



## Organic compounds in PM<sub>2.5</sub> emitted from fireplace and woodstove combustion of typical Portuguese wood species

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### ABSTRACT

The aim of this study is the further characterisation of PM<sub>2.5</sub> emissions from the residential wood combustion of common woods grown in Portugal. This new research extends to eight the number of biomass fuels studied and tries to understand the differences that the burning appliance (fireplace versus woodstove) and the combustion temperature (cold and hot start) have on emissions. *Pinus pinaster* (Maritime pine), *Eucalyptus globulus* (eucalypt), *Quercus suber* (cork oak), *Acacia longifolia* (Golden wattle), *Quercus faginea* (Portuguese oak), *Olea europea* (Olive), *Quercus ilex rotundifolia* (Holm oak) and briquettes produced from forest biomass waste were used in the combustion tests. Determinations included fine particle emission factors, carbonaceous content (OC and EC) by a thermal–optical transmission technique and detailed identification and quantification of organic compounds by gas chromatography–mass spectrometry. Fine particle emission factors from the woodstove were lower than those from the fireplace. For both combustion appliances, the OC/EC ratio was higher in “cold start” tests ( $1.56 \pm 0.95$  for woodstove and  $2.03 \pm 1.34$  for fireplace). These “cold start” OC/EC values were, respectively, for the woodstove and the fireplace, 51% and 69% higher than those obtained in “hot start” experiments. The chromatographically resolved organics included *n*-alkanes, *n*-alkenes, PAHs, *n*-alkanal, ketones, *n*-alkanols, terpenoids, triterpenoids, phenolic compounds, phytosterols, alcohols, *n*-alkanoic acids, *n*-di-acids, unsaturated acids and alkyl esters of acids. The smoke emission rate and composition varied widely depending on fuel type, burning appliance and combustion temperature.

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### 1. Introduction

Residential wood log combustion is considered to be a major emission source of local and regional air pollution, especially for particulate matter and hydrocarbons, such as polycyclic aromatics (Fine et al., 2004b; Rogge et al., 1998; Schmidl et al., 2008a). The flue gases from residential biomass combustion are dominated by submicron particles ( $<1 \mu\text{m}$ ) by number and often also by mass, and there is an increasing interest in their characteristics and implications to human health (Lighty et al., 2000). Besides the health-related implications, these aerosols have climate-forcing impacts, either contributing to, or balancing, the effects of greenhouse gases (Danny and Kaufmann, 2002). In Europe, emissions from biomass combustion are one of the major sources of atmospheric aerosol mass during winter (Puxbaum et al., 2007; Gelencsér et al., 2007). Modelling results showed that in Portugal

18% of PM<sub>10</sub> could be related to this emission source, which may deeply impact the levels in the atmosphere (Borrego et al., 2010). Source apportionment of PM<sub>2.5</sub> aerosol applied to ambient measurements in a coastal/rural area in Portugal showed that 52–69% of the organic carbon is assigned to residential wood burning for heating (Gelencsér et al., 2007). Responses to a national survey (unpublished data) indicated that, on average, 34% of the Portuguese population uses residential wood combustion for heating purposes, but this percentage can reach 62% in cold inland districts, such as Viseu. In Portugal and other Mediterranean countries, there is a lack of information concerning the characteristics of particulate emissions from biomass combustion systems. Emission inventories and source apportionment studies (e.g. Caseiro et al., 2009; Kupiainen and Limonet, 2007; Yin et al., 2010) have been using default values obtained for United States (e.g. Fine et al., 2004a,b), mid-European Alpine region (Schmidl et al., 2008a), or Scandinavian (Hedberg et al., 2002; Johansson et al., 2004) biofuels, uncommon in Southern Europe. Because of the lack of biomass burning profiles for Southern Europe, positive matrix factorisation or principal components analysis (unknown sources)

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instead of chemical mass balance (known sources) have been used to apportion different inputs to the ambient aerosol (e.g. Callen et al., 2009). To overcome the lack of information, a series of source tests were made to evaluate the chemical composition of particulate matter (PM<sub>10</sub>) emissions from the woodstove combustion of four prevalent Portuguese species of wood: *Pinus pinaster*, *Eucalyptus globulus*, *Quercus suber* and *Acacia longifolia*. The burning tests were carried out at the combustion facility of the Vienna University of Technology, on a highly efficient “chimney type” log woodstove and the results were published by Gonçalves et al. (2010). The objectives of this new investigation are to extend to eight the number of biomass fuels studied and try to understand the effects of traditional Portuguese burning appliances (a brick open fireplace versus a cast iron woodstove) and combustion conditions on emissions. In addition to a larger number of wood species involved in the present study in comparison to that in Gonçalves et al. (2010), the two major differences between both investigations are related to the use of burning appliances with distinct characteristics (“chimney type” stove in Austria with high efficiency versus traditional Portuguese equipments with lower efficiency) and sampling of particulate matter with distinct aerodynamic diameters (PM<sub>10</sub> for the Austrian stove, PM<sub>2.5</sub> for the Portuguese appliances).

Characterisation of the emissions for different types of appliances during different operation conditions (cold and hot start phases) makes it possible to identify when the major parts of the emissions occur and actions for emission reduction can then be achieved where the savings can be highest. On the other hand, by weighting the source test results in proportion to the availability of firewood from specific tree species, the quantities of wood burned in each region, type and number of household burning appliances, and prevailing combustion conditions in “ordinary” domestic operation, it will be possible to develop composite regional source profiles for Chemical Mass Balance receptor models, to account for particulate organic emissions at a country-scale and to quantify the regional differences in wood smoke composition.

## 2. Experimental work

### 2.1. Biomass fuel selection

According to the Portuguese Forest Inventory (2005), the top seven nationally predominant tree species are *P. pinaster* (Maritime pine), *E. globulus* (Eucalypt), *Q. suber* (Cork oak), *A. longifolia* (Golden wattle), *Quercus faginea* (Portuguese oak), *Olea europea* (olive) and *Quercus ilex rotundifolia* (Holm oak). The burning emissions of all these species were studied and results are presented here. In addition, biomass briquettes made of wastes from forest cleaning activities and/or wastes from local wood processing industries, common in home heating nowadays, were also studied and evaluated. The elemental composition, ash and moisture content of all tested fuels are presented in Table 1.

### 2.2. Sampling details

The burning tests were carried out at the Department of Environment, University of Aveiro, combustion facility. The facility structure and operational conditions were described in detail by Fernandes (2009). Two types of residential biomass combustion appliances were selected for the source tests: i) a cast iron woodstove (Solzaima, model Sahara), operated manually in batch mode with handheld control of combustion air, and ii) a traditional Portuguese brick open fireplace operated manually in batch mode and with no control of combustion air. In order to evaluate the

**Table 1**  
Elemental composition, ash and moisture content of biofuels (% w/w).

Biomass	% Moisture content	Elemental composition (dry basis)					Ashes
		C	H	N	S	O (by difference)	
Maritime pine	9.10	51.4	6.20	0.160	n/d	41.9	0.360
Eucalypt	11.3	48.6	6.20	0.160	n/d	44.3	0.750
Cork oak	12.2	51.6	6.03	0.180	n/d	40.8	1.41
Olive	15.5	53.6	7.68	0.180	n/d	36.6	1.94
Portuguese oak	14.1	50.3	7.32	0.190	n/d	41.8	0.380
Holm oak	8.70	50.6	7.14	0.180	n/d	39.7	2.32
Golden wattle	8.40	50.8	6.43	0.180	n/d	41.8	0.750
Briquettes	8.40	50.8	7.01	0.160	n/d	41.2	0.910

n/d – not determined because the concentration level was below detection level of 0.01% w/w.

influence of the temperature and fuel ignition process on the combustion flue emission characteristics, two sets of experiments were performed for each appliance and wood fuel type: cold start and hot start. In the experiments with cold start, the combustion began with the appliance at ambient temperature. Thus, the “cold start” experiments represent the post-ignition combustion phase. The hot start experiments were initiated with the load of a batch of fuel to the combustion chamber already at a temperature of around 100 °C and with the presence of a small amount of burning char from a batch of fuel already burned previously. The continuous monitoring of temperatures was made with K-type thermocouples in the middle point of each combustion chamber. The temperature in the combustion chamber of the fireplace, on average, was 128 °C ± 66 °C for “cold start” and 179 °C ± 63 °C for “hot start”. The temperature in the combustion chamber of the woodstove, on average, was 248 °C ± 69 °C for “cold start” and 307 °C ± 67 °C for “hot start”. It should be noted that Tiegs (1995) reported that the cold start-up PM emissions can be about half of the emissions from a full combustion cycle. Thus, emissions from different combustion phases should be accounted for in order to develop composite emission profiles for further application in source apportionment methodologies.

The wood was cut into logs of 30–40 cm in length. Before each burning test, a batch of dry wood was weighed in a balance. The weights ranged between 1.9 and 2.2 kg. The ignition of the wood was achieved using small pieces cut from the same wood being burned. Burn times ranged from 45 to 90 min. Particle sampling began immediately prior to ignition and was ceased at the end of combustion. Collection of particulate matter with aerodynamic diameters below 2.5 μm (PM<sub>2.5</sub>) was performed in a dilution tunnel. Dilution sampling is used to characterise particle emissions from combustion because it simulates the rapid cooling and dilution that occurs as exhaust mixes with the atmosphere (Lipsky and Robinson, 2005). The dilution tunnel consisted of a cylindrical tube with 0.20 m internal diameter and 11 m length. The sampling of PM<sub>2.5</sub> was made at a dilution ratio of 25:1. PM<sub>2.5</sub> were collected using an Echo sampling head connected to a TECORA sampler (model 2.004.01, Italy) operating at a flow of 2.3 m<sup>3</sup> h<sup>-1</sup>, onto quartz fibre filters (47 mm diameter), located at 10 m downstream the dilution tunnel entering. The temperature in the particle sampling point in the dilution tunnel was in the range 25–35 °C.

After each combustion experiment, the PM<sub>2.5</sub> sampling head was cleaned to minimise contamination of the subsequent experiments. Background samples were collected to assess any contamination arising from the dilution air; negligible levels of particulate matter, organic carbon and elemental carbon were found. The conditions at the exit of the chimney of the woodstove or fireplace are different from those in the dilution tunnel. For this reason, the PM<sub>2.5</sub> concentrations at the exit of the chimney were

obtained by correcting the concentrations measured at the dilution tunnel, considering the respective values of temperature, pressure and dilution ratio.

### 2.3. Analytical methods

Gravimetric analysis was performed with a microbalance (Sartorius M5P) after 24 h equilibration in a room with controlled temperature and humidity. Quartz fibre filters used in this work were pre-baked at 500 °C for 6 h. Filter weight before and after sampling was obtained as the average of three measurements, when observed variations were less than 5%.

The elemental carbon (EC) and organic carbon (OC) of particulate matter in quartz fibre filters were analysed by a thermal–optical technique. The carbon analyser was a home-made thermo-optical system, based on the thermal desorption/oxidation of particulate carbon to CO<sub>2</sub>, which is subsequently analysed by non-dispersive infrared spectrophotometry (Pio et al., 1993). 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 (Alves et al., 2011).

Half of the area of each quartz fibre filter was consecutively extracted with dichloromethane and methanol (Fisher Scientific) and the total organic extract was separated into five different organic fractions by flash chromatography with silica gel and various solvents of increasing polarity. After elution, the different fractions were vacuum concentrated and evaporated by ultra pure nitrogen stream. The detailed description of the methodology for the extraction of organic compounds can be found in Alves et al. (2011, in press). The fractionated extracts were analysed by gas chromatography–mass spectrometry (GC model 6890, quadrupole MSD 5973 from Hewlett–Packard and GC Trace Ultra, quadrupole DSQ II from Thermo Scientific). 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). Calibration for GC–MS analysis was based on a total of about 110 standards in different concentration levels with relative response factors determined individually for the majority of compounds. For those with no authentic standards available, relative response factors were calculated as an average of the relative response factors 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-D<sub>50</sub> (Sigma–Aldrich) and 1-chlorohexadecane (Merck). The EPA 8270 Semivolatile Internal Standards Mix (Supelco), with six deuterated compounds (acenaphthene-d<sub>10</sub>, chrysene-d<sub>12</sub>, 1,4-dichlorobenzene-d<sub>4</sub>, naphthalene-d<sub>8</sub>, perylene-d<sub>12</sub>, phenanthrene-d<sub>10</sub>) was used for the determination of PAHs. Compound identification was based on comparison of resulting spectra with mass spectra libraries (Wiley

275 and NIST MS Search 2.0), co-injection with authentic standards and analysis of fragmentation patterns.

## 3. Results and discussion

### 3.1. PM<sub>2.5</sub> emission factors and carbonaceous content

PM<sub>2.5</sub> emission factors and the carbonaceous content were calculated for the woodstove and fireplace with both cold and hot starts, as shown in Figs. 1 and 2. The PM<sub>2.5</sub> emission factors were in the range from 5.62 to 25.8 g kg<sup>-1</sup> (dry basis) (cold start) and from 1.66 to 16.0 g kg<sup>-1</sup> (dry basis) (hot start) of fuel burned in the woodstove. The emission factors for fireplace were between 8.11 and 29.0 g kg<sup>-1</sup> (dry basis) (cold start) and 0.84–21.7 g kg<sup>-1</sup> of fuel burned (dry basis) (hot start). The emission factor of PM<sub>2.5</sub> was always higher during the combustion experiments in the fireplace than in the woodstove. In general, particulate matter emissions were higher during the experiments with cold start for both equipments (Fig. 1). This is related to the fact that under those conditions the temperature in the combustion chamber is lower. Lower temperatures results in a lower degree of conversion (oxidation) of the biomass (solid and pyrolysis products), thus originating a higher emission of unburned chemical compounds. The emissions from the combustion of maritime pine whether in the woodstove or in the fireplace were the lowest among all biomass fuels. Fine et al. (2001, 2002, 2004b) obtained PM<sub>2.5</sub> emission factors for the fireplace and woodstove combustion of American tree species lower than those observed in this study; the PM<sub>2.5</sub> emission factors were in the range 0.88–3.4 g kg<sup>-1</sup> of wood burned (as fired) in a woodstove, and between 1.6 and 11.4 g kg<sup>-1</sup> of wood burned (as fired) in the fireplace. As stated in the literature, particle emission factors from residential biomass combustion may show wide variation due to the type of fuel, the characteristics of combustion facility, dilution techniques used, sampling procedures, burning rate and the moisture content of the fuel (Fine et al., 2004b; Kowalczyk et al., 1981; Lipsky and Robinson, 2005; Wardoyo et al., 2006). Burning wood of poor quality (e.g. high moisture content), overloading the firebox or insufficient air supply, are examples of conditions that can lead to incomplete combustion, characterised by low temperature (Bølling et al., 2009). Lipsky and Robinson (2005) tested the effects of dilution on fine particle mass concluding that too little dilution can potentially overestimate the fine particle mass emissions, and too much dilution can underestimate them. At low levels of dilution semi-volatile species largely occur in the particle phase, but increasing dilution reduces the concentration of semivolatile species, shifting this material to the gas phase in order to maintain phase equilibrium. It should be noted, however, that the dilution ratio used in our study is comparable to the majority of values reported in the literature for biomass burning experiments (Lipsky and Robinson, 2005). The PM<sub>2.5</sub> emission factors for the fireplace and the woodstove are in the range of values reported for identical household combustion appliances in Scandinavia (Bølling et al., 2009; and references therein). However, particle emissions from the woodstove are much higher than those obtained in the “chimney type” stove (Gonçalves et al., 2010) and in other modern combustion devices (Bølling et al., 2009). Thus, it seems that the major differences in emission factors are due to large variations in combustion appliance types.

Total carbon represented 38% w/w (hot start) to 52% w/w (cold start) and 21% w/w (cold start) to 55% w/w (hot start) of the particle mass emitted during the combustion processes in the woodstove and fireplace, respectively (can be deduced in Fig. 2). Combustion of maritime pine, the only softwood among all species studied, in both combustion equipments generated the highest EC content in PM<sub>2.5</sub>

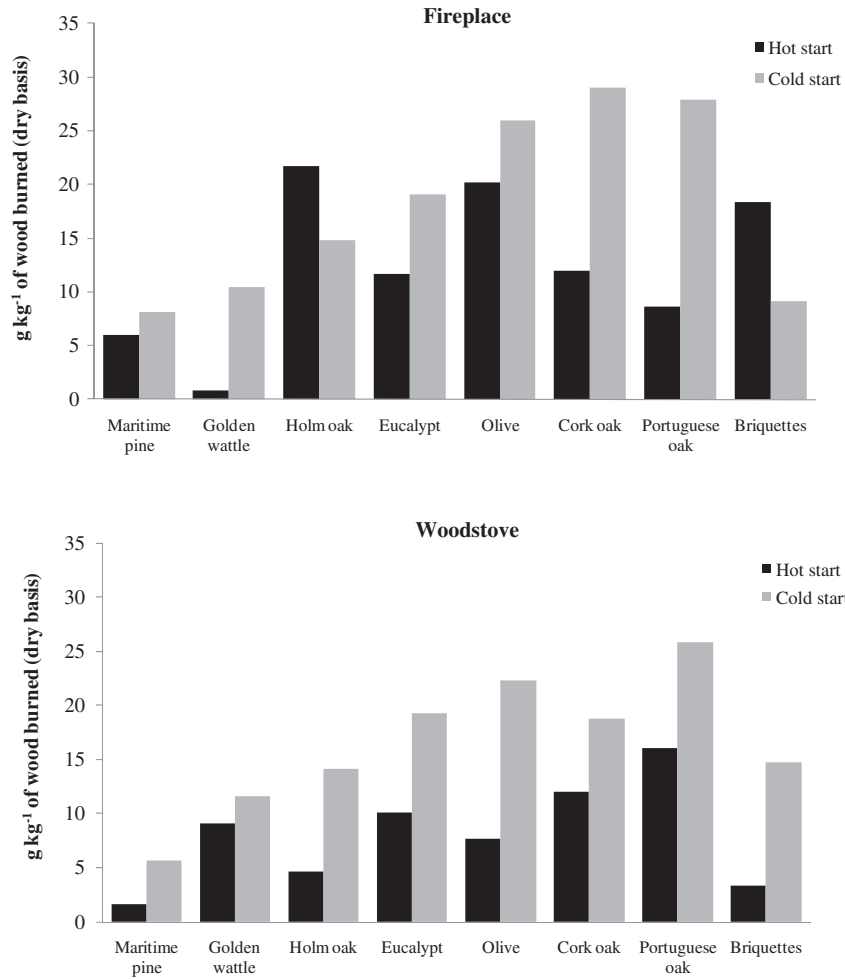


Fig. 1. PM<sub>2.5</sub> emission factors (dry fuel basis).

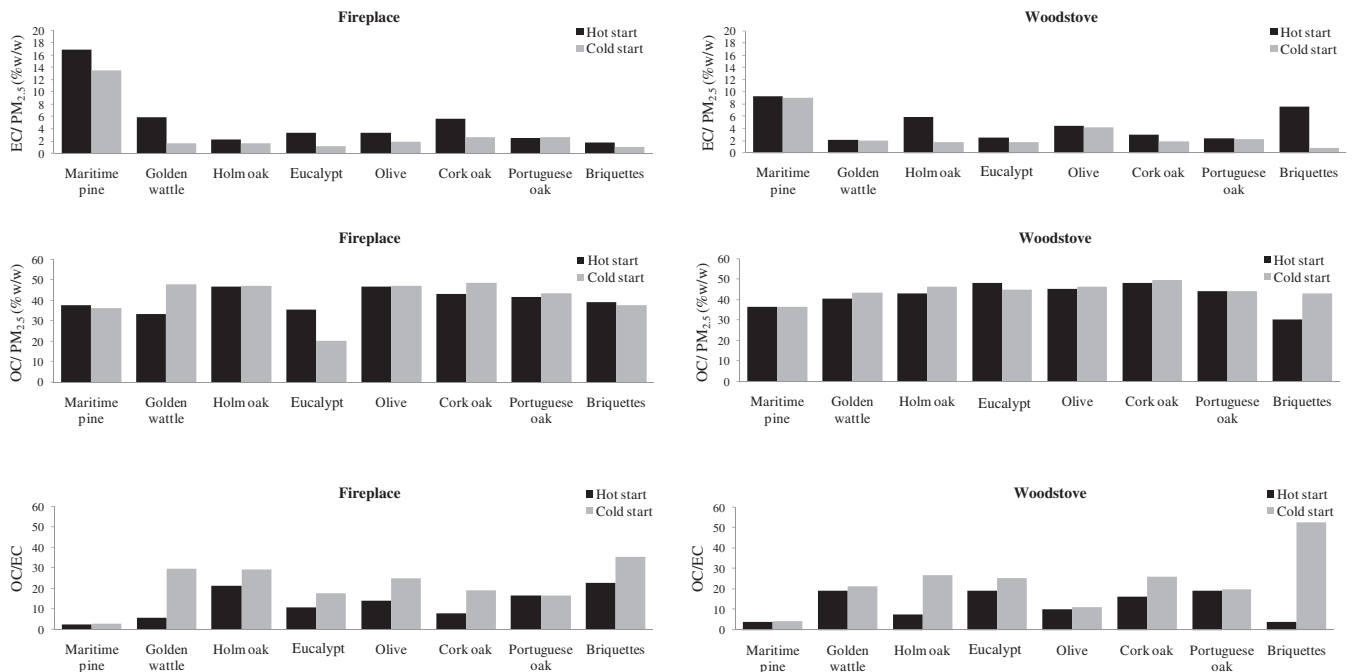


Fig. 2. Carbonaceous components: elemental carbon (EC), organic carbon (OC) and OC/EC in PM<sub>2.5</sub>.

(fireplace with hot start: 17% w/w; woodstove with hot start: 9.3% w/w), while briquette-derived smoke presented the lowest EC content (fireplace with cold start: 1.1% w/w; woodstove with cold start: 0.82% w/w). The OC content of PM<sub>2.5</sub> ranged between 30% w/w (briquettes – hot start) and 50% w/w (cork oak – cold start) for tests carried out in the woodstove. In the fireplace, the lowest OC content (cold start: 20% w/w) was observed during eucalypt combustion, while the smoke aerosols from the combustion of cork oak were the most OC-enriched (cold start: 48% w/w) (Fig. 2). The carbon content of particle emissions from the combustion of Portuguese woods was compared with that determined by Fine et al. (2001, 2002, 2004b) and by Gonçalves et al. (2010) in Table 2. The OC values obtained by Fine et al. (2002) for the fireplace combustion of selected American wood species are about two times higher than those obtained in our study. It should be noted, however, that Fine et al. (2002) obtained, in several tests, OC/PM ratios higher than 100%. They explained the results by increased organic vapour adsorption onto the quartz fibre filters used for organics collection relative to the Teflon filters from which gravimetric mass measurements were taken. Since no reliable method exists to correct for this positive adsorption artefact, and considering the possibility of a negative artefact caused by desorption of particle phase compounds, no correction was made by the researchers to the OC data.

It should be noted that the carbonaceous content obtained from thermal–optical technique does not account for associated O, H, N, and other elements, from the measured C mass concentrations attributed to OC. To estimate the organic matter content in particulate matter, the OC measurements have to be multiplied by a factor ranging from 1.4 to 2 (Alves et al., 2011; Gonçalves et al., 2010). Thus, up to 90% of the PM<sub>2.5</sub> in the wood smoke is constituted by organic matter. The inorganic composition of smoke particles from these residential biomass burning samples was discussed in detail by Alves et al. (in press), who found that the water-soluble ions accounted for about 1–14% of the PM<sub>2.5</sub> mass, while trace elements represented 0.4–2.5%.

The OC/EC ratio of PM<sub>2.5</sub> in the woodstove ranged between 3.99 (briquettes – hot start) and 52.58 (briquettes – cold start). For the fireplace emissions, the OC/EC varied from 2.23 (maritime pine – hot start) to 35.49 (briquettes – cold start) (Fig. 2). The OC/EC ratio can be helpful in distinguishing carbonaceous sources. Lower ratios are characteristic of fresh emissions from fossil fuel, while higher ratios are generally typical of biomass burning. High OC production in wood combustion emissions 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). Values ranging from 2.6 to 5.7 were reported for residential wood

burning of Austrian biofuels (Schmidl et al., 2008a). McDonald et al. (2000) obtained an OC/EC ratio of 3.9 for softwood and 7.9 for hardwood in a woodstove. Gonçalves et al. (2010) reported ratios ranging from 0.9 for maritime pine PM<sub>10</sub> emissions to 4.4 for the smoke of cork oak emitted from the combustion in a “chimney type” stove. Higher OC/EC ratios have been reported for low-temperature combustion in conventional fireplaces and stoves, confirming that particulate matter from these appliances are dominated by OC (Bølling et al., 2009), while higher EC mass fractions in smoke particles from the combustion of woody biomass in more efficient modern small scale units (modern logwood stoves with secondary air and automated air supply, and pellet stoves) contributed to lower OC/EC ratios, sometimes comparable to those from vehicular emissions. Ratios <1 have been determined at tunnel and roadside sites, where vehicle exhausts were the dominant sources of aerosols (Cheng et al., 2010). Monitoring campaigns in a busy roadway tunnel in central Lisbon showed OC/EC ratios between 0.3 and 0.4 (Pio et al., in press).

### 3.2. Organic speciation

The organic compounds found in biomass burning emissions can have two distinct origins: may result, either from volatilisation of organic molecules originally present in the wood that recondense into particle phase, or from pyrolysis products of combustion reactions (Fine et al., 2001). Thus, some organic compounds may be directly released by a steam stripping/volatilisation effect, while others are pyrolysis derivatives from the thermal breakdown of cellulose, lignin and other biopolymers. Natural (unaltered) and thermally altered (pyrolysis) derivative compounds emitted by biomass burning can be utilised as specific indicators for identifying inputs from this specific source. In this study, more than one hundred eighty organic compounds were identified. The OC-normalised concentrations of all these constituents can be found in appendix (Table A1), as Supplementary material. The database obtained is potentially useful to improve existing emission inventories. In addition, these results will supply important information on the variability in wood smoke tracer emission rates for those organic compounds that are presently used in receptor models.

#### 3.2.1. Homologous compound series

Aliphatic compounds comprised the *n*-alkane homologous series from C<sub>14</sub> to C<sub>34</sub> and *n*-alkenes from C<sub>16</sub> to C<sub>28</sub>. In accordance to what has been observed in other studies of domestic biomass burning smoke (Rogge et al., 1998; Schmidl et al., 2008b), the *n*-alkane homologous series did not show any clear preference for molecules with an odd or even number of carbon atoms. The homologues with the highest concentrations (C<sub>max</sub>) were C<sub>14</sub> and

**Table 2**  
Carbonaceous content in smoke particles (minimum and maximum values).

Carbonaceous content	Woodstove (% w/w)	Fireplace (% w/w)	
TC	38 (h.s.) – 52 (c.s.)	21 (c.s.) – 55 (h.s.)	
EC	0.82 (c.s. – briquettes) – 9.3 (h.s. – maritime pine)	1.1 (c.s. – briquettes) – 17 (h.s. – maritime pine)	This study
OC	30 (h.s. – briquettes) – 50 (c.s. – cork oak)	20 (c.s. – eucalypt) – 48 (c.s. – cork oak)	
EC	3.3–22.8 (hardwood) 7.6–13.4 (softwood)	1.2–22.0 (hardwood) 5.4–31.3 (softwood)	Fine et al., 2001, 2002, 2004b
OC	51.2–59.4 (hardwood) 43.6–77.8 (softwood)	74.2–87.5 (hardwood) 73.4–102.3 (softwood)	
TC	43.9–63.2		Gonçalves et al., 2010
EC	11.3 (cork oak) – 37.1 (maritime pine)		
OC	19.7 (golden wattle) – 42.8 (cork oak)		

h.s. – hot start; c.s. – cold start.

This study – PM<sub>2.5</sub>; Fine et al. – PM<sub>2.5</sub>; Gonçalves et al. – PM<sub>10</sub>.



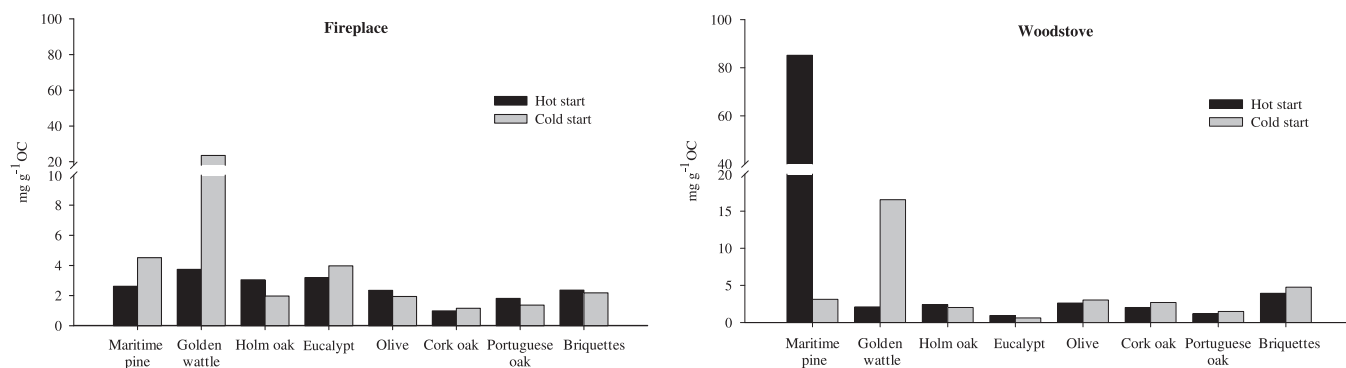


Fig. 3. OC-normalised concentrations of  $\Sigma$  alkanes in the  $PM_{2.5}$  from the various biomass fuels.

$C_{23}$ . For alkenes, the  $C_{max}$  was at  $C_{22}$ . Alkenes are probably derived from the dehydration of  $n$ -alkanols (Simoneit et al., 2000). A similar distribution is observed for the  $n$ -alkanols and thus an origin from reduction of  $n$ -alkanoic acids or cracking of wax  $n$ -alkanes is less likely (Simoneit, 2002). Independently from the burning appliance, the highest alkane concentrations were observed in tests with cold start. Wiesenberget al. (2009) showed that the distribution patterns of  $n$ -alkanes in biomass burning samples (maize and rye straw) changed as a function of temperature. At higher combustion temperatures,  $n$ -alkanes seem to be less stable than other compounds (Schmidl et al., 2008b). During the charring process, the long-chain  $n$ -alkanes may suffer thermal breakdown, causing short-chain homologues with a maximum at  $<C_{20}$ . Hence, the predominance of short-chain homologues, instead of  $C_{max}$  at  $C_{27}$ ,  $C_{29}$  or  $C_{31}$  typical of vegetation waxes, was found to be a useful marker for incomplete burning of biomass (Eckmeier and Wiesenberget al., 2009). The species whose smoke contained the highest amount of alkanes were golden wattle (fireplace with cold start) and maritime pine (woodstove with hot start) (Fig. 3). The alkenes were emitted aplenty by the woodstove with hot start and by fireplace with cold start. Golden wattle was the wood species whose smoke presented the highest  $n$ -alkenes content (Fig. 4). The higher amount of aliphatic compounds in the smoke emitted from maritime pine and golden wattle and the lower content in cork oak emissions are consistent with previous measurements in a "chimney type" stove (Gonçalves et al., 2010).

The smoke samples revealed the presence of an incomplete homologous series of  $n$ -alkanols from  $C_{10}$  to  $C_{30}$ . Depending on the sample, various  $C_{max}$ , in the range from  $C_{18}$  to  $C_{28}$ , were found. The  $C_{22}$  homologue was the most representative. In general, the  $n$ -alkanols in the smoke from the combustion in the fireplace contributed to a higher fraction of OC (average =  $2.02 \text{ mg g}^{-1}$ ) than that observed in emissions from the woodstove (average =  $1.21 \text{ mg g}^{-1}$ ). Olive (fireplace with cold start) and eucalypt (fireplace with cold start) were the wood species with the highest  $n$ -alkanol content in  $PM_{2.5}$  emissions, whilst the smallest amounts were

detected in the Maritime pine smoke (woodstove with cold start and fireplace with cold start) (Fig. 5).

A series of  $n$ -alkanoic acids were identified in the smoke of all samples, ranging from  $C_8$  to  $C_{24}$ . These homologous series are ubiquitous in biomass burning smoke (Simoneit, 2002). These acids were generally emitted in large amount by both combustion equipments with hot start. All wood smokes contained high levels of both hexadecanoic and tetracosanoic acids, as found in previous biomass burning studies (Fine et al., 2001, 2004b; Schmidl et al., 2008b; Simoneit, 2002; Gonçalves et al., 2010).

The total OC-normalised concentrations of all  $n$ -alkanoic acids were in the range from  $0.548 \text{ mg g}^{-1} \text{ OC}$  (cork oak – fireplace with cold start) to  $39.9 \text{ mg g}^{-1} \text{ OC}$  (Portuguese oak – fireplace with hot start) (Fig. 6). The only alkenoic acid found in all types of wood smokes was 9,12-octadecadienoic acid (linoleic acid), in a range between  $0.11 \text{ mg g}^{-1} \text{ OC}$  (fireplace with hot start – olive) and  $7.05 \text{ mg g}^{-1} \text{ OC}$  (woodstove with cold start – briquettes).

Dicarboxylic acids were represented by an incomplete homologous series from  $C_3$  to  $C_{16}$ . The  $C_{max}$  was observed for heptanedioic acid in a concentration range from  $0.28 \text{ mg g}^{-1} \text{ OC}$  (woodstove with cold start – cork oak) to  $10.2 \text{ mg g}^{-1} \text{ OC}$  (fireplace with hot start – Holm oak). Dicarboxylic acids in the same carbon range have been detected previously in the emissions from residential wood burning (Fine et al., 2004a,b; Gonçalves et al., 2010) and from wildfires (Alves et al., 2010, 2011, in press; Kundu et al., 2010). Average concentrations of total dicarboxylic acids in  $PM_{2.5}$  samples collected during the burning season in Amazonia were 2–8 times higher than those reported in urban aerosols (Kundu et al., 2010). However, dicarboxylic acids are ubiquitous compounds that can be generated from several primary sources or secondary processes and, thus, cannot be regarded as biomass burning tracers. Some alkyl esters of acids were detected in minor amounts, with a range from  $0.02 \text{ mg g}^{-1} \text{ OC}$  (fireplace with hot start – eucalypt) to  $1.40 \text{ mg g}^{-1} \text{ OC}$  (fireplace with cold start – maritime pine).

It should be noted that a significant fraction of other acids, whose individual characterisation was not possible, have a large

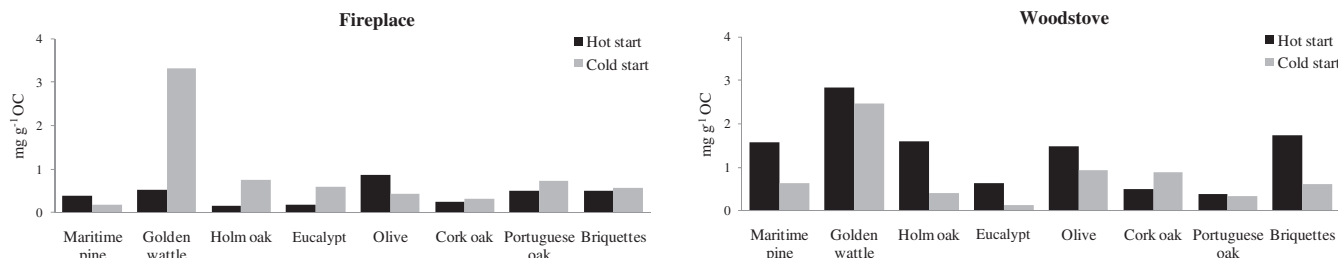


Fig. 4. OC-normalised concentrations of  $\Sigma$  alkenes in the  $PM_{2.5}$  from the various biomass fuels.

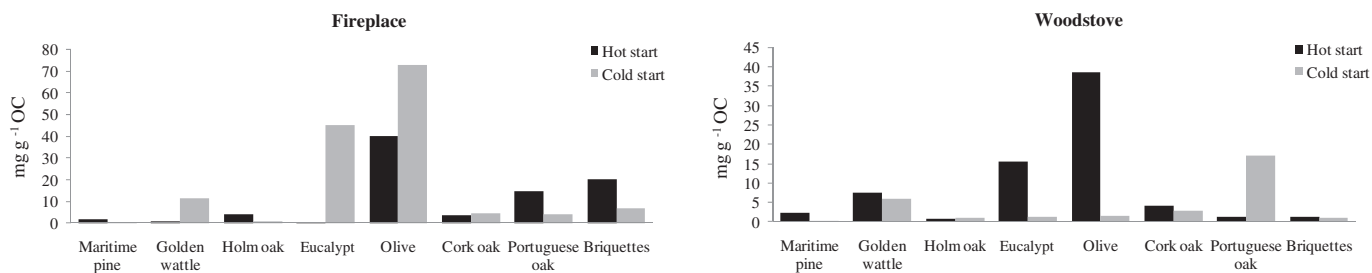


Fig. 5. OC-normalised concentrations of  $\Sigma$  alcohols in the PM<sub>2.5</sub> from the various biomass fuels.

contribution to the OC of smoke particles. Those other acids are mostly dicarboxylic acids and related compounds (e.g. keto-carboxylic acids) (Kundu et al., 2010), hydroxy-acids (e.g. glycolic acid) and oxo-acids (e.g. levulinic acid).

### 3.2.2. Polycyclic aromatic hydrocarbons

Polycyclic aromatic hydrocarbons (PAHs) are a group of compounds that is formed during incomplete combustion. More than twenty PAHs were identified in the smoke samples. It is difficult to draw firm conclusions about the relative PAH content in emissions resulting from cold or hot start combustions. The total

OC-normalised concentrations of all PAHs ( $\Sigma$  PAHs) were in the range 1.47–10.7 mg g<sup>-1</sup> OC for fireplace with hot start, 4.05–27.6 mg g<sup>-1</sup> OC for fireplace with cold start, 2.27–29.3 mg g<sup>-1</sup> OC for woodstove with hot start and 3.12–23.3 mg g<sup>-1</sup> OC for woodstove with cold start (Fig. 7). Emissions from the woodstove at higher temperatures possess a higher PAH content than those of the fireplace. Comparable average total PAH emissions were obtained in the woodstove and fireplace tests with cold start (~8.8 mg g<sup>-1</sup> OC). The influence of these two parameters could explain the results. It is known that PAH amounts increase with the increase of temperatures (Lu et al., 2009; and references therein).

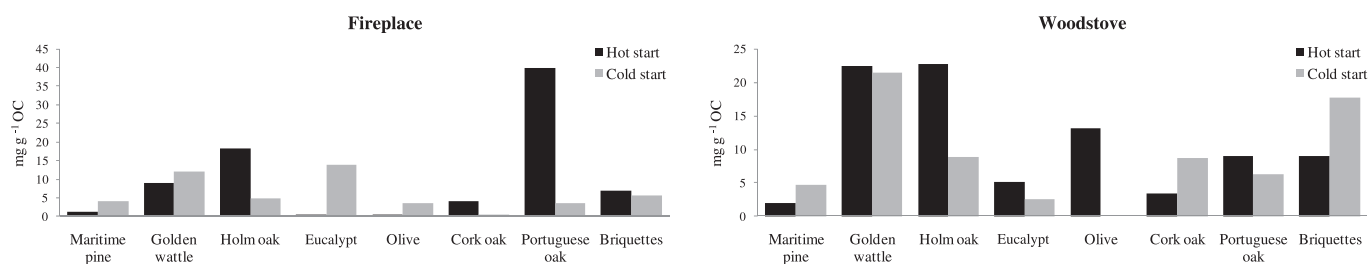


Fig. 6. OC-normalised concentrations of  $\Sigma$  alkanolic acids in the PM<sub>2.5</sub> from the various biomass fuels.

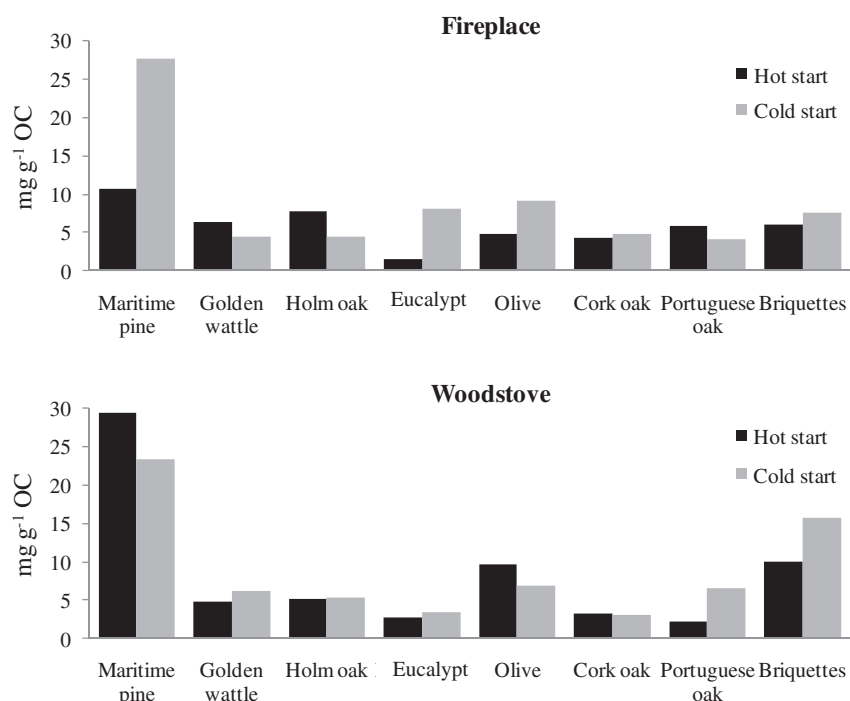


Fig. 7. OC-normalised concentrations of  $\Sigma$  PAHs in the PM<sub>2.5</sub> from the various biomass fuels.

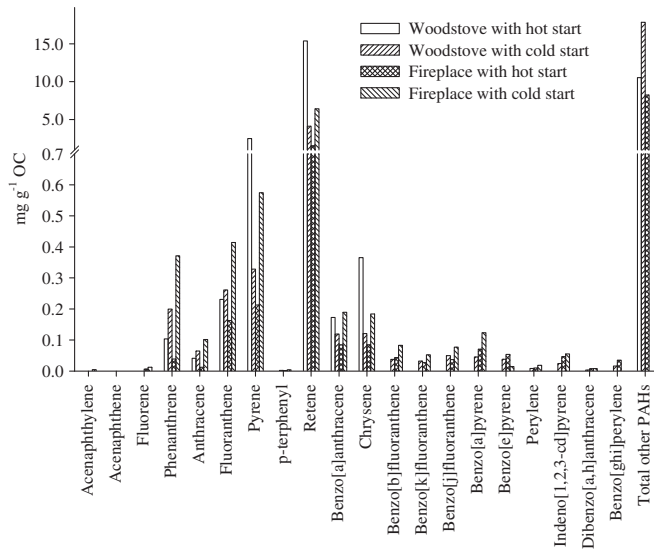


Fig. 8. OC-normalised concentrations of PAHs in the PM<sub>2.5</sub> from Maritime pine.

On the other hand, it is also observed that total PAH emissions increase with the increase of O<sub>2</sub> content in supplied air (Lu et al., 2009). In the present study, the fireplace operated at lower temperatures than those in the woodstove, but the O<sub>2</sub> content in supplied air was around 20%, while values lower than 15% were provided to the woodstove.

The PAH emissions from pine combustion were significantly higher than those of the other wood types, especially in emissions from woodstove. A great inter-study variation for the PAH content in emissions from burning pine species has been reported. This variation may be due to the large concentration range of flammable resin in the different pine woods tested (Gullett et al., 2003). Retene was the dominant aromatic hydrocarbon found in the softwood smoke (maritime pine – 6.43 mg g<sup>-1</sup> OC for fireplace with cold start; 15.4 mg g<sup>-1</sup> OC for woodstove with hot start) (Fig. 8), whilst it was present at very small levels in the hardwood combustion emissions. Retene is the fully aromatised thermal alteration product of the resin acids present in conifer woods (Ramdahl, 1983). The very high proportion of retene in softwood smoke was also verified by Fine et al. (2004b) in PM<sub>2.5</sub> emissions resulting from the combustion of USA prevalent trees (red maple, Douglas fir, white oak and loblolly pine) in a catalyst-equipped woodstove. In the smoke from these American wood species, retene represented

Table 3  
PAH diagnostic parameters.

			Woodstove			
			Flu/(Flu+Pyr)	IcdP/(BghiP+IcdP)	BFs/BghiP	BeP/(BeP+BaP)
<i>This study</i>	Maritime pine	Hot start				
		Cold start	0.44	0.60	7.51	0.46
	Golden wattle	Hot start	0.38	0.57	4.00	0.46
		Cold start	0.45	0.59	4.91	0.40
	Holm oak	Hot start	0.44	0.60	5.09	0.50
		Cold start	0.44	0.55	4.47	0.41
	Eucalypt	Hot start	0.46	0.58	3.41	0.43
		Cold start	0.44	0.53	3.75	0.40
	Olive	Hot start	0.18	0.73	38.1	0.57
		Cold start	0.45	0.54	6.23	0.49
	Cork Oak	Hot start	0.20	0.69	42.4	0.52
		Cold start	0.37	0.58	5.03	0.38
	Portuguese oak	Hot start	0.45	0.57	3.83	0.47
		Cold start	0.42	0.57	4.75	0.38
	Briquettes	Hot start	0.47	0.57	8.28	0.61
		Cold start	0.46	0.57	5.98	0.48
	<b>Fireplace</b>					
	Maritime pine	Hot start	0.43	0.57	3.08	0.43
		Cold start	0.42	0.58	5.26	0.11
	Golden wattle	Hot start	0.48	0.59	3.10	0.45
		Cold start	0.39	0.59	4.90	0.42
	Holm oak	Hot start	0.41	0.57	4.40	0.40
		Cold start	0.39	0.61	6.16	0.40
Eucalypt	Hot start	0.45	1.00		0.47	
	Cold start	0.44	0.57	4.29	0.44	
Olive	Hot start	0.46	0.60	6.69	0.46	
	Cold start	0.36	0.59	3.77	0.38	
Cork Oak	Hot start	0.49	0.58	3.60	0.43	
	Cold start	0.39	0.57	4.09	0.44	
Portuguese oak	Hot start					
	Cold start	0.35	0.54	3.14	0.41	
Briquettes	Hot start	0.44			0.48	
	Cold start	0.47	0.64	7.86	0.49	
Wang et al., 2009	Broad-leaf trees	0.50–0.55				
Wang et al., 2009	Shrubs	0.54–0.60				
Oros et al., 2006	Grasses	0.53–0.63				
Hays et al., 2005	Cereal straw	0.50–0.53		0.52–1.0		
Chen et al., 2004	Coal	0.48	0.43	1.86	0.91	
Rogge et al., 1993	Noncatalyst-equip. vehicles	0.61	0.04	0.58		
Rogge et al., 1993	Catalyst-equip. vehicles	0.44	0.09	1.16		

Flu – Fluoranthene; Pyr – Pyrene; IcdP – Indeno[1,2,3-cd]pyrene; BghiP – Benzo[ghi]perylene; BFs – Benzofluoranthenes; BeP – Benzo[e]pyrene; BaP – Benzo[a]pyrene.



0.008–0.018 and 1.987–3.893 mg g<sup>-1</sup> OC for hardwood and softwood, respectively. In this study, besides retene, fluoranthene, pyrene, and phenanthrene were the most prevalent PAHs found in both hardwood and softwood smoke. Because the major PAHs in wood smoke are generally the same as from other anthropogenic combustion emissions, diagnostic ratios are used for assessing the contribution of different sources (Alves, 2008). The IcdP/(BghiP + IcdP), BFs/BghiP, Flu/(Flu + Pyr) and BeP/(BeP + BaP) ratios are listed and compared with those of other sources in Table 3. In general, the diagnostic ratios can be differentiated from those of other combustion sources. The Flu/(Flu + Pyr) ratios of 0.40 ± 0.09 and 0.42 ± 0.04 for woodstove and fireplace, respectively, are below the values reported for broad-leaf trees, shrubs, grasses and cereal straw (Hays et al., 2005; Oros et al., 2006; Wang et al., 2009). The values of this diagnostic ratio can be differentiated from those of other combustion sources, such as vehicular exhausts and coal combustion, which are slightly higher (Chen et al., 2004; Rogge et al., 1993). The BFs/BghiP ratio was 5.2 ± 1.5 and 4.6 ± 1.5 for woodstove and fireplace, respectively. The comparatively high values for olive and cork oak for woodstove with hot start were not included in the average calculation. The high BFs/BghiP ratios obtained for olive (38.14) and cork oak (42.40) are due to the very low concentrations of BghiP in the smoke of these two wood species. The values of this diagnostic ratio can be distinguished from those of other combustion sources, such as vehicular exhausts and coal combustion, which have lower values (Chen et al., 2004; Rogge et al., 1993). The IcdP/(BghiP + IcdP) ratio was 0.59 ± 0.05 and 0.61 ± 0.11 for woodstove and fireplace, respectively. Much lower values have been obtained for vehicular emissions (Rogge et al., 1993) and coal combustion (Chen et al., 2004). The BeP/

(BeP + BaP) ratios were 0.46 ± 0.07 and 0.41 ± 0.01 for woodstove and fireplace, respectively. These values differ from the higher ratio produced by coal combustion.

### 3.2.3. Phenolic compounds

Phenolic compounds included polyphenols, methoxyphenols and alkyl phenols. Methoxyphenols have been identified as prominent 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 et al., 1993). 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) compounds because of a different lignin structure. These compounds were emitted in higher amounts by woodstove with cold start (10.6–236.5 mg g<sup>-1</sup> OC) and by fireplace with cold start (47.8–242.1 mg g<sup>-1</sup> OC) (Table 4). The predominant methoxyphenols found in the smoke were the vanillic and syringic acids. Vanillic acid was emitted in higher amounts by pine (softwood) than by hardwood species, while the opposite was observed for syringic acid. Vanillin, catechol, methylcatechol and pyrogallol are other phenolic compounds that are quite impressive in the smoke of all species (Table 4).

### 3.2.4. Other biomarkers

Phytosterols, terpenoids, including resin acids, and saccharides represent biomarker constituents in the smoke from residential wood combustion. The most abundant phytosterol in all smoke samples was β-sitosterol, followed by stigmasterol, at lower abundances. The

**Table 4**

OC-normalised concentrations of the most abundant phenolic compounds in the emissions from the various biomass fuels (mg g<sup>-1</sup> OC).

		Woodstove						
		Vanillic acid	Syringic acid	Coniferyl alcohol	Catechol	Methylcatechol	Pyrogallol	Vanillin
Maritime pine	Hot start	1.72	0.126	0.0176	4.21	3.38	2.22	2.59
	Cold start	14.8	0.233	0.355	18.9	18.2	3.56	8.34
Golden wattle	Hot start	1.46	2.74	0.956	27.7	19.6	3.43	5.81
	Cold start	3.72	2.23	0.946	23.7	29.7	29.6	65.2
Holm oak	Hot start	1.83	8.55	0.583	25.8	12.4	5.57	12.3
	Cold start	5.45	11.4	0.535	16.8	17.6	32.7	5.64
Eucalypt	Hot start	1.02	6.73	0.129	26.1	11.1	59.2	3.33
	Cold start	1.37	8.72	0.311	–	9.04	25.8	4.90
Olive	Hot start	2.66	5.30	1.52	4.63	2.98	–	8.38
	Cold start	+	+	3.14	+	–	+	6.89
Cork oak	Hot start	1.34	4.93	0.756	34.0	37.3	59.7	7.09
	Cold start	7.44	14.2	1.49	24.1	13.1	29.0	7.56
Portuguese oak	Hot start	2.66	10.6	0.511	35.2	34.0	50.9	7.02
	Cold start	3.84	12.5	0.188	48.2	34.2	110	6.53
Briquettes	Hot start	9.52	20.9	–	15.6	6.05	–	–
	Cold start	17.7	34.8	1.33	38.7	51.9	77.5	13.0
		<i>Fireplace</i>						
Maritime pine	Hot start	0.553	+	0.759	2.25	3.41	0.842	3.94
	Cold start	3.46	0.0665	1.26	15.0	25.3	2.73	–
Golden wattle	Hot start	1.68	3.91	1.79	26.0	25.8	5.73	–
	Cold start	1.32	2.90	3.15	10.1	18.9	22.1	6.47
Holm oak	Hot start	5.14	22.1	7.66	16.8	13.8	23.3	14.0
	Cold start	2.41	9.63	1.13	19.0	10.2	38.7	5.36
Eucalypt	Hot start	1.25	12.8	0.143	16.7	9.88	70.9	–
	Cold start	2.94	19.2	0.418	64.8	50.6	88.9	10.8
Olive	Hot start	0.811	2.06	0.829	6.21	6.33	12.3	17.3
	Cold start	1.41	2.16	4.85	11.6	9.57	29.0	5.67
Cork oak	Hot start	1.59	5.41	2.03	29.2	20.8	37.7	8.18
	Cold start	0.694	2.42	4.11	8.97	8.71	29.5	24.7
Portuguese oak	Hot start	1.53	8.16	0.681	36.9	24.2	53.1	11.2
	Cold start	3.05	8.46	2.94	14.7	13.6	28.3	14.0
Briquettes	Hot start	8.84	12.9	0.268	32.0	23.4	40.7	16.2
	Cold start	10.1	8.54	0.673	38.2	18.5	36.6	6.65

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

high  $\beta$ -sitosterol normalised-OC concentrations in maritime pine (fireplace with hot start – 39.9 mg g<sup>-1</sup> OC) emissions deserve consideration. However, as  $\beta$ -sitosterol emissions vary greatly with wood species, it cannot be regarded as a candidate to separate hardwood from softwood combustion emissions in source apportionment studies. Stigmaterol was only present in the smoke of hardwood species. This result is in accordance with the study by Fine et al. (2004b). Thus, stigmaterol may be pointed out as a potential tracer for the smoke from deciduous trees. Several products from the thermal alteration of sterol precursors were identified (e.g. stigmastan-4,5,22-triene, and stigmastan-3,5,22-triene). Among these, the most abundant was stigmastan-3,5-diene. Some terpenoids were also found, mostly in trace amounts, except lupeol that appeared with great expression in maritime pine PM<sub>2.5</sub> emissions (4.73 mg g<sup>-1</sup> OC). Resin acids, such as isopimaric, dehydroabietic and pimaric acids, were detected as significant components of softwood emissions, but were found only in trace quantities in the emissions from hardwoods (Table 5). 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). These constituents were emitted at higher concentrations in cold start tests, independently from the burning appliance used. In addition to differences related to the presence or absence of ducts filled with resin and distinct combustion temperatures, moisture may play an important role in the abundance of the resin acids as compared to other carbonaceous species (Mazzoleni et al., 2007).

**Table 5**  
OC-normalised concentrations of resin acids in the emissions from the various biomass fuels (mg g<sup>-1</sup> OC).

		Woodstove			
		Dehydroabietic acid	Isopimaric acid	Pimaric acid	Abietic acid
Maritime pine	Hot start	83.1	4.71	94.8	+
	Cold start	154	30.9	198	12.0
Golden wattle	Hot start	1.18	0.466	2.75	0.0661
	Cold start	21.2	3.41	26.9	7.81
Holm oak	Hot start	0.779	–	0.779	+
	Cold start	12.3	1.94	15.1	0.264
Eucalypt	Hot start	2.74	–	2.74	0.00778
	Cold start	1.62	0.524	2.14	0.460
Olive	Hot start	0.504	0.165	0.669	+
	Cold start	5.43	0.982	6.41	3.25
Cork oak	Hot start	0.385	0.0630	0.448	0.0151
	Cold start	15.9	5.61	26.0	11.7
Portuguese oak	Hot start	0.256	0.118	0.374	0.00859
	Cold start	25.5	2.25	30.8	1.60
Briquettes	Hot start	7.60	2.26	10.6	0.0390
	Cold start	21.5	5.88	29.3	0.429
<i>Fireplace</i>					
Maritime pine	Hot start	67.9	10.3	80.0	9.07
	Cold start	306	37.7	355	29.4
Golden wattle	Hot start	6.23	1.03	8.51	–
	Cold start	–	0.631	0.631	0.515
Holm oak	Hot start	–	0.305	0.305	–
	Cold start	0.659	0.0472	0.706	–
Eucalypt	Hot start	1.29	0.748	2.05	–
	Cold start	26.6	1.80	28.5	–
Olive	Hot start	–	0.451	0.754	1.13
	Cold start	8.14	0.860	9.00	–
Cork oak	Hot start	–	0.117	0.471	–
	Cold start	1.24	–	1.24	0.285
Portuguese oak	Hot start	50.9	2.79	53.7	1.47
	Cold start	1.13	0.462	1.59	0.235
Briquettes	Hot start	6.53	3.54	10.1	–
	Cold start	13.7	3.19	18.5	–

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

The major organic components of smoke particles from biomass burning were monosaccharide derivatives from the breakdown of cellulose and hemicelluloses, such as levoglucosan, mannosan and galactosan (Simoneit et al., 1999). In general, these compounds were emitted in larger amounts by the woodstove with hot start and by the fireplace with cold start (Table 6). As expected, levoglucosan, a specific marker for wood combustion in ambient PM samples (Fine et al., 2004a; Schmidl et al., 2008a), was the most abundant organic compound (Table 6). The global amounts of anhydrosugars were generically higher in the smoke resulting from experiments with hot start than those obtained at lower combustion temperatures. While the average values for the hot start tests were 426 mg g<sup>-1</sup> OC (fireplace) and 466 mg g<sup>-1</sup> OC (woodstove), the corresponding values for cold start tests were 379 and 415 mg g<sup>-1</sup> OC. However, for the majority of biofuels, the levoglucosan emissions were usually higher for the hot woodstove tests (average = 383 mg g<sup>-1</sup> OC) at higher temperatures and for the fireplace with cold start (average = 278 mg g<sup>-1</sup> OC).

Mannosan was the second most abundant anhydrosugar product from the hemicellulose pyrolysis. Galactosan was the third most abundant anhydrosugar in the wood smoke samples. Levoglucosan, mannosan, and galactosan were emitted in varying ratios, probably due to differences in the relative content of cellulose and hemicellulose in different biofuels (Engling et al., 2006). Biomass pyrolysis products are a complex combination of the products from the individual pyrolysis of cellulose, hemicellulose, and extractives, each of which has its own chemical degradation pathways. In addition, secondary reaction products result from cross-reactions of primary pyrolysis products and between pyrolysis products and the original feedstock molecules (Mohan et al., 2006). Pyrolysis of each constituent is itself a complex process that is dependent of many factors, rendering difficult the attainment of simple relationships between the combustion temperature and the amounts of products in the smoke. It is known that cellulose degradation occurs at 240–350 °C to produce anhydrocellulose and levoglucosan, while hemicelluloses decomposes at temperatures of 200–260 °C, yielding more volatiles, less tars, and less chars than cellulose (Mohan et al., 2006). However, in slow pyrolysis, the loss of hemicelluloses of wood starts taking place at temperatures from 130 to 194 °C, which are in the range of values registered in the cold start tests in the fireplace. Most hemicelluloses do not give rise to significant amounts of levoglucosan (Mohan et al., 2006), although the slow pyrolysis of some hemicellulosic constituents of wood could result in the formation of the carbohydrate as a main product (Aho et al., 2008).

The relative proportions of levoglucosan to mannosan (L/M) have been used for source reconstruction of combustion derived by-products in atmospheric aerosols. For example, inputs from very specific poor-quality brown coals gave L/M ratios greater than 50 in atmospheric aerosols (Fabbri et al., 2009). Differences in the L/M ratio in smoke from softwood and hardwood/grass combustion (~5 versus ~10–20, respectively) can further support discrimination between inputs from these combustion sources to the atmosphere (Louchouart et al., 2009; and references therein). Herbaceous tissues can produce relatively high L/M ratios, in the range from 25 to 50 (Engling et al., 2009). In the present study, lower ratios than those reported for soft- and hardwood smoke were obtained. In addition to differences in the cellulosic content of the different biofuels, the emission of saccharidic compounds may strongly depend on combustion characteristics that are not well-understood. Under controlled combustion conditions (150–1050 °C), Kuo et al. (2008) determined the levoglucosan content in samples from 3 wood species. The anhydrosugar was only detectable in low-temperature samples (150–350 °C), with maximum yield obtained from samples produced at 250 °C, regardless of plant species. A

**Table 6**  
OC-normalised concentrations of sugars in the emissions from the various biomass fuels ( $\text{mg g}^{-1}$  OC).

		Woodstove				
		Galactosan	Mannosan	Levogluconan	Other sugars	L/M
Maritime pine	Hot start	114	232	335	35.0	1.44
	Cold start	81.8	237	291	140	1.23
Golden wattle	Hot start	56.0	42.3	374	206	8.85
	Cold start	48.6	115	159	147	1.39
Holm oak	Hot start	34.9	12.5	205	70.4	16.5
	Cold start	40.8	81.2	126	150	1.55
Eucalypt	Hot start	94.6	66.6	463	170	6.95
	Cold start	23.3	289	+	83.6	
Olive	Hot start	19.4	30.1	99.2	199	3.30
	Cold start	+	+	+	–	
Cork oak	Hot start	53.1	52.9	293	77.4	5.53
	Cold start	53.0	108	241	88.5	2.23
Portuguese oak	Hot start	65.2	+	349	190	
	Cold start	125	320	506	216	1.58
Briquettes	Hot start	226	31.9	948	307	29.7
	Cold start	191	293	410	284	1.40
		<i>Fireplace</i>				
Maritime pine	Hot start	37.6	108	148	83.4	1.37
	Cold start	170	+	378	345	
Golden wattle	Hot start	41.4	91.5	301	293	3.29
	Cold start	35.2	15.9	101	113	6.35
Holm oak	Hot start	38.7	15.2	106	51.0	7.00
	Cold start	66.0	26.9	186	82.4	6.93
Eucalypt	Hot start	98.1	45.9	506	274	11.0
	Cold start	177	61.3	582	402	9.49
Olive	Hot start	24.4	23.5	79.6	96.8	3.39
	Cold start	30.7	58.1	133	65.7	2.28
Cork oak	Hot start	44.7	26.4	184	87.5	6.98
	Cold start	25.9	15.2	112	44.3	7.35
Portuguese oak	Hot start	50.3	91.0	327	166	3.60
	Cold start	55.7	+	199	177	
Briquettes	Hot start	133	85.4	+	484	
	Cold start	183	265	532	192	2.01

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

laboratory emission study of wood and pellet boilers gave 0.3% w/w to 22% w/w levoglucosan to particle mass, indicating that the levoglucosan fraction may be highly dependent on combustion parameters, making it uncertain to use it as a quantitative tracer under real-world burning conditions (Hedberg et al., 2006). Another variable that has a strong influence on the yield of levoglucosan from cellulose is the presence of inorganic ions (Dobele et al., 2005). It has been observed that the presence of mineral matter in wood decreases the temperature of cellulose pyrolysis (Williams and Horne, 1994). Thus, quantitative estimates of wood burning inputs to atmospheric particles will be very doubtful using exclusively levoglucosan as a tracer.

Other saccharidic compounds included inositol, glycerol among others, especially in the smoke from briquettes and eucalypt.

#### 4. Conclusions

The traditional Portuguese burning appliances tested in this study present higher  $\text{PM}_{2.5}$  emission factors, a lower EC content of the fine particle mass, and a higher OC mass fraction compared to those described in the literature for the residential wood combustion in countries where certification of stoves is required to meet certain emission limits. In Portugal, the certification process is still in progress and, therefore, catalytic elements in the woodstove designs or high-efficiency woodstoves that reduce emissions by careful control of air flow and temperature are not common.

This work provides detailed information on organic composition of smoke particles from residential combustion of the most prevalent Portuguese woods in an attempt of contributing with

new data for source apportionment methodologies. Two types of residential biomass combustion appliances were tested: woodstove and fireplace. In order to evaluate the influence of temperature on the combustion flue emissions characteristics, two sets of experiments were performed for each wood fuel type: cold start and hot start. Some differences between particle emissions from softwood and hardwood burning were observed. Maritime pine, the only softwood studied, was the wood species that contributed to the lowest  $\text{PM}_{2.5}$  emission in both fireplace and woodstove. In general, the  $\text{PM}_{2.5}$  emissions were higher during the experiments with cold start. Concerning the carbonaceous content of  $\text{PM}_{2.5}$ , maritime pine produced the highest EC emissions (fireplace and woodstove), while Holm oak and briquettes presented the lowest EC content in  $\text{PM}_{2.5}$  from fireplace. For woodstove, the golden wattle smoke encompassed the lowest EC emissions. The OC content did not show appreciable differences between species, combustion appliances or combustion temperatures. In general, high OC/EC ratios were obtained for all species, especially in the fireplace. The lowest OC/EC ratios were obtained for the maritime pine. Alkanes, PAHs, ketones, alkanols, resin acids and alkyl esters of acids were emitted in large concentrations in cold start tests, independently of the burning appliance used. Alkenes and anhydrosugars were emitted in higher amounts by the woodstove with hot start and by fireplace with cold start. Phenolic compounds were emitted in highest concentration by woodstove with cold start and by fireplace with cold start. The major organic components in particles from biomass burning were anhydrosugars, in particular levoglucosan, acids and aliphatic compounds. Retene was the dominant aromatic hydrocarbon found in the softwood smoke, whilst it was present at very small levels in the hardwood combustion emissions. Guaiacyl, like

vanillic acid, and synapyl compounds were identified in softwood smoke, whereas hardwood burning contributed mainly to the formation of syringyl compounds, such as syringic acid. Stigmasterol was only present in the smoke of hardwood species; thus, this compound may be pointed out as a potential tracer for smoke from deciduous trees.  $\beta$ -Sitosterol has a great expression in the smoke of softwood species. However, as  $\beta$ -sitosterol emissions vary greatly with wood species, it cannot be regarded as a candidate to separate hardwood from softwood combustion emissions in source apportionment studies. Since important differences between hardwood and softwood combustion were seen among the substituted phenols, aromatic compounds and phytosterols, composite emission profiles, weighted based on the estimated usage of the distinct wood types, should be accounted for in chemical mass balance models that use organic compounds as tracers. Weighted composite residential wood combustion source profiles based on the woodstove and fireplace usage patterns in a particular region should also be developed for further mass balance calculations, which attempt to determine the contribution of wood smoke sources to ambient fine particle samples.

Taking into account that the distributions and abundances of the biomass smoke constituents are dependent on combustion temperature, the emission profiles obtained in this study should not be used as absolute but as relative chemical fingerprints for residential wood burning. Besides differences in combustion temperatures and biofuel types, the variability in emission profiles may be due to several factors, including differences in fuel array and configuration, composition and dimensions of branches and bark, fuel moisture content, flame temperature, aeration, or the presence of other constituents (e.g. acids, bases, or salts, either catalysing or inhibiting the formation of certain combustion products). Future studies would require a more strict control of these variables and more replicate burning tests.

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## Appendix. Supplementary material

Supplementary data related to this article can be found online at doi:10.1016/j.atmosenv.2011.05.071.

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