1.3	0.27-0.64	0.11	0.57-2.2	0.086	5.1
<i>n</i> -Heptacosanol	C <sub>27</sub> H <sub>56</sub> O	0.089-0.20	0.0024-0.095	0.010	0.022-0.17	---	0.21
<i>n</i> -Octacosanol	C <sub>28</sub> H <sub>58</sub> O	0.52-1.6	0.10-0.50	0.11	0.25-1.0	0.020-0.29	2.5
<i>n</i> -Nonacosanol	C <sub>29</sub> H <sub>60</sub> O	0.160	0.220	+	+	+	+
<i>n</i> -Triacontanol	C <sub>30</sub> H <sub>62</sub> O	0.40-1.4	0.081-0.74	0.27	0.18-0.81	0.018-0.076	2.5
<b>Other alcohols</b>							
(-)-Myrtenol	C <sub>10</sub> H <sub>16</sub> O	0.0053-0.023	0.059-0.15	+	+	+	+
Benzyl alcohol	C <sub>7</sub> H <sub>8</sub> O	0.25-0.40	0.086-1.1	0.054	0.20-0.91	0.078-1.5	1.3
<i>cis</i> -2-Methylcyclohexanol	C <sub>7</sub> H <sub>14</sub> O	+	0.0014	+	+	+	+
(1S,2S,3R,5S) -(+)-2,3-Pinandediol	C <sub>10</sub> H <sub>18</sub> O <sub>2</sub>	0.042-0.064	0.11	+	+	+	+

**Fatty alcohol**

2-ethylhexanol	C <sub>8</sub> H <sub>18</sub> O	0.11-0.63	0.12-0.86	1.9	1.8	0.039-1.0	2.1
<b>Fatty acids</b>							
Methyl tetradecanoate	C <sub>15</sub> H <sub>30</sub> O <sub>2</sub>	+	0.034	+	+	+	---
Isopropyl Myristate	C <sub>17</sub> H <sub>34</sub> O <sub>2</sub>	0.28	+	+	+	+	+
<b><i>n</i>-Alkanoic acids</b>							
Hexanoic acid	C <sub>6</sub> H <sub>12</sub> O <sub>2</sub>	+	0.11	0.024	+	+	+
Heptanoic acid	C <sub>7</sub> H <sub>14</sub> O <sub>2</sub>	+	0.045-0.37	0.049	+	+	+
Octanoic acid	C <sub>8</sub> H <sub>16</sub> O <sub>2</sub>	0.050-0.22	0.14-1.0	0.37	0.24-0.28	0.057-0.21	0.73
Nonanoic acid	C <sub>9</sub> H <sub>18</sub> O <sub>2</sub>	0.094-0.35	0.22-0.97	0.38	0.22-1.5	0.067-0.26	0.58
Decanoic acid	C <sub>10</sub> H <sub>20</sub> O <sub>2</sub>	0.29-0.38	0.39-1.5	0.47	0.40-0.83	0.088-0.39	1.8
Undecanoic acid	C <sub>11</sub> H <sub>22</sub> O <sub>2</sub>	0.13-0.16	0.010-0.027	0.26	0.18-0.44	0.038-0.20	0.73
Dodecanoic Acid	C <sub>12</sub> H <sub>24</sub> O <sub>2</sub>	0.52-0.83	1.6-4.6	1.1	0.64-2.5	0.0044-0.45	3.5
Tridecanoic acid	C <sub>13</sub> H <sub>26</sub> O <sub>2</sub>	0.014-0.035	0.29-2.1	0.057	0.16-0.46	--- -1.4	1.0
Tetradecanoic acid	C <sub>14</sub> H <sub>28</sub> O <sub>2</sub>	2.6-3.8	1.30-2.2	2.0	1.7-5.0	0.26-2.4	9.2
Pentadecanoic acid	C <sub>15</sub> H <sub>30</sub> O <sub>2</sub>	0.40-0.64	0.26-0.95	0.79	0.58-1.8	0.054-0.56	2.8
Hexadecanoic acid	C <sub>16</sub> H <sub>32</sub> O <sub>2</sub>	4.9-6.5	3.3-5.8	4.5	4.5-14	0.99-4.8	20.1
Heptadecanoic acid	C <sub>17</sub> H <sub>34</sub> O <sub>2</sub>	0.27-0.48	0.81-1.2	0.65	0.33-0.87	0.031-0.81	1.5
Octadecanoic acid	C <sub>18</sub> H <sub>36</sub> O <sub>2</sub>	1.4-2.2	1.2-2.6	1.9	1.5-4.2	1.4-4.5	8.6
Nonadecanoic acid	C <sub>19</sub> H <sub>38</sub> O <sub>2</sub>	0.046-0.16	0.0065-0.56	1.1	0.086-0.28	0.010-0.043	0.73
Eicosanoic acid	C <sub>20</sub> H <sub>40</sub> O <sub>2</sub>	0.70-0.90	1.7-2.9	3.4	0.97-3.4	0.10-0.43	6.7
Heneicosanoic acid	C <sub>21</sub> H <sub>42</sub> O <sub>2</sub>	0.150	0.065	0.29	+	0.29	+
Docosanoic acid	C <sub>22</sub> H <sub>44</sub> O <sub>2</sub>	1.6-2.1	3.9-7.0	7.0	2.1-8.0	0.20-1.2	12
Tricosanoic acid	C <sub>23</sub> H <sub>46</sub> O <sub>2</sub>	0.23-0.38	0.48-0.86	0.43	+	0.30	2
Tetracosanoic acid	C <sub>24</sub> H <sub>48</sub> O <sub>2</sub>	1.0-2.0	4.1-6.0	7.7	1.5-5.7	0.19-0.92	11
Pentacosanoic acid	C <sub>25</sub> H <sub>50</sub> O <sub>2</sub>	0.12-0.12	0.15-0.29	0.18	+	+	+
Hexacosanoic acid	C <sub>26</sub> H <sub>52</sub> O <sub>2</sub>	0.090-0.65	0.44-0.77	0.71	+	+	2.3
Heptacosanoic acid	C <sub>27</sub> H <sub>54</sub> O <sub>2</sub>	0.052	0.062-0.16	0.14	+	+	+
Octacosanoic acid	C <sub>28</sub> H <sub>56</sub> O <sub>2</sub>	0.22	0.18-0.43	0.61	+	+	+
Nonacosanoic acid	C <sub>29</sub> H <sub>58</sub> O <sub>2</sub>	+	+	0.18	+	+	+

## Supplementary Material

Triacontanoic acid	C <sub>30</sub> H <sub>60</sub> O <sub>2</sub>	0.160	0.17-0.39	0.49	+	+	+
<b>n-di-Acids</b>							
Propanedioic acid	C <sub>3</sub> H <sub>4</sub> O <sub>4</sub>	--- -0.043	---	+	0.042-0.052	0.0023-0.35	0.84
Butanedioic acid	C <sub>4</sub> H <sub>6</sub> O <sub>4</sub>	0.0028-0.16	0.26-1.7	0.033	1.1-1.8	0.57-5.8	4.5
Pentanedioic acid	C <sub>5</sub> H <sub>8</sub> O <sub>4</sub>	0.0071-0.36	0.061-1.8	0.012	0.97-1.6	0.12-10	5.8
Hexanedioic acid	C <sub>6</sub> H <sub>10</sub> O <sub>4</sub>	0.0045-0.038	0.037-0.057	0.0044	0.076-0.10	0.010-0.69	0.31
Heptanedioic acid	C <sub>7</sub> H <sub>12</sub> O <sub>4</sub>	0.047-0.077	0.040-0.25	+	0.16-0.35	0.078-0.36	0.64
Octanedioic acid	C <sub>8</sub> H <sub>14</sub> O <sub>4</sub>	0.12-0.32	0.012-0.013	0.10	0.19-0.51	0.022-0.20	0.65
Nonanedioic acid	C <sub>9</sub> H <sub>16</sub> O <sub>4</sub>	0.014-0.035	0.29-2.1	0.074	0.14-0.33	--- -1.4	1.0
Decanedioic acid	C <sub>10</sub> H <sub>18</sub> O <sub>4</sub>	0.0050-0.0088	0.036-1.5	0.015	0.035-0.074	0.0052-0.035	0.18
Hexadecanedioic acid	C <sub>16</sub> H <sub>30</sub> O <sub>4</sub>	0.0056	0.020-0.11	0.040	0.050-0.15	+	0.51
<b>n-Alkenoic acids</b>							
Oleic acid(C <sub>18:1</sub> )	C <sub>18</sub> H <sub>34</sub> O <sub>2</sub>	1.2-1.5	2.1-3.6	3.1	0.65-2.5	0.21-1.3	4.2
Linoleic acid (C <sub>18:2</sub> )	C <sub>18</sub> H <sub>32</sub> O <sub>2</sub>	0.27-0.48	1.3-2.1	1.5	0.44-1.6	0.088-0.61	2.4
Palmitoleic acid (C <sub>16:1</sub> )	C <sub>16</sub> H <sub>30</sub> O <sub>2</sub>	+	+	0.35	+	+	+
<b>Dicarboxylic acids</b>							
Methylmalonic acid	C <sub>4</sub> H <sub>6</sub> O <sub>4</sub>	0.012-0.042	0.0056-0.041	+	0.030-0.041	0.077	0.19
Pinic acid	C <sub>11</sub> H <sub>18</sub> O <sub>4</sub>	0.048-0.51	0.045-0.16	0.37	0.24-15	0.017-0.18	3.1
<b>Oxo-acids</b>							
Levulinic acid	C <sub>5</sub> H <sub>8</sub> O <sub>3</sub>	0.083-0.31	0.17-1.6	0.24	0.93-1.0	0.25-5.3	4.0
<b>Hydroxy-acids</b>							
Glycolic acid	C <sub>2</sub> H <sub>4</sub> O <sub>3</sub>	0.17-0.28	0.51-5.5	0.66	1.2-3.7	4.1-26	7.9
L-(-)-Malic acid	C <sub>4</sub> H <sub>6</sub> O <sub>5</sub>	--- -0.0025	0.0030-0.0049	0.023	0.0070-0.024	0.0050-0.023	0.18
2-Hydroxybutyric acid	C <sub>4</sub> H <sub>8</sub> O <sub>3</sub>	0.020	0.0095-0.23	+	0.10-0.26	0.16-0.57	0.33
4-Hydroxybutyric acid	C <sub>4</sub> H <sub>8</sub> O <sub>3</sub>	0.054	+	+	+	0.081-1.0	0.35
Propanoic acid	C <sub>3</sub> H <sub>6</sub> O <sub>2</sub>	---	0.16	+	---	0.16	-

**Ketones**

<i>γ</i> -Heptalactone	C <sub>7</sub> H <sub>12</sub> O <sub>2</sub>	0.002	0.0019	+	+	+	+
2-Decanone	C <sub>10</sub> H <sub>20</sub> O	+	+	0.054	+	+	+
2-Tridecanone	C <sub>13</sub> H <sub>26</sub> O	0.020-0.24	0.0014-0.36	0.015	0.018-0.020	---	0.0022
2-Pentadecanone	C <sub>15</sub> H <sub>30</sub> O	0.18-0.93	0.0064-0.37	0.054	0.055-0.079	0.004	0.023
3-Hexadecanone	C <sub>16</sub> H <sub>32</sub> O	0.81-1.3	0.036-1.5	0.11	0.17-0.27	0.017-0.049	0.16
2-Octadecanone	C <sub>18</sub> H <sub>36</sub> O	0.15-0.21	0.0073-0.14	0.027	0.034-0.041	0.017	0.037
2-Pentadecanone. 6.10.14-trimethyl-	C <sub>18</sub> H <sub>38</sub> O	0.58-0.90	0.030-1.2	0.093	0.31-0.36	0.037	0.36
Benzophenone	C <sub>13</sub> H <sub>10</sub> O	+	+	+	+	+	+
1-(10-Methylanthracen-9-yl)ethanone	C <sub>17</sub> H <sub>14</sub> O	+	1.2-1.3	0.12	+	+	+
<i>Other Ketones</i>		3.1-3.8	0.29-2.0	0.45	0.24-0.61	---	0.95

***n*-Alkanals**

Decanal	C <sub>10</sub> H <sub>20</sub> O	0.062	+	0.025	0.0068	+	+
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**Terpenoids**

Isopulegol	C <sub>10</sub> H <sub>18</sub> O	0.0026	0.0058-0.023	0.0016	0.0020	0.016	0.013
<i>β</i> -Amyrin	C <sub>30</sub> H <sub>50</sub> O	+	0.35-0.36	0.026	+	+	+
Eucalyptol	C <sub>10</sub> H <sub>18</sub> O	0.010	0.0074	+	0.0047-0.0065	+	+

**Steroids and alteration products**

Stigmasterol	C <sub>29</sub> H <sub>48</sub> O	0.028-0.056	0.025-0.15	0.088	0.051-0.17	0.0059	0.23
<i>β</i> -Sitosterol	C <sub>29</sub> H <sub>50</sub> O	0.18-0.23	0.29-0.59	0.25	0.17-0.63	0.074-0.26	1.4
Stigmasta-3,5-dien-7-one	C <sub>29</sub> H <sub>46</sub> O	---	0.44-0.76	0.067	0.66	---	---
Stigmast-4-en-3-one	C <sub>29</sub> H <sub>48</sub> O	+	+	0.33	+	+	+
Stigmastan-3,5-diene	C <sub>29</sub> H <sub>48</sub>	+	+	+	+	0.061	+

**Triterpenoids and alteration products**

4-Cholesten-3-one	C <sub>27</sub> H <sub>44</sub> O	0.0063-0.022	0.025-0.048	0.0117	0.0033	+	+
Urs-12-en-one ( <i>α</i> -amyrenone)	C <sub>30</sub> H <sub>48</sub> O	0.11-0.27	0.055-0.32	0.0030	0.0077-0.010	0.0083-0.025	0.018

## Supplementary Material

Lupeol	C <sub>30</sub> H <sub>50</sub> O	0.094-0.15	0.050-0.18	0.032	0.022-0.066	0.010-0.040	0.19
Cholesterol	C <sub>27</sub> H <sub>46</sub> O	0.073-0.10	0.18	+	0.10	0.088	0.19
<b>Diterpenoids and alteration products</b>							
Isopimaric	C <sub>20</sub> H <sub>30</sub> O <sub>2</sub>	0.016-0.061	5.0-11	1.3	0.57-1.9	0.70-4.3	3.1
Pimaric acid	C <sub>20</sub> H <sub>30</sub> O <sub>2</sub>	+	8.8-14	1.1	1.1-2.6	1.3-5.5	4.6
Abietic acid	C <sub>20</sub> H <sub>30</sub> O <sub>2</sub>	0.026-0.044	15-27	1.2	0.47-1.1	1.7-2.6	3.1
Methyl dehydroabietate	C <sub>21</sub> H <sub>30</sub> O <sub>2</sub>	0.17-0.45	2.2-11	0.34	0.60-1.4	1.0-3.9	1.6
Dehydroabietic acid	C <sub>20</sub> H <sub>28</sub> O <sub>2</sub>	0.62-1.1	49-120	17	9.8-24	16-51	42
7-Oxodehydroabietic acid	C <sub>20</sub> H <sub>26</sub> O <sub>3</sub>	+	0.51-3.7	0.21	+	+	+
<b>Phenols and alteration products</b>							
Vanillin	C <sub>8</sub> H <sub>8</sub> O	3.900	13-91	14	5.6-9.2	4.4-20	9.1
Vanillic acid	C <sub>8</sub> H <sub>8</sub> O <sub>4</sub>	2.0-3.8	0.81-2.3	1.6	1.8-5.5	0.26-2.4	9.2
Homovanillic acid	C <sub>9</sub> H <sub>10</sub> O <sub>4</sub>	0.13-0.16	0.18-4.6	0.30	0.60-1.4	1.300	2.3
Vanillyl acetic acid	-	+	0.20-6.8	+	+	+	+
Homovanillyl alcohol	C <sub>10</sub> H <sub>14</sub> O <sub>3</sub>	+	0.66	0.12	+	+	+
Methyl homovanillate	C <sub>10</sub> H <sub>12</sub> O <sub>4</sub>	+	0.46	+	+	+	+
3-Vanillylpropanol	C <sub>10</sub> H <sub>14</sub> O <sub>3</sub>	0.230	1.1-1.7	0.59	0.080-0.29	1.0-4.3	+
Coniferyl aldehyde	C <sub>10</sub> H <sub>10</sub> O <sub>3</sub>	0.240	0.0031	0.020	0.020	+	+
Coniferyl alcohol	C <sub>10</sub> H <sub>12</sub> O <sub>3</sub>	0.0032-0.017	0.034-0.071	0.044	0.0013-0.0074	0.00085-0.0028	0.0031
Syringaldehyde	C <sub>9</sub> H <sub>10</sub> O <sub>4</sub>	+	+	+	0.0040-0.011	0.0073	+
Syringic acid	C <sub>9</sub> H <sub>10</sub> O <sub>5</sub>	0.22-0.26	0.20-1.8	0.28	1.0-2.8	0.035-0.16	2.6
Sinapyl alcohol	C <sub>11</sub> H <sub>14</sub> O <sub>4</sub>	--- -0.00072	0.0018-0.0019	0.00028	+	---	+
Sinapic acid	C <sub>11</sub> H <sub>12</sub> O <sub>5</sub>	0.00068-0.0010	0.0013-0.0039	0.0012	0.0030-0.012	0.00062-0.0035	0.0051
p-Ethylguaiacol	C <sub>9</sub> H <sub>12</sub> O <sub>2</sub>	+	0.042	0.030	+	+	+
(±)-α-Tocopherol = Vitamin E	C <sub>29</sub> H <sub>50</sub> O <sub>2</sub>	0.071-0.55	0.051-0.22	0.066	0.039-0.12	0.0041-0.0064	0.29
3-Hydroxybenzoic acid	C <sub>7</sub> H <sub>6</sub> O <sub>3</sub>	0.21-0.35	0.071-1.9	0.26	+	+	+
4-Hydroxybenzoic acid	C <sub>7</sub> H <sub>6</sub> O <sub>3</sub>	0.081-0.58	0.12-0.35	0.15	0.39-1.6	0.049-0.49	2.1
Benzoic acid	C <sub>7</sub> H <sub>6</sub> O <sub>2</sub>	2.6-5.8	0.62-3.7	1.8	2.4-3.4		7.2

Resorcinol	C <sub>6</sub> H <sub>6</sub> O <sub>2</sub>	--- -0.72	0.75-2.1	0.14	0.38-0.98	+	1.4
5-methylresorcinol	C <sub>7</sub> H <sub>8</sub> O <sub>2</sub>	0.36	+	+	+	+	+
Catechol	C <sub>6</sub> H <sub>6</sub> O <sub>2</sub>	1.4-2.9	2.4-14	4.8	1.2-3.7	2.9-6.2	2.2
3-Methylcatechol	C <sub>7</sub> H <sub>8</sub> O <sub>2</sub>	+	0.70-2.9	0.58	+	+	+
4-methylcatechol	C <sub>7</sub> H <sub>8</sub> O <sub>2</sub>	0.73-1.2	1.6-4.3	1.4	0.59-1.3	2.5-3.2	+
Pyrogallol	C <sub>9</sub> H <sub>14</sub> O <sub>3</sub>	+	0.092-2.2	+	+	+	+
<i>trans</i> -Cinnamic acid	C <sub>9</sub> H <sub>8</sub> O <sub>2</sub>	0.030-0.063	0.080-0.43	+	0.19-0.62	0.30-1.3	0.84
Isoeugenol	C <sub>10</sub> H <sub>12</sub> O <sub>2</sub>	+	0.31-0.95	0.20	+	0.27	+
Hydroquinone	C <sub>6</sub> H <sub>4</sub> (OH) <sub>2</sub>	0.29	0.82-1.2	0.37	0.160	+	+
<b>Carbohydrates</b>							
Galactosan	C <sub>6</sub> H <sub>10</sub> O <sub>5</sub>	0.36-0.60	0.96-21	2.0	+	1.1-4.3	5.9
Mannosan	C <sub>6</sub> H <sub>10</sub> O <sub>5</sub>	0.54-0.80	1.6-41	2.9	1.6-4.0	1.9-8.2	8.1
Levoglucozan	C <sub>6</sub> H <sub>10</sub> O <sub>5</sub>	2.5-3.9	2.7-70	5.3	8.6-22	8.7-25	32.2
Glycerol	C <sub>3</sub> H <sub>8</sub> O <sub>3</sub>	0.0013-0.12	0.20	---	---	---	-
Erythrose	C <sub>4</sub> H <sub>8</sub> O <sub>4</sub>	0.92-1.4	0.69-17	2.9	+	1.5-15	9.7
Erythritol	C <sub>4</sub> H <sub>10</sub> O <sub>4</sub>	+	+	0.50	+	+	+
Arabinose	C <sub>5</sub> H <sub>10</sub> O <sub>5</sub>	+	---	+	+	+	+
l-Lyxose	C <sub>5</sub> H <sub>10</sub> O <sub>5</sub>	+	+	+	+	+	+
D-(-)-Ribose	C <sub>5</sub> H <sub>10</sub> O <sub>5</sub>	---	0.064-2.5	1.7	---	--- -0.22	0.33
Xylitol	C <sub>5</sub> H <sub>12</sub> O <sub>5</sub>	0.070	+	+	+	+	0.21
D-(+)-Arabitol	C <sub>5</sub> H <sub>12</sub> O <sub>5</sub>	0.025	0.60	0.054	+	0.055-0.24	0.80
Ribitol	C <sub>5</sub> H <sub>12</sub> O <sub>5</sub>	+	+	+	+	+	+
D-Mannitol	C <sub>6</sub> H <sub>14</sub> O <sub>6</sub>	+	0.0040-0.095	+	+	0.069	1.0
Sorbitol	C <sub>6</sub> H <sub>14</sub> O <sub>6</sub>	0.003	+	+	+	0.0076	+
D-Galactose	C <sub>6</sub> H <sub>12</sub> O <sub>6</sub>	0.010-0.036	0.0084-0.26	---	--- -0.098	---	---
Glucose	C <sub>6</sub> H <sub>12</sub> O <sub>6</sub>	+	+	+	+	---	-
Inositol	C <sub>6</sub> H <sub>12</sub> O <sub>6</sub>	+	0.002	+	+	+	0.19
Sucrose	C <sub>12</sub> H <sub>22</sub> O <sub>11</sub>	0.022-0.035	0.038	+	0.043-0.069	0.16	0.29
Maltose	C <sub>12</sub> H <sub>22</sub> O <sub>11</sub>	+	0.098	+	+	+	+
D-Erythronic acid $\gamma$ -lactone	C <sub>4</sub> H <sub>6</sub> O <sub>4</sub>	+	0.066-0.48	+	+	+	+

## Supplementary Material

<b>Other Aldehydes</b>		4.2-9.4	--- -0.79	4.3	5.1-12	---	9.6
<b>Methyl esters</b>		3.7-4.4	0.37-2.0	1.4	1.4-3.1	0.41-3.0	2.7
<b>Other Phenols</b>							
Phenol, 2,4-di-ter-butyl	C <sub>14</sub> H <sub>22</sub> O	0.21-6.5	---	+	--- -0.074	---	-
4-Octylphenol	C <sub>14</sub> H <sub>22</sub> O	0.0038	+	+	+	+	0.024
<i>Other Phenols</i>		0.032-1.0	--- -0.12	0.034	---	---	---
<b>Other compounds</b>							
5 $\alpha$ -Cholestan-3 $\beta$ -ol	C <sub>27</sub> H <sub>48</sub> O	0.063	0.065	0.023	0.017-0.032	0.010-0.069	0.17
Lactic acid	C <sub>3</sub> H <sub>6</sub> O <sub>3</sub>	--- -0.0023	0.041-3.2	0.56	1.3-3.7	2.0-8.1	17
Hydracrylic acid	C <sub>3</sub> H <sub>6</sub> O <sub>3</sub>	0.93	0.12-2.8	0.33	2.500	2.0-9.7	5.7
(R)-3-hydroxybutyric acid	C <sub>4</sub> H <sub>8</sub> O <sub>3</sub>	0.042-0.33	0.021-0.45	0.089	0.19-0.27	0.15-0.52	0.69
Benzaldehyde	C <sub>7</sub> H <sub>6</sub> O	0.016-0.16	0.56-1.6	0.34	0.44-0.74	0.30-1.4	0.25
<i>cis</i> -Pinonic acid	C <sub>10</sub> H <sub>16</sub> O <sub>3</sub>	0.010-0.026	---	+	0.037-0.059	0.36	0.18
D-Glucuronic acid lactone	C <sub>6</sub> H <sub>8</sub> O <sub>6</sub>	--- -0.0024	0.074-1.8	0.18	---	0.24	1.0
D-Glucuronic acid	C <sub>6</sub> H <sub>10</sub> O <sub>7</sub>	0.0065-0.0088	0.0062-0.015	0.017	0.0019-0.014	0.0015-0.0086	0.031
2-Furoic acid	C <sub>5</sub> H <sub>4</sub> O <sub>3</sub>	0.14-0.19	0.048-1.1	0.27	0.60	2.0	2.3
Benzeneacetic acid	C <sub>8</sub> H <sub>8</sub> O <sub>2</sub>	+	0.13-1.0	1.3	+	+	+
Benzenepropanoic acid	C <sub>9</sub> H <sub>10</sub> O <sub>2</sub>	+	0.20-0.26	+	+	+	+
Hydrocinnamic acid	C <sub>6</sub> H <sub>10</sub> O <sub>2</sub>	0.13-0.13	+	+	+	+	+
Butanoic acid	C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>	0.044	0.059-1.6	+	0.34-0.69	0.37-2.6	0.63
3-Hydroxypyridine	C <sub>5</sub> H <sub>4</sub> O <sub>3</sub>	4.0-4.4	0.18-5.9	1.6	+	+	4.0
<i>p</i> -hydroxyacetophenone	C <sub>8</sub> H <sub>8</sub> O <sub>2</sub>	0.15	0.30-0.67	0.23	+	0.18-0.92	+
Methylmaleic acid	C <sub>5</sub> H <sub>6</sub> O <sub>4</sub>	0.28	0.53	+	+	10	+
Isocitric acid	C <sub>6</sub> H <sub>8</sub> O <sub>7</sub>	0.79	+	+	1.700	+	+
Diethylene glycol	C <sub>4</sub> H <sub>10</sub> O <sub>3</sub>	0.26-0.50	+	+	+	0.42-1.2	0.14
<i>m</i> -Anisic acid	C <sub>8</sub> H <sub>8</sub> O <sub>3</sub>	+	0.63-2.8	+	+	+	+
Ferulic acid	C <sub>10</sub> H <sub>10</sub> O <sub>4</sub>	+	+	+	+	+	+

Phosphoric acid	H <sub>3</sub> PO <sub>4</sub>	---	0.55-2.7	+	2.5-3.6	2.8	52
Nitriles	-	---	--- -12	---	0.21-0.41	---	0.35
1,4-Anhydro-3-deoxypentitol-2-carboxylic acid, TMS	C <sub>12</sub> H <sub>26</sub> O <sub>4</sub> Si <sub>2</sub>	2.2-3.8	6.1	+	7.9-22	58	39
2,3-Dihydroxypropyl octadecanoate (Monoglyceride)	C <sub>21</sub> H <sub>42</sub> O <sub>4</sub>	0.51-0.58	--- -0.85	---	0.38-1.3	0.12-3.2	4.1
D-arabino-Hexonic acid, 3-deoxy-2,5,6-tris-O-(TMS)-, lactone		0.59	0.60-14	0.67	0.840	3.6	2.2

(+) not detected; (---) detected, but not quantified, because of abundances close to the detection limit; (a) sample damage

## Supplementary Material A4

## Supplementary Information from Chapter 6.

Table A4.1. Concentration ranges (and average) for water-soluble ions ( $\mu\text{g mg}^{-1}$  PM) in smoke particles from wildfires.

Wildfire		Na <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>	K <sup>+</sup>	Mg <sup>2+</sup>	Ca <sup>2+</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>
Mangualde	PM <sub>2.5</sub>	---	---	---	0.80	4.7	---	1.5	1.8
	PM <sub>2.5-10</sub>	---	0.59	2.5	---	---	8.1	---	3.3
Sever do Vouga	PM <sub>2.5</sub>	---	4.1-9.3 (6.7)	---	0.10-0.82 (0.46)	0.99-3.4 (2.2)	6.2-6.8 (6.4)	--- -0.46 (0.23)	1.6-3.0 (2.3)
	PM <sub>2.5-10</sub>	---	0.53-1.5 (1.0)	0.20-1.4 (0.79)	--- -1.2 (0.59)	--- - 1.4 (0.68)	1.1-1.8 (1.4)	---	0.75-2.9 (1.8)
Dornelas (Sever do Vouga)	PM <sub>2.5</sub>	10	6.3	14	2.7	3.4	15	2.3	5.5
	PM <sub>2.5-10</sub>	---	0.72	22	---	7.1	6.9	---	14
Rebordelo (Santa Maria da Feira)	PM <sub>2.5</sub>	--- -8.1 (2.7)	--- -11 (5.0)	2.6-8.4 (5.4)	1.5-2.7 (2.0)	1.4-7.6 (4.6)	--- -20 (8.2)	2.0-13 (8.0)	6.1-6.9 (6.5)
	PM <sub>2.5-10</sub>	---	0.69-2.0 (1.3)	1.9-5.8 (3.3)	--- -4.7 (1.6)	--- -5.8 (3.8)	--- -7.8 (2.6)	--- -3.2 (1.1)	6.1-11 (9.4)
Albergaria-a-Velha	PM <sub>2.5</sub>	--- -3.66 (1.83)	4.4-4.7 (4.5)	5.2-8.4 (6.8)	0.28-0.97 (0.62)	1.8-6.4 (4.1)	5.9-6.4 (6.1)	1.3-1.8 (1.6)	2.8-4.4 (3.6)
	PM <sub>2.5-10</sub>	---	0.39-0.80 (0.60)	6.0-7.8 (6.9)	1.3-2.0 (1.65)	3.6-9.9 (6.8)	2.3-2.9 (2.6)	0.77-0.91 (0.84)	6.9-8.4 (7.7)
Fontanheiras (Nelas)	PM <sub>2.5</sub>	---	0.79	---	0.48	3.7	---	0.76	0.97
	PM <sub>2.5-10</sub>	---	---	2.5	1.7	6.9	---	---	3.2
Albergaria-a-Velha	PM <sub>2.5</sub>	--- -10.47 (5.24)	6.0-12 (9.2)	6.0-14 (10)	3.2-3.4 (3.3)	8.8-10 (9.6)	14-25 (19)	2.6-3.4 (3.0)	6.7-8.0 (7.3)
	PM <sub>2.5-10</sub>	---	0.34-0.56 (0.45)	5.1-7.6 (6.4)	4.1-8.7 (6.4)	12-15 (13)	13-17 (15)	--- -2.6 (1.3)	6.7-14 (10)

<b>Albergaria-a-Velha</b>	PM <sub>2.5</sub>	---	2.3	---	1.5	7.1	4.6	7.5	8.0
	PM <sub>2.5-10</sub>	---	0.41	1.2	1.8	6.8	2.5	3.6	8.1
<b>Chão do Coto (Oliveira de Frades)</b>	PM <sub>2.5</sub>	---	---	9.2	3.8	12	7.6	4.9	4.2
	PM <sub>2.5-10</sub>	---	1.1	6.7	7.7	21	---	---	11
<b>Sobrosa (São Pedro do Sul)</b>	PM <sub>2.5</sub>	--- -22.4 (10)	4.8-14.6 (8.7)	--- -3.4 (1.4)	0.45-2.1 (0.93)	1.8-5.4 (3.0)	4.4-13 (7.7)	2.0-5.3 (3.0)	2.7-4.4 (3.5)
	PM <sub>2.5-10</sub>	---	0.89-2.1 (1.4)	2.1-4.6 (3.7)	1.4-5.0 (3.2)	4.1-9.8 (6.6)	--- -2.8 (1.8)	---	5.3-14 (9.4)
<b>Junqueira (Vale de Cambra)</b>	PM <sub>2.5</sub>	---	4.3-9.0 (6.6)	--- -1.7 (0.84)	0.61-1.6 (1.1)	2.5-5.1 (3.8)	--- -5.1 (2.6)	3.6-3.7 (3.7)	3.9-5.2 (4.6)
	PM <sub>2.5-10</sub>	---	0.73-1.2 (0.96)	3.7-3.9 (3.8)	1.4-2.2 (1.8)	3.8-6.8 (5.3)	--- -1.2 (0.61)	---	5.0-7.1 (6.1)
<b>Vila Nova de Tazem (Gouveia)</b>	PM <sub>2.5</sub>	--- -40.25 (6.71)	1.7-36 (13)	3.6-11 (7.0)	0.56-2.8 (1.4)	1.4-8.4 (4.5)	5.5-18 (12)	0.71-8.4 (3.6)	2.3-5.6 (4.0)
	PM <sub>2.5-10</sub>	---	0.54-2.4 (1.2)	5.4-17 (10)	--- -5.6 (2.6)	4.2-16 (10)	--- -7.8 (3.0)	---	--- -13 (5.8)

(---) below detection limit.

Table A4.2. Average concentrations (mg g<sup>-1</sup> PM) of trace elements found in the smoke particles.

	PM <sub>2.5</sub>															
	As	Ce	Co	Cs	Eu	Hf	La	Nd	Sb	Sc	Sm	Ta	Tb	Th	U	Yb
<b>Mangualde</b>																
<b>Sever do Vouga</b>		0.21	0.61		0.0077	0.067			1.9	0.37		0.091				
<b>Dornelas (Sever do Vouga)</b>			0.23	0.013		0.15			1.3	0.19		0.049			0.0065	
<b>Rebordelo (Santa Maria da Feira)</b>		0.10	0.15		0.0043				0.73	0.10		0.033			0.0087	
<b>Albergaria-a-Velha</b>		0.082	0.058	0.037	0.00070		0.030		0.60			0.015		0.016	0.00013	
<b>Fontanheiras (Nelas)</b>			0.15													
<b>Albergaria-a-Velha</b>			0.67		0.035	0.087	0.55		0.40	0.54			0.022	1.1		
<b>Albergaria-a-Velha</b>	2.3	0.72	0.38	0.076					0.94	0.33	0.11					
<b>Chão do Coto (Oliveira de Frades)</b>			0.20													
<b>Sobrosa (São Pedro do Sul)</b>		0.44	0.64	0.46	0.073	1.4				0.26		0.067	0.052	0.66	0.066	
<b>Junqueira (Vale de Cambra)</b>		0.74	0.24	0.051	0.13	0.41	0.43	0.47		0.15	0.15	0.084	0.015	0.41	0.11	0.041
<b>Vila Nova de Tazem (Gouveia)</b>		0.96	0.22	0.32	0.034	0.17	0.28		0.59	0.058	0.060	0.085	0.0047	0.45	0.052	0.019

<b>PM<sub>2.5-10</sub></b>																
	<b>As</b>	<b>Ce</b>	<b>Co</b>	<b>Cs</b>	<b>Eu</b>	<b>Hf</b>	<b>La</b>	<b>Nd</b>	<b>Sb</b>	<b>Sc</b>	<b>Sm</b>	<b>Ta</b>	<b>Tb</b>	<b>Th</b>	<b>U</b>	<b>Yb</b>
<b>Mangualde</b>									5.8							
<b>Sever do Vouga</b>							0.85		2.0	0.34	0.29					
<b>Dornelas (Sever do Vouga)</b>			2.6				0.40		3.5	0.70	0.50				0.44	0.74
<b>Rebordelo (Santa Maria da Feira)</b>	0.26	1.5	1.6	0.45		0.47	0.34	22	5.9	0.47		0.034	0.073	0.07	1.4	0.83
<b>Albergaria-a-Velha</b>		2.7	0.48	0.23		0.13	1.2	5.0	1.6	0.29	0.35	0.025	0.033	0.21	0.066	0.19
<b>Fontanheiras (Nelas)</b>				1.5		0.23	0.34		4.2		0.45		0.29		1.0	0.56
<b>Albergaria-a-Velha</b>	12	2.3	1.9	0.18		0.045	0.89	7.1	3.6	0.39		0.066	0.10		2.0	0.20
<b>Albergaria-a-Velha</b>	0.045	3.3	1.3	0.38	0.064	0.0087	0.65		4.0	0.66		0.14	0.15	0.050	2.8	
<b>Chão do Coto (Oliveira de Frades)</b>	0.64	9.6	2.1	0.56			0.30		16	0.32		0.14	0.74		3.7	2.3
<b>Sobrosa (São Pedro do Sul)</b>	6.8	7.7	0.51	0.81	0.0070	1.9	2.5			0.51		0.20	0.11	0.66	2.3	0.33
<b>Junqueira (Vale de Cambra)</b>	1.2	3.5	0.11	0.27		0.49	1.3	2.2		0.30		0.22		0.71	3.8	0.13
<b>Vila Nova de Tazem (Gouveia)</b>	7.1	10	0.38	1.0		2.5	3.4			0.39		0.46		1.1	3.7	0.24

The concentrations of all organic compounds from Chapter 6.

Table A4.3. Detailed speciation of organic compounds in smoke particles ( $\text{mg g}^{-1}$  OC).

		PM <sub>2.5</sub>					
Wildfires		Dornelas (Sever do Vouga)	Rebordelo (Santa Maria da feira)	Albergaria-a-Velha	Albergaria-a-Velha	Junqueira (Vale de Cambra)	Vila Nova de Tazem (Gouveia)
Compounds	Formula						
<b>Alcohols</b>							
<i>n</i> -Decanol	C <sub>10</sub> H <sub>22</sub> O	nd	0.0011-0.0014	0.00051	nd	0.0043	0.0023 - 0.089
<i>n</i> -Dodecanol	C <sub>12</sub> H <sub>26</sub> O	nd	nd	nd	nd	nd	nd
<i>n</i> -Tetradecanol	C <sub>14</sub> H <sub>30</sub> O	nd	nd	nd	nd	nd	nd
<i>n</i> -Pentadecanol	C <sub>15</sub> H <sub>32</sub> O	nd	0.072 - 1.0	0.014	0.14	0.00040 - 0.40	0.056 - 0.13
<i>n</i> -Hexadecanol	C <sub>16</sub> H <sub>34</sub> O	nd	0.053 - 0.053	nd	0.16	0.17	0.074 - 0.097
<i>n</i> -Octadecanol	C <sub>18</sub> H <sub>38</sub> O	---	--- - 0.28	---	---	--- - 0.33	0.0088 - 0.19
<i>n</i> -Eicosanol	C <sub>20</sub> H <sub>42</sub> O	nd	0.075 - 0.16	nd	0.13	0.36	0.18
<i>n</i> -Heneicosanol	C <sub>21</sub> H <sub>44</sub> O	nd	nd	nd	nd	nd	nd
<i>n</i> -Docosanol	C <sub>22</sub> H <sub>46</sub> O	0.039	0.075 - 0.78	0.22	0.97	0.0038 - 0.88	0.0017 - 0.43
<i>n</i> -Tricosanol	C <sub>23</sub> H <sub>48</sub> O	0.19	0.0092 - 0.11	0.023	0.061	0.11	0.016 - 0.079
<i>n</i> -Tetracosanol	C <sub>24</sub> H <sub>50</sub> O	nd	0.11 - 0.40	0.22	0.31	0.56	0.036 - 0.44
<i>n</i> -Hexacosanol	C <sub>26</sub> H <sub>54</sub> O	0.17	0.14 - 0.53	0.13	0.32	0.011 - 1.1	0.036 - 0.62
<i>n</i> -Pentacosanol	C <sub>25</sub> H <sub>52</sub> O	0.010	0.012 - 0.086	0.013	0.035	0.00055 - 0.10	0.00049 - 0.038
<i>n</i> -Heptacosanol	C <sub>27</sub> H <sub>56</sub> O	0.013	0.017 - 0.048	0.010	0.032	0.0015 - 0.12	0.0028 - 0.14
<i>n</i> -Octacosanol	C <sub>28</sub> H <sub>58</sub> O	0.13	0.16 - 0.42	0.098	0.27	0.012 - 0.53	0.078 - 0.59
<i>n</i> -Nonacosanol	C <sub>29</sub> H <sub>60</sub> O	nd	0.035 - 0.076	nd	nd	0.09	0.013 - 0.083
<i>n</i> -Triacontanol	C <sub>30</sub> H <sub>62</sub> O	0.21	0.34 - 0.72	0.060	0.36	0.019 - 0.56	0.12 - 0.57

<b>Other alcohols</b>							
(-)-Myrtenol	C <sub>10</sub> H <sub>16</sub> O	0.0013	0.00083 - 0.0044	0.0016	nd	0.019	0.0021 - 0.014
Benzyl alcohol	C <sub>7</sub> H <sub>8</sub> O	0.10	0.044 - 0.84	1.0	1.1	3.5	0.015 - 1.4
<i>cis</i> -2-Methylcyclohexanol	C <sub>7</sub> H <sub>14</sub> O	0.0024	0.00071 - 0.0022	nd	0.0017	0.00030 - 0.0027	0.00044 - 0.00084
(1 <i>S</i> ,2 <i>S</i> ,3 <i>R</i> ,5 <i>S</i> )-(+)-2,3-Pinane-1,3-diol	C <sub>10</sub> H <sub>18</sub> O <sub>2</sub>	0.0023	0.0048 - 0.037	nd	0.0048	0.027	0.016
<b><i>n</i>-alkanoic acids</b>							
Hexanoic acid	C <sub>6</sub> H <sub>12</sub> O <sub>2</sub>	0.011	nd	nd	0.030	nd	0.0062
Heptanoic acid	C <sub>7</sub> H <sub>14</sub> O <sub>2</sub>	nd	0.013	nd	0.039	0.038	0.0087 - 0.046
Octanoic acid	C <sub>8</sub> H <sub>16</sub> O <sub>2</sub>	0.027	0.017 - 0.042	0.020	0.15	0.0034 - 0.15	0.0016 - 0.11
Nonanoic acid	C <sub>9</sub> H <sub>18</sub> O <sub>2</sub>	0.044	0.028 - 0.035	0.025	0.31	0.0012 - 0.22	0.0018 - 0.15
Decanoic acid	C <sub>10</sub> H <sub>20</sub> O <sub>2</sub>	0.0024	0.0027 - 0.022	0.15	0.017	0.035 - 0.028	0.0028 - 0.097
Undecanoic acid	C <sub>11</sub> H <sub>22</sub> O <sub>2</sub>	-	0.0033 - 0.011	0.016	0.014	0.0049 - 0.0212	0.0037 - 0.079
Dodecanoic Acid	C <sub>12</sub> H <sub>24</sub> O <sub>2</sub>	0.49	0.041 - 0.18	0.048	0.70	0.048 - 2.2	0.016 - 1.2
Tridecanoic acid	C <sub>13</sub> H <sub>26</sub> O <sub>2</sub>	0.0063	0.0045 - 0.024	0.0085	0.020	0.040 - 0.31	0.011 - 0.22
Tetradecanoic acid	C <sub>14</sub> H <sub>28</sub> O <sub>2</sub>	0.81	0.54 - 1.1	0.26	4.0	0.085 - 1.9	0.10 - 1.5
Pentadecanoic acid	C <sub>15</sub> H <sub>30</sub> O <sub>2</sub>	0.0074	0.0064 - 0.40	0.019	1.2	0.0058 - 1.9	0.0033 - 0.84
Hexadecanoic acid	C <sub>16</sub> H <sub>32</sub> O <sub>2</sub>	0.64	0.70 - 1.2	0.66	4.0	0.016 - 1.3	0.16 - 3.0
Heptadecanoic acid	C <sub>17</sub> H <sub>34</sub> O <sub>2</sub>	0.17	0.0089 - 0.51	0.0080	1.3	0.0036 - 0.96	--- -1.1
Octadecanoic acid	C <sub>18</sub> H <sub>36</sub> O <sub>2</sub>	0.43	0.39 - 1.0	0.60	2.1	0.0099 - 2.4	0.27 - 2.1
Nonadecanoic acid	C <sub>19</sub> H <sub>38</sub> O <sub>2</sub>	0.011	0.0066 - 0.18	0.0063	0.56	0.0033 - 0.016	0.0036 - 0.018
Eicosanoic acid	C <sub>20</sub> H <sub>40</sub> O <sub>2</sub>	0.20	0.26 - 0.65	0.036	1.6	0.036 - 1.9	0.0039 - 1.3
Heneicosanoic acid	C <sub>21</sub> H <sub>42</sub> O <sub>2</sub>	nd	nd	nd	nd	nd	nd
Docosanoic acid	C <sub>22</sub> H <sub>44</sub> O <sub>2</sub>	0.57	0.47 - 1.5	0.97	3.3	0.013 - 3.1	0.059 - 2.9
Tricosanoic acid	C <sub>23</sub> H <sub>46</sub> O <sub>2</sub>	0.060	0.26 - 0.63	0.19	0.96	1.1	0.036 - 0.76

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Tetracosanoic acid	C <sub>24</sub> H <sub>48</sub> O <sub>2</sub>	0.88	0.59 - 1.8	1.3	3.9	0.067 - 3.4	0.088 - 3.4
Pentacosanoic acid	C <sub>25</sub> H <sub>50</sub> O <sub>2</sub>	nd	0.081 - 0.23	nd	0.51	0.43	0.025 - 0.43
Hexacosanoic acid	C <sub>26</sub> H <sub>52</sub> O <sub>2</sub>	0.088	0.40 - 0.92	0.37	1.8	1.4	0.038 - 0.95
Heptacosanoic acid	C <sub>27</sub> H <sub>54</sub> O <sub>2</sub>	0.082	0.088 - 0.20	nd	0.33	0.30	0.032 - 0.24
Octacosanoic acid	C <sub>28</sub> H <sub>56</sub> O <sub>2</sub>	0.48	0.40 - 0.76	nd	1.0	0.035 - 1.3	0.12 - 0.99
Nonacosanoic acid	C <sub>29</sub> H <sub>58</sub> O <sub>2</sub>	0.11	0.19 - 0.34	0.17	nd	0.32	0.039 - 0.32
Triacontanoic acid	C <sub>30</sub> H <sub>60</sub> O <sub>2</sub>	nd	0.39 - 0.55	nd	0.76	0.81	0.15 - 0.74
<i>n-di-acids</i>							
Propanedioic acid	C <sub>3</sub> H <sub>4</sub> O <sub>4</sub>	0.0017	0.00066 - 0.0051	0.014	0.0075	0.00039 - 0.0058	0.00013 - 0.0045
Butanedioic acid	C <sub>4</sub> H <sub>6</sub> O <sub>4</sub>	0.47	0.39 - 0.75	0.72	0.79	0.46 - 0.86	0.27 - 1.2
Pentanedioic acid	C <sub>5</sub> H <sub>8</sub> O <sub>4</sub>	0.11	0.11 - 0.23	0.21	0.17	0.11 - 0.16	0.048 - 0.19
Hexanedioic acid	C <sub>6</sub> H <sub>10</sub> O <sub>4</sub>	0.063	0.059 - 0.099	0.028	0.13	0.067 - 0.080	0.031 - 0.12
Heptanedioic acid	C <sub>7</sub> H <sub>12</sub> O <sub>4</sub>	0.28	0.31 - 0.92	0.11	0.41	0.55 - 1.2	0.35 - 0.86
Octanedioic acid	C <sub>8</sub> H <sub>14</sub> O <sub>4</sub>	0.45	0.31 - 0.52	nd	nd	0.12	0.031 - 0.31
Nonanedioic acid	C <sub>9</sub> H <sub>16</sub> O <sub>4</sub>	0.76	0.92 - 1.0	0.11	1.7	0.39 - 0.89	0.088 - 0.62
Decanedioic acid	C <sub>10</sub> H <sub>18</sub> O <sub>4</sub>	0.089	0.11 - 0.21	0.018	0.30	0.067 - 0.12	0.033 - 0.20
Hexadecanedioic acid	C <sub>16</sub> H <sub>30</sub> O <sub>4</sub>	0.48	0.34 - 0.48	0.051	0.35	0.24 - 0.33	0.064 - 0.30
<i>Dicarboxylic acids</i>							
Methylmalonic acid	C <sub>4</sub> H <sub>6</sub> O <sub>4</sub>	0.00015	0.0097 - 0.024	0.0045	0.0083	nd	0.0023
Pinic acid	C <sub>11</sub> H <sub>18</sub> O <sub>4</sub>	5.4	0.30 - 0.52	1.2	0.43	0.43 - 1.1	0.21 - 0.82
<i>Oxo-acids</i>							
Levulinic acid	C <sub>5</sub> H <sub>8</sub> O <sub>3</sub>	0.075	0.044 - 0.29	0.40	0.21	0.15 - 0.28	0.072 - 0.29

<b>Hydroxy-acids</b>							
Glycolic acid	C <sub>2</sub> H <sub>4</sub> O <sub>3</sub>	0.45	0.18 - 0.46	2.0	0.32	0.78 - 0.89	0.25 - 1.0
L-(-)-Malic acid	C <sub>4</sub> H <sub>6</sub> O <sub>5</sub>	nd	0.0062 - 0.019	0.011	0.010	0.0046 - 0.0089	0.0017 - 0.024
2-Hydroxybutyric acid	C <sub>4</sub> H <sub>8</sub> O <sub>3</sub>	nd	nd	0.11	nd	0.036 - 0.060	0.019 - 0.043
4-Hydroxybutyric acid	C <sub>4</sub> H <sub>8</sub> O <sub>3</sub>	nd	nd	nd	nd	nd	nd
Propanoic acid	C <sub>3</sub> H <sub>6</sub> O <sub>2</sub>	0.059	0.029 - 0.046	0.063	0.011	0.062 - 0.064	0.026 - 0.057
<b>Unsaturated Fatty acid</b>							
Oleic acid (C <sub>18:1</sub> )	C <sub>18</sub> H <sub>34</sub> O <sub>2</sub>	1.2	0.97 - 1.1	0.77	4.4	2.1	0.16 - 3.0
Linoleic acid (C <sub>18:2</sub> )	C <sub>18</sub> H <sub>32</sub> O <sub>2</sub>	0.57	0.38 - 0.80	0.087	0.80	0.019 - 1.4	0.024 - 1.9
Palmitoleic acid	C <sub>16</sub> H <sub>30</sub> O <sub>2</sub>	nd	nd	nd	nd	nd	0.66
<b>Other acids</b>							
Lactic acid	C <sub>3</sub> H <sub>6</sub> O <sub>3</sub>	0.068	0.031 - 0.17	0.59	nd	0.12 - 0.24	0.041 - 0.24
Hydracrylic acid	C <sub>3</sub> H <sub>6</sub> O <sub>3</sub>	nd	0.11	nd	nd	nd	nd
(R)-3-hydroxybutyric acid	C <sub>4</sub> H <sub>8</sub> O <sub>3</sub>	0.016	0.094 - 0.052	0.0066	0.027	0.013 - 0.046	0.0049 - 0.054
<i>cis</i> -Pinonic acid	C <sub>10</sub> H <sub>16</sub> O <sub>3</sub>	0.10	0.012 - 0.090	0.038	0.087	0.053 - 0.71	0.047 - 0.048
D-Glucuronic acid lactone	C <sub>6</sub> H <sub>8</sub> O <sub>6</sub>	nd	0.0070 - 0.85	0.019	0.0088	0.0048 - 0.019	0.0035 - 0.024
D-Glucuronic acid	C <sub>6</sub> H <sub>10</sub> O <sub>7</sub>	0.11	0.021 - 0.030	0.091	0.015	0.012	0.0090 - 0.037
2-Furoic acid	C <sub>5</sub> H <sub>4</sub> O <sub>3</sub>	nd	0.022 - 0.047	0.16	0.047	0.19 - 0.26	0.053 - 0.10
Benzenepropanoic acid	C <sub>9</sub> H <sub>10</sub> O <sub>2</sub>	0.075	0.05	nd	nd	nd	0.070 - 0.11
Hydrocinnamic acid	C <sub>6</sub> H <sub>10</sub> O <sub>2</sub>	nd	0.051	nd	nd	0.086	0.15 - 0.16
Butanoic acid	C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>	0.17	0.12 - 0.21	nd	0.21	0.12 - 0.17	0.052 - 0.22
Maleic acid	C <sub>4</sub> H <sub>4</sub> O <sub>4</sub>	nd	0.075 - 0.13	0.097	0.10	nd	0.068
Methylmaleic acid	C <sub>5</sub> H <sub>6</sub> O <sub>4</sub>	nd	nd	nd	0.21	nd	0.11

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<i>m</i> -Anisic acid	C <sub>8</sub> H <sub>8</sub> O <sub>3</sub>	nd	nd	nd	nd	nd	0.44
Ferulic acid	C <sub>10</sub> H <sub>10</sub> O <sub>4</sub>	0.12	0.085 - 0.096	0.14	0.10	0.061 - 0.10	0.037 - 0.086
Phosphoric acid	H <sub>3</sub> PO <sub>4</sub>	0.045	0.21 - 0.28	0.25	0.16	0.14 - 0.20	0.065 - 1.2
Pyrotartaric acid (2-methylbutanedioic acid)	C <sub>5</sub> H <sub>8</sub> O <sub>4</sub>	nd	nd	nd	nd	nd	0.051 - 0.24
Boric acid	H <sub>3</sub> BO <sub>3</sub>	nd	nd	nd	nd	nd	
<b>Phenols and alteration products</b>							
Vanillin	C <sub>8</sub> H <sub>8</sub> O	nd	nd	0.94	nd	nd	nd
Vanillic acid	C <sub>8</sub> H <sub>8</sub> O <sub>4</sub>	2.9	0.63 - 1.5	1.4	1.9	1.1 - 2.6	0.69 - 2.1
Homovanillic acid	C <sub>9</sub> H <sub>10</sub> O <sub>4</sub>	0.64	0.23 - 0.51	0.63	0.41	0.30 - 0.60	0.075 - 0.74
Vanillyl acetic acid	-	4.0	nd	nd	nd	nd	nd
3-Vanillylpropanol	C <sub>10</sub> H <sub>14</sub> O <sub>3</sub>	1.6	0.34 - 0.65	0.57	1.0	0.25 - 1.1	0.53 - 1.6
Coniferyl alcohol	C <sub>10</sub> H <sub>12</sub> O <sub>3</sub>	0.21	0.011 - 0.091	0.029	0.0061	0.016 - 0.10	0.036 - 0.27
Syringaldehyde	C <sub>9</sub> H <sub>10</sub> O <sub>4</sub>	nd	0.25	nd	nd	0.21	0.37
Syringic acid	C <sub>9</sub> H <sub>10</sub> O <sub>5</sub>	1.9	0.98 - 2.9	1.5	3.8	1.3 - 1.5	0.42 - 0.98
Sinapyl alcohol	C <sub>11</sub> H <sub>14</sub> O <sub>4</sub>	0.027	0.024 - 0.24	0.018	0.039	0.041 - 0.39	0.025 - 0.86
Sinapic acid	C <sub>11</sub> H <sub>12</sub> O <sub>5</sub>	0.0061	0.069 - 0.020	0.0086	0.022	0.0063 - 0.0081	0.0028 - 0.011
<i>p</i> -Coumaric acid	C <sub>9</sub> H <sub>8</sub> O <sub>3</sub>	0.17	0.14	nd	nd	nd	0.071 - 0.091
(±)- $\alpha$ -Tocopherol = Vitamin E	C <sub>29</sub> H <sub>50</sub> O <sub>2</sub>	0.096	0.12 - 0.43	0.26	0.34	0.0052 - 0.69	0.035 - 0.49
3-Hydroxybenzoic acid	C <sub>7</sub> H <sub>6</sub> O <sub>3</sub>	0.51	0.18 - 0.26	0.029	-	0.30 - 0.40	0.20 - 0.39
4-Hydroxybenzoic acid	C <sub>7</sub> H <sub>6</sub> O <sub>3</sub>	0.53	0.48 - 0.97	0.55	1.0	0.37 - 1.2	0.18 - 0.96
Benzoic acid	C <sub>7</sub> H <sub>6</sub> O <sub>2</sub>	0.43	0.34 - 0.50	0.38	0.31	0.66 - 1.6	0.23 - 0.52
Resorcinol	C <sub>6</sub> H <sub>6</sub> O <sub>2</sub>	0.82	0.22 - 0.77	0.51	0.13	0.68 - 2.2	1.5 - 10
2-methylresorcinol	C <sub>7</sub> H <sub>8</sub> O <sub>2</sub>	nd	nd	nd	nd	nd	1.1
5-methylresorcinol	C <sub>7</sub> H <sub>8</sub> O <sub>2</sub>	nd	0.30	nd	0.14	0.19	1.4
Catechol	C <sub>6</sub> H <sub>6</sub> O <sub>2</sub>	1.1	0.17 - 0.57	0.90	0.080	2.2 - 3.5	1.1 - 3.4
3-Methylcatechol	C <sub>7</sub> H <sub>8</sub> O <sub>2</sub>	nd	0.096	nd	nd	0.28 - 1.8	0.30 - 0.83
4-methylcatechol	C <sub>7</sub> H <sub>8</sub> O <sub>2</sub>	0.69	0.16 - 0.34	1.2	nd	0.58 - 0.96	0.37 - 2.3

Pyrogallol	C <sub>9</sub> H <sub>14</sub> O <sub>3</sub>	0.36	0.49 - 0.58	0.66	nd	1.1 - 1.2	0.50 - 1.0
Isoeugenol	C <sub>10</sub> H <sub>12</sub> O <sub>2</sub>	nd	nd	nd	nd	nd	nd
trans-Cinnamic acid	C <sub>9</sub> H <sub>8</sub> O <sub>2</sub>	0.022	0.059 - 0.21	0.30	0.12	0.14 - 0.27	0.041 - 0.23
Hydroquinone	C <sub>6</sub> H <sub>4</sub> (OH) <sub>2</sub>	0.80	0.079 - 0.36	0.42	nd	1.1 - 2.1	0.87 - 2.1
4-Octylphenol	C <sub>14</sub> H <sub>22</sub> O	nd	nd	nd	0.043	nd	0.012 - 0.026
4-Nonylphenol	C <sub>15</sub> H <sub>24</sub> O	nd	nd	nd	nd	nd	nd
<b>Terpenoids</b>							
Isopulegol	C <sub>10</sub> H <sub>18</sub> O	0.0017	0.00056 - 0.0021	0.00084	0.0050	0.0022	0.0014 - 0.0018
β-Amyrin	C <sub>30</sub> H <sub>50</sub> O	nd	nd	nd	nd	nd	0.65
<b>Steroids and alteration products</b>							
Stigmasterol	C <sub>29</sub> H <sub>48</sub> O	nd	0.0091	nd	0.037	0.098	0.066 - 0.14
β-Sitosterol	C <sub>29</sub> H <sub>50</sub> O	0.066	0.035 - 0.21	0.15	0.25	0.00026 - 0.42	0.00014 - 0.46
Stigmast-4-en-3-one	C <sub>29</sub> H <sub>48</sub> O	nd	nd	nd	nd	0.34	0.50
<b>Triterpenoids and alteration products</b>							
Lupeol	C <sub>30</sub> H <sub>50</sub> O	0.18	0.052	nd	nd	nd	0.00089 - 0.58
Cholesterol	C <sub>27</sub> H <sub>46</sub> O	nd	nd	nd	nd	nd	0.26 - 0.27
Campesterol	C <sub>28</sub> H <sub>48</sub> O	nd	nd	nd	nd	0.40	0.36
<b>Diterpenoids and alteration products</b>							
Isopimaric acid	C <sub>20</sub> H <sub>30</sub> O <sub>2</sub>	nd	0.0079	2.0	0.54	0.89	0.021 - 2.6
Pimaric acid	C <sub>20</sub> H <sub>30</sub> O <sub>2</sub>	nd	nd	3.4	nd	1.4	1.8 - 2.4

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Abietic acid	C <sub>20</sub> H <sub>30</sub> O <sub>2</sub>	nd	0.044	0.21	nd	0.81	0.012 - 1.0
Dehydroabietic acid	C <sub>20</sub> H <sub>28</sub> O <sub>2</sub>	nd	0.77 - 1.1	12	2.5	0.065 - 5.2	0.16 - 10
<b>Anhydrosugars</b>							
Galactosan	C <sub>6</sub> H <sub>10</sub> O <sub>5</sub>	1.4	1.4 - 1.6	2.6	1.9	1.4 - 2.4	0.53 - 2.1
Mannosan	C <sub>6</sub> H <sub>10</sub> O <sub>5</sub>	1.9	1.9 - 2.8	4.5	2.8	2.1 - 3.2	0.74 - 3.0
Levogluconan	C <sub>6</sub> H <sub>10</sub> O <sub>5</sub>	5.4	4.1 - 7.4	8.7	4.8	3.3 - 6.4	1.6 - 7.8
<b>Saccharides</b>							
Glycerol	C <sub>3</sub> H <sub>8</sub> O <sub>3</sub>	0.054	0.042 - 0.13	0.0081	0.0086	0.026 - 0.047	0.015 - 0.051
Erythrose	C <sub>4</sub> H <sub>8</sub> O <sub>4</sub>	nd	nd	nd	nd	nd	nd
Erythritol	C <sub>4</sub> H <sub>10</sub> O <sub>4</sub>	nd	0.73	nd	nd	nd	0.64 - 1.4
l-Lyxose	C <sub>5</sub> H <sub>10</sub> O <sub>5</sub>	nd	nd	nd	nd	nd	nd
D-(-)-Ribose	C <sub>5</sub> H <sub>10</sub> O <sub>5</sub>	nd	0.17 - 0.19	nd	nd	0.19	0.071 - 0.16
Xylitol	C <sub>5</sub> H <sub>12</sub> O <sub>5</sub>	nd	0.18	nd	nd	nd	0.094
D-(+)-Arabitol	C <sub>5</sub> H <sub>12</sub> O <sub>5</sub>	nd	nd	0.18	0.11	0.13 - 0.16	0.071 - 0.22
Ribitol	C <sub>5</sub> H <sub>12</sub> O <sub>5</sub>	0.92	0.63	0.55	0.49	0.39 - 0.52	0.13 - 0.44
D-Mannitol	C <sub>6</sub> H <sub>14</sub> O <sub>6</sub>	0.070	0.032 - 0.096	nd	nd	nd	0.021 - 0.076
Sorbitol	C <sub>6</sub> H <sub>14</sub> O <sub>6</sub>	nd	0.032	nd	nd	nd	0.024 - 0.025
D-Galactose	C <sub>6</sub> H <sub>12</sub> O <sub>6</sub>	0.16	0.048	nd	nd	nd	0.016 - 0.040
Glucose	C <sub>6</sub> H <sub>12</sub> O <sub>6</sub>	nd	0.025	0.023	nd	nd	0.031 - 0.042
Inositol	C <sub>6</sub> H <sub>12</sub> O <sub>6</sub>	0.081	0.013 - 0.054	nd	nd	0.012	0.0051 - 0.035
Sucrose	C <sub>12</sub> H <sub>22</sub> O <sub>11</sub>	nd	0.033 - 0.049	nd	0.012	nd	0.016
Maltose	C <sub>12</sub> H <sub>22</sub> O <sub>11</sub>	0.17	0.10 - 0.18	0.082	0.046	0.039 - 0.073	0.023 - 0.19
<b>Σ Other compounds</b>		6.4	3.6	6.3	5.9	5.3	3.7

(nd) not detected; (---) detected, but not quantified, because of abundances close to the detection limit.

		PM <sub>2.5-10</sub>					
Wildfires		Dornelas (Sever do Vouga)	Rebordelo (Santa Maria da feira)	Albergaria-a-Velha	Albergaria-a-Velha	Junqueira (Vale de Cambra)	Vila Nova de Tazem (Gouveia)
Compounds	Formula						
<b>Alcohols</b>							
<i>n</i> -Decanol	C <sub>10</sub> H <sub>22</sub> O	nd	--- - 0.0046	nd	nd	0.01	--- - 0.0012
<i>n</i> -Dodecanol	C <sub>12</sub> H <sub>26</sub> O	nd	0.12	nd	nd	nd	nd
<i>n</i> -Tetradecanol	C <sub>14</sub> H <sub>30</sub> O	nd		nd	nd	nd	0.0086 - 0.72
<i>n</i> -Pentadecanol	C <sub>15</sub> H <sub>32</sub> O	---	0.084 - 0.11	0.041	0.10	0.12	0.12 - 0.58
<i>n</i> -Hexadecanol	C <sub>16</sub> H <sub>34</sub> O	0.017	--- - 0.090	0.080	0.11	0.021 - 0.076	0.035 - 0.23
<i>n</i> -Octadecanol	C <sub>18</sub> H <sub>38</sub> O	---	---	---	---	--- - 0.002	--- - 0.18
<i>n</i> -Eicosanol	C <sub>20</sub> H <sub>42</sub> O	nd	0.054 - 0.059	0.069	0.14	0.15 - 0.28	0.12 - 0.38
<i>n</i> -Heneicosanol	C <sub>21</sub> H <sub>44</sub> O	nd	nd	nd	0.10	nd	nd
<i>n</i> -Docosanol	C <sub>22</sub> H <sub>46</sub> O	0.44	0.021 - 0.51	0.36	2.00	0.38 - 0.72	0.24 - 0.84
<i>n</i> -Tricosanol	C <sub>23</sub> H <sub>48</sub> O	0.043	0.0045 - 0.032	0.034	0.17	0.041 - 0.10	0.042 - 0.12
<i>n</i> -Tetracosanol	C <sub>24</sub> H <sub>50</sub> O	0.84	0.078 - 0.29	0.23	0.82	0.32 - 0.58	0.30 - 0.71
<i>n</i> -Pentacosanol	C <sub>25</sub> H <sub>52</sub> O	0.025	0.0020 - 0.018	0.017	0.11	0.021 - 0.056	0.024 - 0.083
<i>n</i> -Hexacosanol	C <sub>26</sub> H <sub>54</sub> O	0.89	0.077 - 0.29	0.19	0.87	0.36 - 1.6	0.60 - 1.8
<i>n</i> -Heptacosanol	C <sub>27</sub> H <sub>56</sub> O	0.023	0.00071 - 0.015	0.015	0.17	0.020 - 0.084	0.039 - 0.23
<i>n</i> -Octacosanol	C <sub>28</sub> H <sub>58</sub> O	1.0	0.013 - 0.39	0.18	0.88	0.17 - 0.62	0.39 - 2.8
<i>n</i> -Nonacosanol	C <sub>29</sub> H <sub>60</sub> O	nd	nd	nd	0.17	0.10	0.018 - 0.15

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<i>n</i> -Triacontanol	C <sub>30</sub> H <sub>62</sub> O	0.65	0.34	0.23	1.4	0.099 - 69	0.39 - 2.6
<b>Other alcohols</b>							
(-)-Myrtenol	C <sub>10</sub> H <sub>16</sub> O	0.0084	0.034	0.0011	nd	nd	0.0040 - 0.0062
Benzyl alcohol	C <sub>7</sub> H <sub>8</sub> O	0.17	0.0079 - 4.9	2.0	1.2	0.44 - 1.4	0.040 - 4.0
<i>cis</i> -2-Methylcyclohexanol	C <sub>7</sub> H <sub>14</sub> O	-	0.0027	nd	nd	0.00085 - 0.0013	0.0010
(1 <i>S</i> ,2 <i>S</i> ,3 <i>R</i> ,5 <i>S</i> )-(+)-2,3-Pinane-1,2-diol	C <sub>10</sub> H <sub>18</sub> O <sub>2</sub>	0.021	0.0073 - 0.0083	0.016	nd	0.037 - 0.061	0.028 - 0.056
<b><i>n</i>-alkanoic acids</b>							
Hexanoic acid	C <sub>6</sub> H <sub>12</sub> O <sub>2</sub>	nd	nd	nd	nd	nd	
Heptanoic acid	C <sub>7</sub> H <sub>14</sub> O <sub>2</sub>	nd	nd	nd	nd	0.034	0.027 - 0.12
Octanoic acid	C <sub>8</sub> H <sub>16</sub> O <sub>2</sub>	0.85	0.15 - 0.16	0.082	0.15	0.16 - 0.17	0.12 - 0.26
Nonanoic acid	C <sub>9</sub> H <sub>18</sub> O <sub>2</sub>	1.4	0.080 - 0.20	0.14	0.085	0.097 - 0.22	0.15 - 0.31
Decanoic acid	C <sub>10</sub> H <sub>20</sub> O <sub>2</sub>	1.8	0.18 - 0.21	0.23	0.33	0.23 - 0.34	0.15 - 0.47
Undecanoic acid	C <sub>11</sub> H <sub>22</sub> O <sub>2</sub>	0.18	0.029 - 0.10	0.084	0.099	0.18 - 0.82	0.11 - 0.38
Dodecanoic Acid	C <sub>12</sub> H <sub>24</sub> O <sub>2</sub>	1.2	0.41 - 0.92	0.49	0.67	1.2 - 1.8	0.69 - 2.9
Tridecanoic acid	C <sub>13</sub> H <sub>26</sub> O <sub>2</sub>	0.18	0.12 - 0.18	0.075	0.17	0.18	0.11 - 0.50
Tetradecanoic acid	C <sub>14</sub> H <sub>28</sub> O <sub>2</sub>	15	0.61 - 3.0	0.78	nd	1.50	1.1 - 4.0
Pentadecanoic acid	C <sub>15</sub> H <sub>30</sub> O <sub>2</sub>	4.0	0.20 - 0.41	0.33	0.93	0.71 - 1.1	0.67 - 2.1
Hexadecanoic acid	C <sub>16</sub> H <sub>32</sub> O <sub>2</sub>	19	4.9 - 15	5.6	12	3.7 - 7.4	3.4 - 26
Heptadecanoic acid	C <sub>17</sub> H <sub>34</sub> O <sub>2</sub>	5.0	0.44 - 2.1	0.22	1.1	1.1 - 1.2	0.66 - 2.2
Octadecanoic acid	C <sub>18</sub> H <sub>36</sub> O <sub>2</sub>	20	2.9 - 20	7.2	6.8	2.8 - 8.4	3.4 - 33
Nonadecanoic acid	C <sub>19</sub> H <sub>38</sub> O <sub>2</sub>	1.8	0.29	---	0.61	--- - 0.26	--- - 0.22
Eicosanoic acid	C <sub>20</sub> H <sub>40</sub> O <sub>2</sub>	8.5	0.54 - 2.0	0.75	1.8	1.8	0.83 - 3.0
Heneicosanoic acid	C <sub>21</sub> H <sub>42</sub> O <sub>2</sub>	2.4	0.30 - 0.33	-	0.65	0.41 - 0.58	0.28 - 0.64
Docosanoic acid	C <sub>22</sub> H <sub>44</sub> O <sub>2</sub>	19	1.0 - 2.7	1.7	4.6	3.6 - 3.8	2.0 - 5.4
Tricosanoic acid	C <sub>23</sub> H <sub>46</sub> O <sub>2</sub>	5.2	0.35 - 0.61	nd	0.89	1.1 - 1.6	0.53 - 1.4

Tetracosanoic acid	C <sub>24</sub> H <sub>48</sub> O <sub>2</sub>	18	1.2 - 2.9	2.3	5.8	4.1 - 4.3	2.4 - 6.6
Pentacosanoic acid	C <sub>25</sub> H <sub>50</sub> O <sub>2</sub>	nd	nd	nd	nd	0.21	0.13 - 0.15
Hexacosanoic acid	C <sub>26</sub> H <sub>52</sub> O <sub>2</sub>	5.8	0.26 - 0.52	nd	1.6	1.3	0.53 - 1.2
Heptacosanoic acid	C <sub>27</sub> H <sub>54</sub> O <sub>2</sub>	nd	0.12	nd	-	0.15	0.11 - 0.27
Octacosanoic acid	C <sub>28</sub> H <sub>56</sub> O <sub>2</sub>	2.6	4.5	nd	0.86	1.0 - 1.2	0.55 - 1.2
Nonacosanoic acid	C <sub>29</sub> H <sub>58</sub> O <sub>2</sub>	nd	nd	nd	nd	0.14	0.16 - 0.37
Triacontanoic acid	C <sub>30</sub> H <sub>60</sub> O <sub>2</sub>	nd	0.22	nd	nd	0.50 - 0.62	0.48 - 1.1
<i>n-di-acids</i>							
Propanedioic acid	C <sub>3</sub> H <sub>4</sub> O <sub>4</sub>	0.00030	0.0090 - 0.56	0.15	0.33	0.019 - 0.058	0.0016 - 0.22
Butanedioic acid	C <sub>4</sub> H <sub>6</sub> O <sub>4</sub>	1.3	0.15 - 0.23	0.92	1.1	0.51 - 0.52	0.13 - 1.9
Pentanedioic acid	C <sub>5</sub> H <sub>8</sub> O <sub>4</sub>	0.0050	0.057 - 0.091	0.26	0.31	0.088 - 0.16	0.030 - 0.64
Hexanedioic acid	C <sub>6</sub> H <sub>10</sub> O <sub>4</sub>	0.048	0.032 - 0.071	0.15	0.28	0.049 - 0.25	0.023 - 0.74
Heptanedioic acid	C <sub>7</sub> H <sub>12</sub> O <sub>4</sub>	nd	0.090 - 0.24	0.084	0.14	0.20 - 0.22	0.081 - 0.57
Octanedioic acid	C <sub>8</sub> H <sub>14</sub> O <sub>4</sub>	0.20	0.098 - 0.17	0.19	0.073	0.20	0.055 - 0.35
Nonanedioic acid	C <sub>9</sub> H <sub>16</sub> O <sub>4</sub>	0.30	0.0038 - 0.28	0.17	0.63	0.37	0.087 - 1.1
Decanedioic acid	C <sub>10</sub> H <sub>18</sub> O <sub>4</sub>	0.041	0.021 - 0.039	0.015	0.079	0.056 - 0.26	0.022 - 0.55
Hexadecanedioic acid	C <sub>16</sub> H <sub>30</sub> O <sub>4</sub>	---	---	---	0.065	0.18	0.0039 - 0.016
<i>Dicarboxylic acids</i>							
Methylmalonic acid	C <sub>4</sub> H <sub>6</sub> O <sub>4</sub>	0.0058	0.0050 - 0.022	0.034	0.025	0.0054 - 0.011	0.0057 - 0.065
Pinic acid	C <sub>11</sub> H <sub>18</sub> O <sub>4</sub>	0.22	0.079 - 0.19	nd	0.10	0.25 - 0.52	0.061 - 0.49
<i>Oxo-acids</i>							
Levulinic acid	C <sub>5</sub> H <sub>8</sub> O <sub>3</sub>	1.6	0.20 - 0.57	1.5	0.71	0.24 - 0.36	0.12 - 1.5

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<b>Hydroxy-acids</b>								
Glycolic acid	C <sub>2</sub> H <sub>4</sub> O <sub>3</sub>	13	1.7 - 4.9	3.3	1.1	1.0 - 2.3	0.30 - 8.2	
L-(-)-Malic acid	C <sub>4</sub> H <sub>6</sub> O <sub>5</sub>	0.24	0.0022 - 0.11	nd	0.017	0.031	0.0026 - 0.12	
2-Hydroxybutyric acid	C <sub>4</sub> H <sub>8</sub> O <sub>3</sub>	0.75	0.12	0.31	nd	0.17	0.044 - 0.35	
4-Hydroxybutyric acid	C <sub>4</sub> H <sub>8</sub> O <sub>3</sub>	0.69	0.14	0.15	nd	0.090	nd	
Propanoic acid	C <sub>3</sub> H <sub>6</sub> O <sub>2</sub>	1.4	0.12 - 0.29	nd	0.24	0.13 - 0.30	0.030 - 1.0	
<b>Unsaturated Fatty acid</b>								
Oleic acid (C <sub>18:1</sub> )	C <sub>18</sub> H <sub>34</sub> O <sub>2</sub>	20	0.44 - 1.2	1.1	6.2	1.5 - 2.1	2.0 - 4.1	
Linoleic acid (C <sub>18:2</sub> )	C <sub>18</sub> H <sub>32</sub> O <sub>2</sub>	0.82	0.34 - 0.74	0.62	1.2	1.1 - 1.4	1.2 - 3.1	
Palmitoleic acid	C <sub>16</sub> H <sub>30</sub> O <sub>2</sub>	nd	nd	nd	nd	nd	nd	
<b>Other acids</b>								
Lactic acid	C <sub>3</sub> H <sub>6</sub> O <sub>3</sub>	8.0	1.4 - 2.3	4.2	5.5	0.85 - 2.9	0.48 - 9.9	
Hydracrylic acid	C <sub>3</sub> H <sub>6</sub> O <sub>3</sub>	nd	0.29	nd	0.29	nd	0.11 - 0.89	
(R)-3-hydroxybutyric acid	C <sub>4</sub> H <sub>8</sub> O <sub>3</sub>	0.97	0.10 - 0.20	0.15	0.13	0.058 - 0.14	--- - 0.21	
D-Glucuronic acid	C <sub>6</sub> H <sub>10</sub> O <sub>7</sub>	0.012	0.035 - 0.11	0.017	0.040	0.014 - 0.044	0.0061 - 0.050	
2-Furoic acid	C <sub>5</sub> H <sub>4</sub> O <sub>3</sub>	2.4	0.14 - 0.16	nd	0.15	0.26 - 0.41	0.041 - 0.39	
Benzenepropanoic acid	C <sub>9</sub> H <sub>10</sub> O <sub>2</sub>	nd	nd	nd	nd	nd	nd	
Hydrocinnamic acid	C <sub>6</sub> H <sub>10</sub> O <sub>2</sub>	0.97	0.30	nd	nd	0.13 - 0.55	0.21 - 0.34	
Butanoic acid	C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>	4.1	0.14 - 0.67	0.59	0.37	0.26 - 0.52	0.076 - 0.97	
cis-Pinonic acid	C <sub>10</sub> H <sub>16</sub> O <sub>3</sub>	nd	0.049 - 0.074	0.081	0.084	0.023 - 0.042	0.013 - 0.17	
D-Glucuronic acid lactone	C <sub>6</sub> H <sub>8</sub> O <sub>6</sub>	0.0061	0.0054 - 0.0075	0.0046	nd	nd	0.0050 - 0.0090	
Maleic acid	C <sub>4</sub> H <sub>4</sub> O <sub>4</sub>	nd	nd	-	nd	nd	nd	
Methylmaleic acid	C <sub>5</sub> H <sub>6</sub> O <sub>4</sub>	nd	nd	0.35	nd	nd	nd	
<i>m</i> -Anisic acid	C <sub>8</sub> H <sub>8</sub> O <sub>3</sub>	nd	---	-	nd	0.33	0.073 - 0.30	

Ferulic acid	C <sub>10</sub> H <sub>10</sub> O <sub>4</sub>	nd	nd	0.19	nd	nd	nd
Phosphoric acid	H <sub>3</sub> PO <sub>4</sub>	2.6	0.013 - 0.13	nd	0.71	1.40	0.16 - 7.0
Pyrotartaric acid (2-methylbutanedioic acid)	C <sub>5</sub> H <sub>8</sub> O <sub>4</sub>	nd	nd	nd	-	nd	nd
Boric acid	H <sub>3</sub> BO <sub>3</sub>	nd	nd	nd	0.34	0.057 - 0.54	0.015 - 1.7
<b>Phenols and alteration products</b>							
Vanillin	C <sub>8</sub> H <sub>8</sub> O	7.3	0.48 - 1.6	5.0	1.9	2.5 - 3.4	0.90 - 8.2
Vanillic acid	C <sub>8</sub> H <sub>8</sub> O <sub>4</sub>	12	0.25 - 1.6	1.3	1.6	2.0 - 2.5	0.46 - 2.3
Homovanillic acid	C <sub>9</sub> H <sub>10</sub> O <sub>4</sub>	nd	0.16	0.33	0.41	0.49 - 0.56	0.26 - 0.50
Vanillyl acetic acid	-	nd	nd	0.22	nd	nd	nd
3-Vanillylpropanol	C <sub>10</sub> H <sub>14</sub> O <sub>3</sub>	nd	nd	2.5	nd	0.45	nd
Coniferyl alcohol	C <sub>10</sub> H <sub>12</sub> O <sub>3</sub>	nd	0.00089 - 0.0012	0.0035	nd	0.09	0.028 - 0.043
Syringaldehyde	C <sub>9</sub> H <sub>10</sub> O <sub>4</sub>	nd	nd	nd	nd	nd	nd
Syringic acid	C <sub>9</sub> H <sub>10</sub> O <sub>5</sub>	0.74	0.26 - 0.97	0.45	1.8	0.67 - 1.4	0.24 - 0.75
Sinapyl alcohol	C <sub>11</sub> H <sub>14</sub> O <sub>4</sub>	0.0052	0.0025 - 0.0086	-	0.0087	nd	nd
Sinapic acid	C <sub>11</sub> H <sub>12</sub> O <sub>5</sub>	0.0044	0.0011 - 0.016	0.020	0.022	0.0080 - 0.017	0.0021 - 0.017
p-Coumaric acid	C <sub>9</sub> H <sub>8</sub> O <sub>3</sub>	nd	nd	nd	nd	nd	nd
(±)-α-Tocopherol = Vitamin E	C <sub>29</sub> H <sub>50</sub> O <sub>2</sub>	0.094	0.063 - 0.18	0.033	0.53	0.088 - 0.34	0.16 - 5.9
3-Hydroxybenzoic acid	C <sub>7</sub> H <sub>6</sub> O <sub>3</sub>	2.8	0.17	0.36	0.35	0.42 - 0.49	0.14 - 0.94
4-Hydroxybenzoic acid	C <sub>7</sub> H <sub>6</sub> O <sub>3</sub>	6.8	0.0039 - 0.57	0.34	0.50	0.85 - 1.1	0.30 - 0.72
Benzoic acid	C <sub>7</sub> H <sub>6</sub> O <sub>2</sub>	6.6	3.2 - 14	2.7	1.4	1.5 - 1.6	0.97 - 2.8
Resorcinol	C <sub>6</sub> H <sub>6</sub> O <sub>2</sub>	nd	0.38	nd	0.30	0.24 - 0.50	0.35 - 4.9
2-methylresorcinol	C <sub>7</sub> H <sub>8</sub> O <sub>2</sub>	nd	nd	nd	nd	nd	0.42 - 0.53
5-methylresorcinol	C <sub>7</sub> H <sub>8</sub> O <sub>2</sub>	nd	nd	nd	nd	0.16	0.36 - 0.36
Catechol	C <sub>6</sub> H <sub>6</sub> O <sub>2</sub>	1.9	0.52	0.64	nd	0.77 - 3.8	0.87 - 1.6
3-Methylcatechol	C <sub>7</sub> H <sub>8</sub> O <sub>2</sub>	nd	nd	nd	nd	nd	nd
4-methylcatechol	C <sub>7</sub> H <sub>8</sub> O <sub>2</sub>	nd	nd	nd	nd	1.2	0.81 - 0.84
Pyrogallol	C <sub>9</sub> H <sub>14</sub> O <sub>3</sub>	nd	nd	nd	nd	nd	nd

## Supplementary Material

Isoeugenol	C <sub>10</sub> H <sub>12</sub> O <sub>2</sub>	nd	nd	nd	nd	0.38	nd
<i>trans</i> -Cinnamic acid	C <sub>9</sub> H <sub>8</sub> O <sub>2</sub>	1.1	0.048 - 0.41	0.50	0.82	0.16 - 0.22	0.070 - 0.27
Hydroquinone	C <sub>6</sub> H <sub>4</sub> (OH) <sub>2</sub>	nd	nd	nd	nd	nd	nd
4-Octylphenol	C <sub>14</sub> H <sub>22</sub> O	0.0013	0.0013	0.0026	0.0025	0.0023	0.0014 - 0.0056
4-Nonylphenol	C <sub>15</sub> H <sub>24</sub> O	nd	nd	nd	nd	nd	nd
<b>Terpenoids</b>							
Isopulegol	C <sub>10</sub> H <sub>18</sub> O	0.0068	0.0037 - 0.0087	0.0039	0.0025	0.0028 - 0.0034	0.0017 - 0.01
β-Amyrin	C <sub>30</sub> H <sub>50</sub> O	nd	0.70	nd	nd	nd	nd
<b>Steroids and alteration products</b>							
Stigmasterol	C <sub>29</sub> H <sub>48</sub> O	nd	0.028	0.0089	0.043	0.11 - 0.12	0.047 - 0.50
β-Sitosterol	C <sub>29</sub> H <sub>50</sub> O	nd	0.12 - 0.16	0.15	0.28	0.47 - 0.66	0.25 - 0.61
Stigmast-4-en-3-one	C <sub>29</sub> H <sub>48</sub> O	nd	nd	nd	nd	0.28	nd
<b>Triterpenoids and alteration products</b>							
Lupeol	C <sub>30</sub> H <sub>50</sub> O	0.034	0.15	nd	nd	nd	0.57 - 2.7
Cholesterol	C <sub>27</sub> H <sub>46</sub> O	nd	nd	nd	nd	0.20 - 0.30	0.27 - 0.27
Campesterol	C <sub>28</sub> H <sub>48</sub> O	nd	nd	nd	nd	0.42	nd
<b>Diterpenoids and alteration products</b>							
Isopimaric acid	C <sub>20</sub> H <sub>30</sub> O <sub>2</sub>	0.61	0.027 - 0.088	1.9	0.19	0.30 - 0.45	0.84 - 2.8
Pimaric acid	C <sub>20</sub> H <sub>30</sub> O <sub>2</sub>	nd	nd	3.3	nd	0.74 - 0.80	0.62 - 2.6
Abietic acid	C <sub>20</sub> H <sub>30</sub> O <sub>2</sub>	1.4	0.028 - 0.038	2.1	0.39	0.33 - 0.36	0.47 - 1.4
Dehydroabietic acid	C <sub>20</sub> H <sub>28</sub> O <sub>2</sub>	24	0.76 - 1.5	14	1.8	3.0 - 3.1	3.9 - 14

**Anhydrosugars**

Galactosan	C <sub>6</sub> H <sub>10</sub> O <sub>5</sub>	12	0.94 - 1.5	1.8	1.3	1.6 - 2.2	0.52 - 1.0
Mannosan	C <sub>6</sub> H <sub>10</sub> O <sub>5</sub>	22	1.4 - 2.7	4.3	2.2	2.9 - 3.4	0.77 - 2.9
Levoglucofan	C <sub>6</sub> H <sub>10</sub> O <sub>5</sub>	56	2.7 - 7.5	12	9.9	7.2 - 8.6	2.8 - 10

**Shaccarides**

Glycerol	C <sub>3</sub> H <sub>8</sub> O <sub>3</sub>	0.86	0.93 - 5.7	1.8	0.12	0.046 - 0.15	0.0014 - 0.054
Erythrose	C <sub>4</sub> H <sub>8</sub> O <sub>4</sub>	nd	nd	nd	nd	3.00	0.97 - 4.33
Erythritol	C <sub>4</sub> H <sub>10</sub> O <sub>4</sub>	nd	0.61 - 0.79	nd	nd	nd	0.93 - 1.0
l-Lyxose	C <sub>5</sub> H <sub>10</sub> O <sub>5</sub>	nd	1.5	14	nd	nd	nd
D-(-)-Ribose	C <sub>5</sub> H <sub>10</sub> O <sub>5</sub>	0.62	0.081 - 0.088	0.12	nd	0.12	0.062 - 0.27
Xylitol	C <sub>5</sub> H <sub>12</sub> O <sub>5</sub>	1.0	0.23 - 0.80	0.15	0.076	nd	0.049 - 0.21
D-(+)-Arabitol	C <sub>5</sub> H <sub>12</sub> O <sub>5</sub>	nd	nd	nd	0.69	0.13	0.075 - 0.081
Ribitol	C <sub>5</sub> H <sub>12</sub> O <sub>5</sub>	nd	nd	0.42	nd	0.25 - 0.51	0.13 - 0.20
D-Mannitol	C <sub>6</sub> H <sub>14</sub> O <sub>6</sub>	nd	0.051 - 0.60	0.050	0.062	0.07	0.031 - 0.10
Sorbitol	C <sub>6</sub> H <sub>14</sub> O <sub>6</sub>	nd	0.045 - 0.097	nd	nd	0.05	0.049 - 0.091
D-Galactose	C <sub>6</sub> H <sub>12</sub> O <sub>6</sub>	0.40	0.074	0.074	0.11	nd	0.096 - 0.14
Glucose	C <sub>6</sub> H <sub>12</sub> O <sub>6</sub>	nd	0.13	0.045	0.10	0.047 - 0.47	0.028 - 0.11
Inositol	C <sub>6</sub> H <sub>12</sub> O <sub>6</sub>	nd	nd	nd	nd	nd	nd
Sucrose	C <sub>12</sub> H <sub>22</sub> O <sub>11</sub>	0.93	0.064 - 0.40	0.11	nd	0.07	0.037 - 0.15
Maltose	C <sub>12</sub> H <sub>22</sub> O <sub>11</sub>	nd	0.19	0.18	nd	nd	nd

**∑ Other compounds**

76	6.8	0.61	8.7	10	8.7
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(nd) not detected; (---) detected, but not quantified, because of abundances close to the detection limit.

