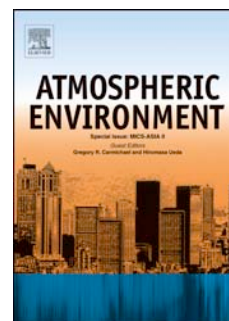


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Atmospheric PM and volatile organic compounds released from Mediterranean shrubland wildfires

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Abstract

Wildfires produce a significant release of gases and particles affecting climate and air quality. In the Mediterranean region, shrublands significantly contribute to burned areas and may show specific emission profiles. Our objective was to depict and quantify the primary-derived aerosols and precursors of secondary particulate species released during shrubland experimental fires, in which fire-line intensity values were equivalent to those of moderate shrubland wildfires, by using a number of different methodologies for the characterization of organic and inorganic compounds in both gas-phase and particulate-phase. Emissions of PM mass, particle number concentrations and organic and inorganic PM_x components during flaming and smouldering phases were characterized in a field shrubland fire experiment. Our results revealed a clear prevalence of K⁺ and SO₄²⁻ as inorganic ions released during the flaming-smouldering processes, accounting for 68 to 80% of the inorganic soluble fraction. During the residual-smouldering phases, in addition to K⁺ and SO₄²⁻, Ca²⁺ was found in significant amounts probably due the predominance of re-suspension processes (ashes and soil dust) over other emission sources during this stage. Concerning organic markers, the chromatograms were dominated by phenols, n-alkanals and n-alkanones, as well as by

alcohol biomarkers in all the PM_x fractions investigated. Levoglucosan was the most abundant degradation compound with maximum emission factors between 182 and 261 mg kg⁻¹ in PM_{2.5} and PM₁₀ respectively. However, levoglucosan was also observed in significant amounts in the gas-phase. The most representative organic volatile constituents in the smoke samples were alcohols, carbonyls, acids, monocyclic and bicyclic arenes, isoprenoids and alkanes compounds. The emission factors obtained in this study may contribute to the validation and improvement of national and international emission inventories of this intricate and diffuse emission source.

Keywords: Biomass burning, Mediterranean shrubland, water soluble ions, trace elements, organic compounds, VOCs.

1. Introduction

In southern Europe, biomass burning emissions are usually linked to wildfires and agriculture practices (Calvo et al., 2013). A recent study evaluating biomass burning contribution in the Barcelona urban area revealed that this source only represents 3% of PM₁₀ and 5% in PM₁, being mostly attributed to agricultural fires (Reche et al., 2012). However, this is not the case in other Mediterranean areas, where biomass burning emissions from different sources (domestic heating, agricultural fires and wildfires) can represent major sources of PM (Sciare et al., 2008; El Haddad et al., 2011).

In the last decades, the influence of climate (Millán et al., 1997) and land-use changes (Vallejo, 1997) has produced an increase in the number and extension of wildfires across the Mediterranean Basin. Fire risk situations include extreme droughts, which may be simultaneous with long periods of high temperatures and/or short periods under intense winds (Vallejo and Alloza, 1998). One of the consequences of these alterations has been the increasing number and magnitude of wildfires during the summer in the last quarter of the 20th century. During the 21st century, Spain has suffered on average around 5800 wildfires per year (>1 ha), being 2012 the most dramatic year (MAGRAMA, 2013), when 226125 ha were burned (0.82 % of the total forested area).

Shrublands have accounted for about 65-70% of total burned area in the last ten years in the Iberia Peninsula (MAGRAMA, 2013). Most of these shrublands are the result of the colonization of old-fields and/or the result of the natural regeneration after

forest fires. A number of parameters such as the type of biomass, moisture content, heat intensity during the fire event and fire behaviour determine the compounds and their abundances in smoke plumes Oros & Simoneit (2001), including the composition of the particulate matter (Alves et al., 2010 and 2011; Vicente et al., 2013) and the volatile organic compounds (Ciccioli et al. 2001; Barboni et al., 2010a and 2010b; Evtyugina et al., 2013) released.

Biomass burning emits large quantities of organic compounds as carboxylic acids, carbonyls, oxygenated multifunctional species and aromatics, including soot particles, but also inorganic species such as ions and certain major and trace metals (Simoneit, 2002; Vicente et al., 2013). Most of the organic compounds released during biomass burning are derived from cellulose, lignocellulose, hemicellulose and products generated during incomplete combustion processes (Simoneit et al., 1999). The most typical inorganic substances associated to biomass burning emissions are those related to vegetation macro-nutrients (Carreira et al., 1996), although soil-derived particles (clays and carbonate minerals among others) may be suspended to the atmosphere. Specific organic and inorganic compounds may be used as tracers of biomass burning emissions, being the most common levoglucosan, mannosan and soluble potassium. Particle size of biomass burning emissions is mainly found below 2.5 μm , being a major source of organic (OC) and elemental (EC) carbon. Generally, organic matter emitted during such events represents over 90% of the total emitted mass.

In addition, the primary organic fraction released to the atmosphere during biomass burning processes (domestic heating, agricultural and wildfires) contains large amounts of polycyclic aromatic hydrocarbons (PAHs), with an important toxicity potential. Likewise, volatile organic compounds (VOCs), as dominant ozone precursors, are emitted in huge quantities during wildfires. It is well known that particulate matter (PM) causes negative human health effects (Pérez et al., 2010 and Belleudi et al., 2010), influence the Earth's climate by absorbing or scattering the solar radiation, affecting clouds formation and their lifetimes (IPCC, 2007). Consequently, the characterization and quantification of primary-derived aerosols and secondary precursors released during wildfires of Mediterranean shrublands will improve emission inventories, may support future climatic projections and will be useful for source apportionment end-users to improve our knowledge about PM sources.

This study complements our previous work by García-Hurtado et al. (2013). Specifically in this study, we focus our investigation on VOCs and PM tracers from

shrublands wildfire experiments carried out in eastern Spain, as well as their emission factors, whereas the previous one was focused on carbon emission.

2. Material and methods

The shrubland burning experiments were conducted in a calcareous terrain in Ayora (Valencia, Eastern Spain) during 3 consecutive days, from 22nd to 24th April 2009, under controlled safety conditions (Ayora burning experiment, Garcia-Hurtado et al., 2013). Three replicated adjacent plots (30x35 m), with a mean slope of 15% and similar biophysical characteristics, were delimited to perform the experimental burnings. Plots were composed by 30-year old shrubland vegetation, senescent Mediterranean gorse shrubland in transition to rosemary shrubland (Baeza et al., 2002). Between 46 and 50% of aboveground fuel was dead, and 30–40% of total fuel (32–57 Mg ha⁻¹) was litter. The values of vegetation moisture were around 35% and the values of the consumed aboveground biomass were around 80%. The burns took place under safe weather conditions with moderate temperatures (around 20° C), low wind speed (less than 10 km h⁻¹), and moderate relative air humidity (around 50%). The duration of each experimental fire ranged between 45 to 60 minutes, and flaming phases lasted between 5 to 10 minutes. Smoke emissions were sampled in situ by using a suction pump. Emissions were suctioned throughout an aluminium tube to a field Teflon chamber where different instruments and sampling inlets for other monitors were placed. A continuous renovation of the air inside the chamber was assured by means of an extraction pump system.

2.1. Online PM measurements

Particulate matter concentrations were measured in terms of mass and number concentrations. The mass concentration of particulate matter (PM) was determined in 15 different size bins between 0.3 and 20 µm. An optical counter (GRIMM model 1108) was employed to measure the number of particles that were subsequently converted into mass concentration by using specific algorithms provided by the instrument manufactures. The results are finally expressed in air quality terms (PM₁₀, PM_{2.5} and PM₁). We calculated the experimental correction factor obtained from the comparison between gravimetric and real-time concentrations ($GRIMM = 0.81 \times \text{gravimetric}$; $R^2 =$

0.94), and we applied it to correct the concentrations recorded by the GRIMM monitor. Particle number concentration (PNC) was provided by a TSI water-based condensable particle counter (CPC, Model 3785), which measured the total particle number from 5 to 1000 nm, using distilled water as the condensing fluid. Flow rates of both instruments were 1 L min⁻¹.

2.2. Offline sampling and determination of chemical compounds in PM

MUNKTELL quartz micro-fibre of (150 mm) filters for PM_{2.5} and fibreglass for PM₁₀ were used to determine inorganic and organic compounds in PM. Before the sampling, filters were heated at 300° C during 4 hours, and they were thereafter flushed with a nitrogen stream to eliminate possible organic compounds. Once collected, filters were kept in a portable fridge at a temperature around 4 °C until the arrival to the lab in the same day, where they were stored in the freezer at -20°C until analysis.

2.2.1. Inorganic compounds

PM₁₀ and PM_{2.5} samples were collected on filters by using MCV-CAV high volume samplers fitted with DIGITEL inlets. The flow rate of these instruments was set to 500 L min⁻¹. During each of the three experiments: one sample was collected during approximately 120 minutes before the fire started (to account for the background conditions); another sample (45-60 minutes) during the fire experiment which included the totality of the flaming phase and a significant part of the smouldering process; and an additional sample during the residual smouldering phase (60-90 minutes). Unfortunately, the PM_{2.5} sample collected during the flame-phase of fire-1 was lost due to technical problems with the sampler.

As fibreglass filters are not appropriate for the analysis of major and trace metals, such elements were only determined in the PM_{2.5} samples. Accordingly, ¼ of each filter was digested in PTFE containers using a HNO₃:HF:HClO₄ under 90°C during 6 h. After digestion the resulting solutions were evaporated to dryness at 200°C, and recovered with HNO₃ and bi-distilled water to obtain a final acidic (5%) solution. After that, the aliquots were analysed by Inductively Coupled Plasma Atomic Emission Spectrometry, ICP-AES (IRIS Advantage TJA Solutions, THERMO) for the determination of the major elements and Inductively Coupled Plasma Mass Spectrometry, ICP-MS, (X Series II, THERMO) for trace elements, following the procedures described in Querol et

al. (2001). To guarantee the quality of the results, blank concentrations were accounted, and a small amount of a certified fly ash standard 1633b was analysed following the same protocol.

$\frac{1}{4}$ of each PM₁₀ and PM_{2.5} filter was leached with bi-distilled water. Anion and cation concentrations were analysed by Ionic Chromatography (DIO-NEX DX-20). The anion separation column was an AS9-HC 250 × 4 mm, with Na₂CO₃ 9 mM as eluent, running at 1.4 mL min⁻¹. Cation analysis was performed using a CS12A 250 × 4 mm cationic column and 20 mM methanesulfonic eluent at a flow rate of 0.8 mL min⁻¹.

2.2.2. Organic compounds

A section of 1.5 cm² was employed to quantify OC and EC concentrations by means of the thermo-optical SUNSET laboratory analyser, with the EUSAAR₂ temperature protocol.

To determine PAH's content in PM₁₀ and PM_{2.5} samples, a TRACE-DSQ II gas chromatograph – mass spectrometer - GC-MS - (Thermo Fisher Scientific Co., Waltham, MA, USA) was used, with a HP-5MS column of 30m x 0.25mm I.D x 0.25 µm film thickness (Crosslinked 5% Ph Me Siloxane) supplied by Agilent Technologies (Santa Clara, USA). We worked in full scan mode (m/z 50–650) with the ion source temperature at 200° C and the quadrupole temperature at 100° C following the protocol proposed by Borrás and Tortajada-Genaro (2007). To quantify the PAH content, a certified standard mixture with 16 compounds of 10 ng L⁻¹ in cyclohexane was used, supplied by Dr Ehrenstorfer (GmbH, Augsburg).

Hydroxycarboxylic compounds content was determined by applying a derivatisation methodology (Borrás and Tortajada-Genaro, 2012). The derivatisation reagents employed were MSTFA (Lancaster, Morecambe, England) and PFBHA (Sigma Aldrich, Steinheim, Germany). Chlorosuccinic acid and 4-Fluorobenzaldehyde were used as surrogate of hydroxyl derivatisation and carbonyl derivatisation, each of them obtained from Sigma Aldrich. 1-phenyldodecane was supplied by Fluka (used as GC internal standard). The same GC-MS system was used as in the analysis of PAH's.

2.3. Sampling and analysis of gaseous compounds

VOC's (Alkanes, monocycle and bicycle arenes and isoprenoids carbonylic and hydroxycarboxylic compounds) were sampled by using cartridges. To this end, three

types of cartridges were used: XAD-2 cartridges (Sigma Aldrich) for the retention of alkanes, monocycle and bicycle arenes and isoprenoids; Silica DNPH coated cartridges with a previous ozone scrubber cartridge (Waters Co) for the sampling of carbonyl compounds; and C₁₈ cartridges (Waters Co) for the collection of alcohols and organic carboxylic acids.

2.3.1. Alkanes, monocycle and bicycle arenes and isoprenoids.

To analyse this group of compounds, an EPA methodology (MTA/MA-030/A92) was used. Resin-Cartridges-XAD-2 were used and extracted with 2 mL of CS₂, then subjected to ultrasonic bath to obtain the first aliquot. Subsequently, a second extraction with a mixture of CS₂ and 50 µL of 2-butanol was performed, resulting in a second aliquot. These solutions were analysed by using a TRACE-DSQ II GC-MS.

2.3.2. Aldehydes and ketones

The determination of carbonyls in samples was performed from a combination of two methods (EPA TO-5 and TO-11A). The cartridges were eluted with 2 mL of acetonitrile liquid chromatograph – mass spectrometer (LC/MS) grade, and were stored under dark conditions during 24 h before the injection in the LC/MS system with a Surveyor quaternary pump, and a Surveyor DAD detector with a Surveyor auto-sampler associated with a mass spectrometer with atmospheric pressure chemical ionization (APCI+) LCQ Advantage, all of them from Thermo-Finnigan Co. Allure AK 200x3,2 mm 5 µm column supplied by Restek was used for the analysis of aldehydes and ketones, using H₂O and CH₃CN as mobile phases.

2.3.3. Alcohols and organic acids

To quantify the content of hydroxyl-carboxylic compounds, a derivatisation methodology was used as for particulate matter, but gaseous phase cartridges C₁₈ were employed as a retention media.

The cartridges were extracted with 2 mL of CH₂Cl₂/CH₃CN (1:1) and the mixture was concentrated in a nitrogen stream, driven to dryness and re-dissolved in 1.5 mL of CH₂Cl₂/CH₃CN (1:1). The following methodology is the same as employed in particulate matter, just modifying the elution methodology. The GC-MS analyser is the same as that used for alkanes.

3. Results and discussion

3.1. PM mass and PNC (particle number concentrations)

Table 1 shows the PM mass concentration and the PNCs obtained during the three experiments, distinguishing between flaming and smouldering phases. Flaming phases lasted no more than 10 minutes and they were characterized by very high particulate matter emissions, showing a similar partitioning between the fine and the coarse mode as the PM_1/PM_{10} ratios varied between 0.44 to 0.52 in fires 2 and 3 (see Garcia-Hurtado et al., 2013 for additional details concerning fire characteristics). Similarly, $PM_1/PM_{2.5}$ ratios ranged from 0.53 to 0.59 for fires 2 and 3. Particle size characteristics were substantially different (PM_1/PM_{10} and $PM_1/PM_{2.5}$ ratios of 0.80 and 0.89 respectively) during the first fire, probably due to the much higher moisture content in dead fuel and soil, as discussed in Garcia-Hurtado et al. (2013). Actually, mass concentration of PM for fires 2 and 3 (Figure 1) peaked between 2 and 3 μm , while much finer emissions (mass peak below 0.3 μm) were recorded during fire 1. Concerning the variability of PNCs of sub-micron PM, levels were extremely high (up to more than 10^6 particles per cm^{-3}) during the flaming phases and almost parallel to those of PM_x mass. Since PNCs are usually driven by the presence of ultra-fine particles (UFP, $< 0.1 \mu m$), the study of the PNC/PM_1 ratio variability is a meaningful tool. Thus, for all the flaming events, PNC/PM_1 ratios varied from 125 for fire 1 to 234 for fire 3. When comparing these ratios with those observed in urban environments, where most of the fine and ultra-fine particles are related to vehicular exhaust emissions, a significant difference is patent. As an example, fine urban aerosols in a typical Mediterranean city such as Barcelona are mainly linked to vehicular emissions, being the PNC/PM_1 ratio between 900 and 1200, and the peak distribution at around 40 nm (Pey et al., 2008). In our study, each microgram of PM_1 is made up of a relatively low number of particles, thus indicating a larger size of biomass burning aerosols (in the range of PM_1) when contrasted with the typical size of other combustion particles such as vehicular exhausts.

Particulate matter characteristics and concentrations measured during the smouldering phases contrasted significantly with respect to those determined during the flaming phases: PM and PNCs were reduced in around two orders of magnitude with respect to those registered during the flaming phases. Besides, the mass concentration of particles shifted to the coarser modes as deduced by the lower PM_1/PM_{10} ratios (0.10-

0.47), although with a high variability between the three fires. For the smouldering phases the mass concentration peak was reached above 5 μm (Figure 1). Much higher PNC/PM₁ ratios (602-1053) were also measured with respect to those of the flaming phases, thus indicating an increasing role of UFPs. In fact, the reduction in the mass concentration of particles may allow new-particle formation processes in the smouldering plumes instead of the condensation sink, the later favoured for high PM loads (Pey et al., 2008). Thus, when elevated PM mass concentrations are registered (flaming phases), coagulation between particles and condensation of semi-volatile species onto pre-existing particles are the dominant routes for the formation on secondary aerosols components. On the other hand, a more diluted air, in terms of PM mass concentration (smouldering phases), favours nucleation processes.

In the context of this campaign, the combination of PM_x and PNCs measurements has been useful to detect the main processes taking place in the smoke plumes. Whilst flaming phases emit large amounts of primary particles in short periods (organic particles in the accumulation mode, and organic and inorganic substances in the PM₁₋₁₀ fraction, probably associated to the ashes generated during the combustion processes), smouldering phases are characterised by much lower emissions per unit of time, shift to coarser sizes, but with intense new-particle formation processes (secondary). In conclusion, our findings show that the smouldering stage is characterized by a coarser PM and by enhanced nucleation processes, the latest probably as a result of the sharp decrease in VOCs, PNC and PM with respect to the flaming stage. Thus, new-particle formation processes occurred significantly but they had little effect on PM_x levels, as expected. Furthermore, since large quantities of deposited burned material were available for re-suspension, a substantial proportion of PM emissions during the smouldering phase was associated to re-suspension processes.

3.2. Inorganic composition of smoke particles

3.2.1. Water-soluble ions

In this study, seven major water-soluble inorganic species (NO_3^- , SO_4^{2-} , Cl^- , NH_4^+ , K^+ , Ca^{2+} , Mg^{2+}) were determined and quantified in PM₁₀ and PM_{2.5} samples (Table 2). As previously described, we obtained during each experiment samples from the flaming process and most of the smouldering phase, and we also sampled the residual smouldering process. The relative abundance of soluble inorganic species may vary

significantly (Chen et al., 2010; Alves et al., 2011; Vicente et al., 2013) according to: 1) their concentration in the flammable plant tissues; 2) their volatility, depending on fire severity; 3) and their intrinsic solubility in the burned plant-tissue particles. Furthermore, the soil type may also influence emissions of mineral dust.

The most abundant soluble inorganic ions released during the flaming-smouldering phase (Table 2) were K^+ and SO_4^{2-} , both accounting for 68 to 80% of the inorganic soluble fraction, and reduced amounts of Cl^- , Ca^{2+} , NO_3^- and Mg^{2+} and NH_4^+ although always above detection limits. During the residual-smouldering phases, K^+ , SO_4^{2-} and Ca^{2+} were the most relevant inorganic compounds, accounting for 7-45, 19-47 and 17-42 % respectively of the total inorganic soluble mass in PM_{10} and $PM_{2.5}$. The high proportion of Ca^{2+} present in the residual-smouldering stage suggests a contribution from re-suspension processes at this stage (deduced above from the coarser PM size), both from ashes generated during the combustion process but also from soil-dust re-suspension, as the experimental area was located on a calcareous terrain. Actually, the ionic balance between cations and anions (Table A1) shows a significant deficit of anions, which could be ascribed to the presence of carbonate in our samples. This hypothesis would support the relevance of soil re-suspension processes during wildfires.

Concerning the partitioning of these components between $PM_{2.5}$ and PM_{10} during the flaming-smouldering phase (Table 3), 49-68% of SO_4^{2-} , 46-67% of Cl^- , 46-68% of K^+ and 47-50% of NH_4^+ were found in the $PM_{2.5}$ fraction. Conversely, nitrate particles occurred predominantly in the coarser fraction (67-89% in $PM_{2.5-10}$), probably due to the reaction between nitric acid (from NO_x emissions) with some mineral dust and/or ash components such as Ca^{2+} and Mg^{2+} . An intermediate partitioning was found for Ca^{2+} and Mg^{2+} .

Overall, the concentration of the water-soluble ions accounted for 2-3% of the $PM_{2.5}$ mass concentration, which is in agreement with the results reported by Alves et al. (2011) from similar experiments. In this study, K^+ , SO_4^{2-} and Cl^- yielded the higher ionic concentrations. In the case of K^+ , the concentrations reached values up to $12 \mu g \text{ mg}^{-1}$ in $PM_{2.5}$, thus 1.0% of the $PM_{2.5}$ mass. According to other studies (Yokelson et al., 2009), this can be considered as a low value, which is interpreted in our case to the prevalence of smouldering conditions. Such assumption is linked with the findings by Chen et al., (2007), who proposed K^+ concentrations in smouldering-prevailing conditions to be <1% in grasses, shrubs and softwood.

Chloride concentrations ranged from 1.6-4.9 $\mu\text{g mg}^{-1}$ in $\text{PM}_{2.5}$ and represents 0.2% of the $\text{PM}_{2.5}$ mass. Chloride concentration in plant tissues is usually low as compared to macronutrients in non-saline soils, though it is very soluble in all biochemical species. Sulphate concentrations ranged from 7.2 to 23.0 $\mu\text{g mg}^{-1}$ in $\text{PM}_{2.5}$ and represents 0.9% of the total $\text{PM}_{2.5}$ mass. Most of the sulphur content in plant is in the form of reduced organic sulphur (Mengel & Kirkby, 2001), which is oxidized during the combustion process to form SO_2 and sulphate. The presence of SO_4^{2-} in the smoke aerosols can be the result of: a) adsorption of SO_2 on black carbon particles through a catalytic process forming H_2SO_4 (Seinfeld & Pandis, 1998); b) the reaction of SO_2 with CaO particles from the burned CaCO_3 mineral dust from this specific high Ca soil and with K_2O particles from burned vegetation to form coarse SO_4^{2-} (the same mechanism may occur with NO_2 to account for the formation of coarse NO_3^-); c) The nucleation or condensation of H_2SO_4 or $\text{H}_2\text{NH}_4\text{SO}_4$ from SO_2 to form fine SO_4^{2-} . In fact, the real time monitoring of SO_2 during the experiments revealed the release of significant concentrations with maximum peaks ranging 677-1341 ppb of this pollutant in flaming phase as a high oxidized compound (Urbanski et al., 2009). Lazaridis et al. (2008) study confirms the presence of SO_2 in the emissions from forest fires in the Mediterranean basin. Calcium, magnesium, ammonium and nitrate made up the remaining inorganic soluble fraction, accounting for 0.2% of the total $\text{PM}_{2.5}$ mass.

3.2.3. Trace elements

The content of trace metals found in $\text{PM}_{2.5}$ samples (Table 4) is dominated by Cu, Zn, Zr, Pb, Ti, and Ba. Some of these trace elements such as Cu and Zn are constituents of enzymes and other proteins in plants (Hall, 2002), and Mn is also an essential plant nutrient (Mengel & Kirkby, 2001). Other trace elements (Ti, Ba, Zr, V and As) may be attributed to soil dust re-suspension (Andreae et al., 1998) or released to the atmosphere due to their presence over leaves and branches. In general, the concentrations of trace elements recorded as emission data during the experiments were reaching levels typical from ambient air concentrations of polluted urban or industrial areas consequently, any of the inorganic trace elements analysed may be considered as a tracer of emissions from our Mediterranean shrublands wildfires when considering source apportionment tracers. It is worth mentioning, however, the high levels of Cu and Zn, as well as As, Ba

and Cd, which could be used as tracers for studies carried out at regional background sites.

3.3. Organic composition of smoke particles

3.3.1. Polyaromatic Hydrocarbons (PAHs)

The organic components of smoke particles identified in this study in PM_{2.5} and PM_{2.5-10} are PAHs, alcohols, hydroxyl-carboxylic compounds and acids.

The main PAHs released during biomass burning emissions are akin to those emitted from other anthropogenic combustion sources. Therefore, they are not specific biomass combustion tracers (Simoneit, 2002). The partitioning of 16 major PAHs in the fine and coarse modes was investigated (Figure 2). Benzo(a)anthracene, fluoranthene (Flu) and pyrene (Py) were the most abundant PAHs. Fluoranthene and pyrene were mentioned in previous studies on fire emissions (Wang et al., 2009). The presence of Benzo(a)anthracene as a major compound from wildfire emissions from Mediterranean ecosystems is proposed by Alves et al. (2010), associated to coarse particles.

Some diagnostic ratios between different PAHs have been used to investigate their origins in the atmosphere. Some of the ratios investigated in this study are presented in Table 5. Our Flu/(Flu + Pyr) ratios are close to those found by Alves et al. (2010) for Mediterranean ecosystems, and also of the same order of magnitude as those from shrubland wildfires (Wang et al. 2009). Similarly, IcdP/(BghiP + IcdP), BghiP/BaP and BFs/BghiP ratios were very close to those found by Alves et al. (2010), and contrast clearly with those linked to other combustion sources such as vehicle exhausts (Rogge et al., 1993). Conversely, the Phe/(Phe + Ant) ratios are higher when compared to other studies (Wang et al., 2009), which could be probably related to the lower Modify Combustion Efficiency (MCE) values (0.76) of our wildfires (Garcia-Hurtado et al., 2013), in contrast to typical MCE values around 0.90-0.95 encountered during flaming processes (Wang et al. 2009).

3.3.2. Alcohols, acids and carbonylic compounds

Around 70 polar organic compounds have been identified in the smoke particles of these experiments. The concentration ranges in absolute values in mass of compound per mass of PM ($\mu\text{g mg}^{-1}$) in PM₁₀ and PM_{2.5}, can be found in the supplementary material (Table A2).

The chromatographically resolved spectra for organic compounds (in both size fractions) were dominated by phenols, n-alkanals and n-alkanones, as well as by alcohol biomarkers. Concerning the partitioning of the different organic compounds between the fine ($PM_{2.5}$) and the coarse mode ($PM_{2.5-10}$), phenil and dicarboxylic compounds (Figure 3) were found almost exclusively in the coarse mode. A similar pattern is observed for alkane carbonilic, aromatic carbonilic, dicarbonilic, methoxy-phenol and alcohol biomarkers compounds, clearly shift to the coarse mode (65-85%). Conversely, alkanoic, unsaturated carboxylic and acid biomarkers were uniformly distributed (40-55% of their mass in the coarse mode) among fine and coarse fractions. Some of these organic compounds (acetaldehyde, glyoxal, methylglyoxal...) are secondary in origin, produced from VOCs and semi-volatile VOCs which condense over the surface of pre-existing particles (soot particles). Others (resins acids, anhydrosugars, phytosterols, furals...) however, are primary compounds derived from the pyrolysis of cellulose, hemicellulose, and ligno-cellulose (Gonçalves et al. 2011).

According to Simoneit et al. (1999), carbonylic compounds (n-alkanals, n-alkanones, aromatics and dicarbonylics) are produced during fragmentation reactions; acid compounds (n-alkanoics, dicarboxylics and unsaturated) are almost released from pyrolysis and/or oxidation of hydroxy acids from vegetation; alcoholic compounds (phenolics and methoxy-phenolics) are the result of the thermal degradation of lignin; and finally anhydrosaccharides, acids, phenol compounds are linked to the degradation of cellulose, hemicellulose and ligno-cellulose.

Levoglucosan, which is commonly used as a biomarker, was the most abundant degradation compound with values between 68.6 and 42.5 $\mu g\ mg^{-1}$ in PM_{10} and $PM_{2.5}$ respectively (Table A1), thus in the range obtained by Simoneit et al. (1999). Moreover, its stereoisomers, mannosan and galactosan, were also noticeable in the smoke samples. The ratios between levoglucosan (L) and its stereoisomers mannosan (M) and galactosan (G) has been recently employed to elucidate the source contribution from different biofuels or types of combustion, therefore, it should be noted a substantial variation in the emission of this ratios. In our study (L/M) ratio in PM_{10} was 73.9 and (L/M+G) value was 18.4. Both values were higher than those presented by Alves et al. (2010) in shrubland fields 5.6 and 3.9 respectively. These differences in the results may be because in that study there was a predominant flaming combustion process unlike in our study where a smouldering combustion process was predominant and thus about our results are more similar to grasses biomass results (Engling et al., 2006).

The reciprocal factor (OC/levoglucosan) is used to account for the amount of OC attributed to biomass combustion in ambient aerosols. Our experimental ratio for shrubland wildfires is 6.9 ± 0.5 , which is only slightly lower (7.6) than the ratio found by Gonçalves et al. (2010) based on the main wood species burned in Portugal. In any case, the experimental ratio obtained in this study falls in the range (4.5-24.6) shown in Harrison et al. (2012).

Other biomarkers such as catechols, b-sitosterol, dehydroabietic acid (a product from resins), and vanillic acid (which is derived from coniferyl alcohol, found in its oxidation state as coniferyl aldehyde) were also detected. Finally, some compounds with amino and nitro groups, as well as hydroxybenzoic acids, hydroxybenzaldehyde and dihydroxybenzaldehyde compounds were also observed but they were not quantified.

3.4. Volatile Organic Compounds

The analysis of the three experimental burning replicates led to the quantification of 71 compounds and their resultant emission factors (EF) (see Table A3). The VOCs were grouped in alkanes, monocyclic and bicyclic arenes, isoprenoids, aldehydes, ketones, alcohols and acids. Benzene was recognized but it could not be quantified due to the high detection limit for that compound in the methodology we used. Similarly, other compounds could not be identified because their mass spectra or retention indices were not included in our database. Overall, VOCs have been detected in a wide range of concentrations, from trace amounts to several hundred of $\mu\text{g m}^{-3}$.

In general, the EFs for most of the VOCs obtained in this study were slightly lower than those reported from wildfires in Mediterranean forests (Evtugina et al., 2013; Ciccioli et al., 2001). However, the EFs for *Erica arborea* (in our plots *Erica multiflora* is very abundant) reported by Barboni et al. (2010a) are akin to our experimental values. Nevertheless, the differences found with respect to other studies can be due to biome specificities, to different combustion efficiencies, and also to the use of different sampling strategies (Evtugina et al., 2013). Thus, it is important to document as much as possible on complementary parameters (fire temperatures, MCE, fuel moisture and type of biomass) to avoid any unrealistic comparison.

For each family of compounds, some of them were clearly enhanced with respect to the others. For example, toluene, m+p xylenes, styrene and naphthalene were the

foremost compounds of the arenes family. In general, isoprenoids, α -pinene and limonene were the most abundant VOCs. In addition, some of our results on aldehydes and ketones were not previously reported for Mediterranean shrubland wildfires.

Mass percentages were calculated according to their abundance with respect to the bulk mass of VOCs. The most abundant VOCs were alcohols (61%), followed by carbonyls (23%) and acids (11%). In contrast, monocyclic and bicyclic arenes (3%), isoprenoids (1%), and alkanes (1%) were found in much lower proportions.

Some of the organic compounds such as levoglucosan were identified both in the gas and in the particulate phase. Such ubiquitous occurrence may be explained as a partitioning effect between the gas and the particle phase because of the high concentrations (Odum et al., 1996). However, the decomposition of levoglucosan in secondary products occurs at temperatures between 675 and 700 °C (Shen et al., 2010), and some previous studies on PM composition from biomass burning emissions reported levoglucosan at temperatures below 350 °C (Kuo et al., 2008). Therefore, we hypothesize that levoglucosan is released as a VOC between 675 and 350 °C, thus during the flaming phase, and it is emitted as particle during the smouldering phase (with temperatures below 350 °C).

4. Conclusions

This work reports detailed inorganic and organic chemical characterisation of smoke particles and volatile organic compounds from experimental wildfires in Mediterranean shrublands. Flaming and smouldering phases are studied independently in this work. The flaming phase emits large amounts of primary particles in short periods, with a prevalent fine mode in terms of mass concentration. The smouldering phase is characterized by much lower emissions per time unit but with a prevalent coarse mode in terms of mass concentration, favoured by the re-suspension of burned materials and the decrease of direct combustion products. Smouldering processes favour new-particle formation processes in the smoke plumes as deduced by the study of PNC/PM₁ ratios.

On average, soluble inorganic components accounted for 2-3% of the PM_{2.5} mass concentration, with a clear dominance of K⁺ and SO₄²⁻ in flaming-smouldering phases, and an increasing role of Ca²⁺ during the residual-smouldering phase due to contributions from ash and soil re-suspension. Trace metals were not identified as tracers of shrublands wildfires.

The main organic components in smoke particles were phenols, n-alkanals and n-alkanones and their alteration products, most of them clearly enhanced in the coarse fraction, and some of them such as acid biomarkers, alkanolic compounds and unsaturated carboxylic compounds which were equally distributed in the fine and coarse modes. Our experimental OC/levoglucosan ratio for shrubland wildfire emissions is 6.5. The concentration in mass of levoglucosan ranged from 68.6 to 42.5 $\mu\text{g m}^{-1}$ in PM_{10} and $\text{PM}_{2.5}$ respectively. Other biomarkers such as catechols, b-sitosterol, dehydroabietic acid and vanillic acid were also detected.

Among more than 70 VOCs detected, alcohols (61%), carbonyls (23%) and acids (11%) prevailed. Conversely, monocyclic and bicyclic arenes (3%) isoprenoids (1%) and alkanes (1%) were found in much lower proportions. To our knowledge, we report for the first time on EFs of some VOCs. Specifically, levoglucosan was identified in the gas phase for the first time, and it is thought to be emitted in the temperature range between 675 and 350°C, in the transition from the flaming towards the smouldering phase. These EFs and chemical profiles may be helpful for further investigations of wildfire emission impacts on air pollution and tropospheric chemistry, as well as to improve chemical transport models.

Appendix. Supplementary material.

Supplementary material is associated with this paper.

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HIGHLIGHTS

- Inorganic and organic speciation of smoke from shrubland wildfires is provided.
- PM mass and PNC allowed us to identify microphysical processes in smoke plumes.
- SO_4^{2-} and K^+ were the foremost inorganic soluble species released.
- Biomarkers acid compounds were mainly found within the fine fraction.
- Levoglucosan is presented in particulate and also in gaseous phase.

Table 1. Average PM₁₀, PM_{2.5}, PM₁ (in $\mu\text{g m}^{-3}$), particle number concentration (PNC, in cm^{-3}) and different ratios during the three fires for each fire phase (F: flaming; S: smouldering).

		PM ₁₀	PM _{2.5}	PM ₁	PNC	PNC/PM ₁	PM ₁ /PM _{2.5}	PM ₁ /PM ₁₀
		$\mu\text{g m}^{-3}$			cm^{-3}			
Fire 1	F	1681	1544	1338	167002	125	0.87	0.80
	S	66	17	13	11291	869	0.75	0.19
Fire 2	F	5704	4768	2549	354592	139	0.53	0.44
	S	75	9	7	7223	1053	0.78	0.10
Fire 3	F	9048	7870	4662	1089901	234	0.59	0.52
	S	36	22	17	10228	602	0.77	0.47

Table 2. Percentages (%) and values ($\mu\text{g}/\text{mg}$) respect to the total inorganic mass in coarse ($\text{PM}_{2.5-10}$) and fine ($\text{PM}_{2.5}$) fraction during the fire (flaming-smouldering) and during the residual smouldering phases.

Soluble ion (%)	Flaming-smouldering		Residual smouldering	
	$\text{PM}_{2.5}$	$\text{PM}_{2.5-10}$	$\text{PM}_{2.5}$	$\text{PM}_{2.5-10}$
NH_4^+	3-5	1-4	<D.L.	<D.L.
K^+	41-42	39-40	7-9	32-45
Mg^{2+}	1-2	1-3	6-11	3-6
Ca^{2+}	5-8	6-14	31-42	17-24
Cl^-	7-9	7-9	5-9	3-6
NO_3^-	1-2	3-6	<D.L.	4-9
SO_4^{2-}	36-39	29-38	31-47	18-32

Soluble ion ($\mu\text{g}/\text{mg}$)	Flaming-smouldering		Residual smouldering	
	$\text{PM}_{2.5}$	$\text{PM}_{2.5-10}$	$\text{PM}_{2.5}$	$\text{PM}_{2.5-10}$
NH_4^+	0.32-0.55	0.64-1.47	<D.L.	<D.L.-0.01
K^+	6.71-7.07	8.65-28.97	0.03-0.23	0.32-1.52
Mg^{2+}	0.17-0.30	0.19-1.05	0.05-0.28	0.03-0.20
Ca^{2+}	0.95-1.46	1.21-10.04	0.20-0.95	0.11-0.82
Cl^-	1.36-1.47	2.02-6.57	0.04-0.315	0.01-0.25
NO_3^-	0.11-0.21	0.64-1.60	<D.L.	0.04-0.44
SO_4^{2-}	6.29-6.48	8.33-21.43	0.14-1.19	0.02-0.94

<D.L.: Bellow the detection limit

Table 3. Partitioning (in %) between coarse (PM_{2.5-10}) and fine (PM_{2.5}) fractions during the fire (flaming-smouldering) and during the residual smouldering phases.

Partitioning	Flaming-smouldering		Residual smouldering	
	PM _{2.5}	PM _{2.5-10}	PM _{2.5}	PM _{2.5-10}
NH ₄ ⁺	47-50	50-53	<D.L.	<D.L.
K ⁺	46-68	32-54	9-11	85-91
Mg ²⁺	17-50	50-83	100	<D.L.
Ca ²⁺	39-64	36-61	94-100	0-6
Cl ⁻	46-67	33-54	100	<D.L.
NO ₃ ⁻	11-33	67-89	<D.L.	<D.L.
SO ₄ ²⁻	49-68	32-51	77-92	8-23

<D.L.: Bellow the detection limit

Table 4. Concentration ranges of trace elements reached in all the experiments.

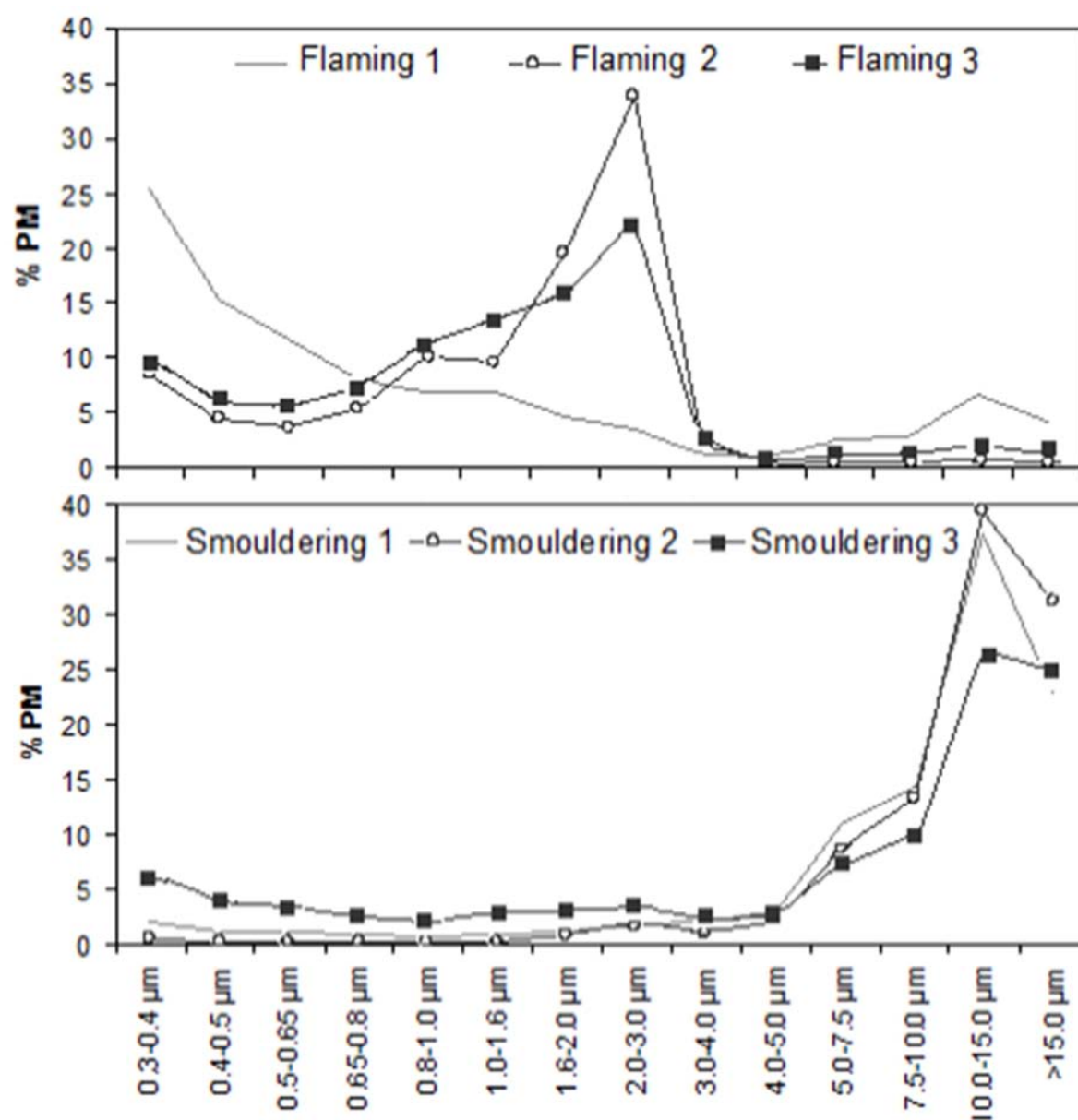
	ng mg ⁻¹ PM _{2.5}
Li	0.3-0.5
Ti	1.9-12
V	1.6-3.9
Mn	2.0-4.8
Cu	27-39
Zn	59-147
As	3.0-3.9
Rb	3.1-4.3
Sr	1.5-2.7
Zr	22-53
Nb	0.3-0.6
Cd	1.3-1.4
Sn	0.8-1.8
Sb	4.3-6.3
Pb	26-30
Ba	8.9-115
Total	163-426

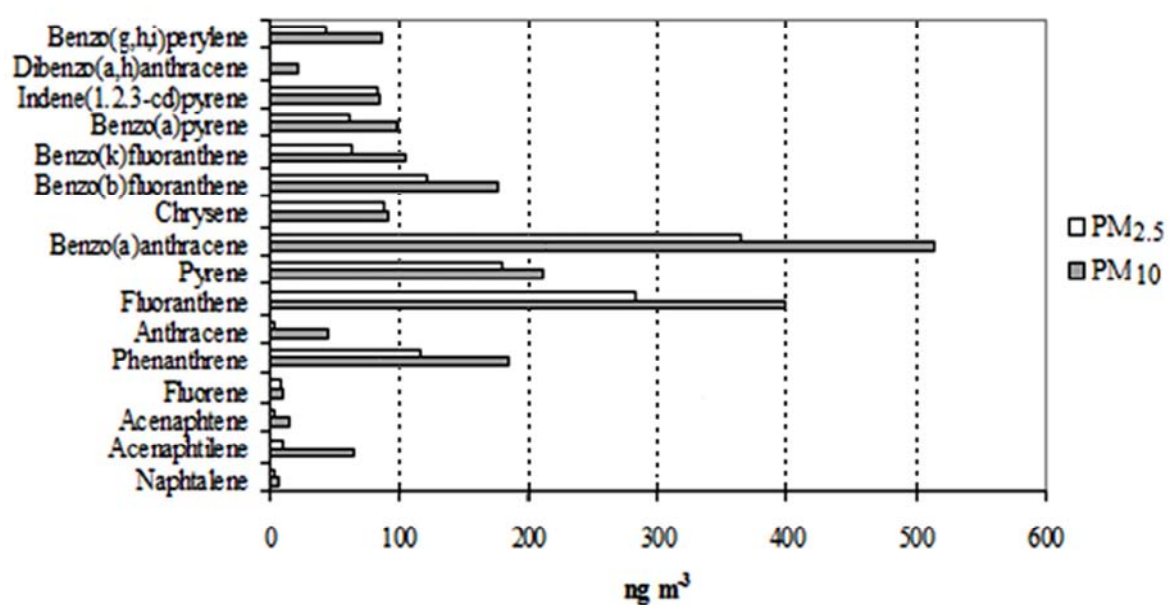
Table 5. Diagnostic ratios of major PAH's in different studies.

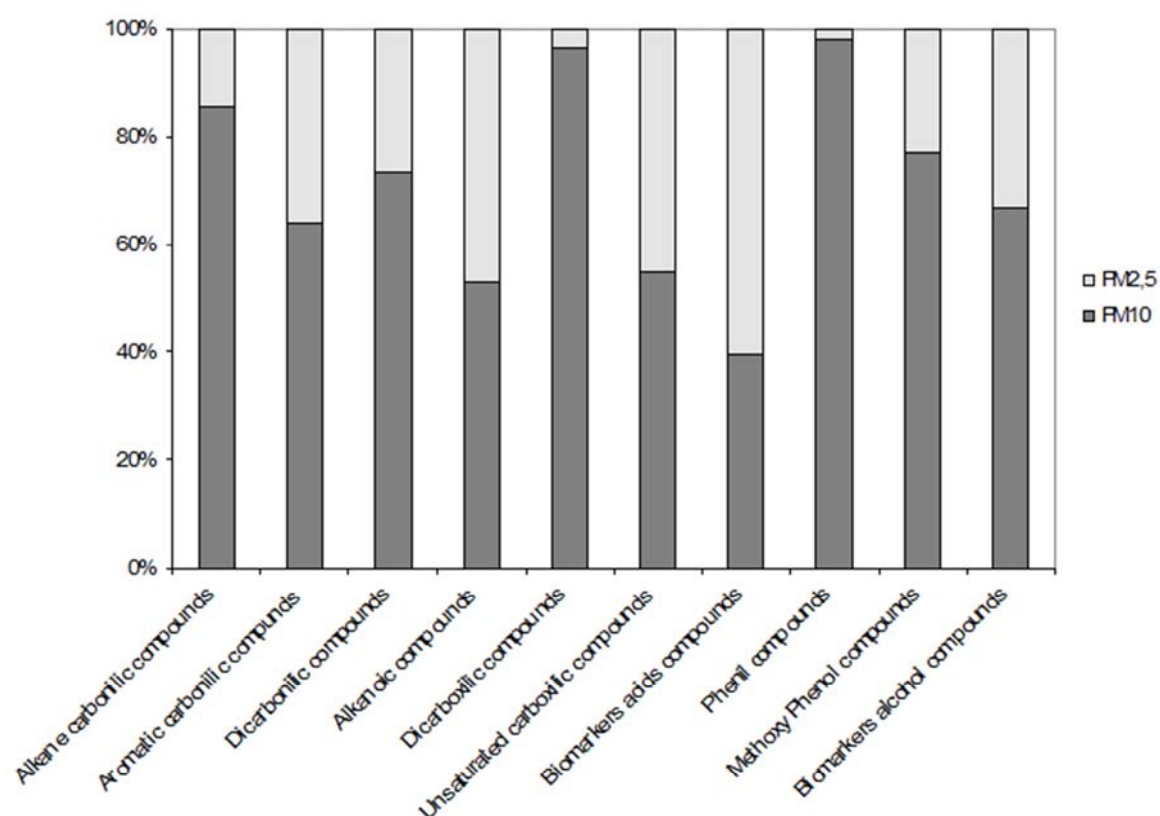
		Flu/ (Flu+Pyr)	Phe/ (Phe+Ant)	IcdP/ (BghiP+IcdP)	BghiP/ BaP	BFs/ BghiP
This study	PM _{2.5-10}	0.64	0.86	0.50	0.87	3.26
	PM _{2.5}	0.61	0.98	0.66	0.70	4.31
Alves et al. (2010) ¹	PM _{2.5-10}	0.56	0.85	0.74	0.82	5.21
	PM _{2.5}	0.6	0.75	0.75	0.86	3.98
Rogge et al. (1993) ²	Non-catalyst auto	0.61	0.77	0.04	3.34	0.58
	Catalyst auto	0.44	0.89	0.09	2.27	1.16

¹ Mediterranean Shrubland in Portugal. ² Exhaust emissions.

(Flu) Fluoranthene; (Phe) Phenanthrene; Anthracene (Ant); Indeno(1,2,3-cd)pyrene (IcdP); Benzo(g,h,i)perylene (BghiP); Benzo(a)pyrene (BaP); Benzo(a)fluoranthene (BfA);







1 **Figure 1.** PM mass-size distributions between 0.3 and 15 μm recorded during flame and smouldering
2 phases in our experiments.

3 **Figure 2.** Concentrations of PAHs in PM_{2.5} and PM₁₀ during the experiments (in ng m^{-3}).

4 **Figure 3.** Partitioning of major organic families between PM_{2.5} and PM₁₀ determined in this study.

5

Table A1. Ionic balances (in neq/m³) during Ayoraburning experiments in PM₁₀ and PM_{2.5}, for fire (flaming phase and most of the smouldering process) and residual emissions (containing some of the smouldering phase). Estimated CO₃²⁻ contribution (in µg/m³) to compensate the anion defect.

			Fire 1		Fire 2		Fire 3	
			PM ₁₀	PM _{2.5}	PM ₁₀	PM _{2.5}	PM ₁₀	PM _{2.5}
Flaming + smouldering	Σ cations	neq/m ³	2488		3712	1515	3151	1997
	Σ anions	neq/m ³	1173		1783	810	2167	1433
	anion defect	neq/m ³	1315		1930	704	984	563
	estimated CO ₃ ²⁻	µg/m ³	39.5		57.9	21.1	29.5	16.9
Residual (including some smouldering	Σ cations	neq/m ³	165	108	228	121	178	105
	Σ anions	neq/m ³	77	53	75	63	37	31
	anion defect	neq/m ³	88	55	153	59	141	74
	estimated CO ₃ ²⁻	µg/m ³	2.7	1.6	4.6	1.8	4.2	2.2

6 **Table A2.** Concentration ranges of mass of compound per mass of total extracts in PM₁₀ and PM_{2.5}

			$\mu\text{g}/\text{mg}$ PM ₁₀	$\mu\text{g}/\text{mg}$ PM _{2.5}
<i>Carbonilic compounds</i>				
<i>rt(min)</i>				
<u>n-alkanals and n-alcanones compounds</u>				
Acetaldehyde peak1	C ₂ H ₄ O	6.95	8.94-70.10	10.37-25.60
Acetaldehyde peak2	C ₂ H ₄ O	7.05	23.37-92.37	17.77-48.44
Acetone	C ₃ H ₆ O	7.81	4.38-168.67	0.42-2.12
Propionaldehyde peak1	C ₃ H ₆ O	8.16	0.05-4.02	0.21-0.85
Propionaldehyde peak2	C ₃ H ₆ O	8.25	0.09-2.01	<D.L.-0.21
2-butanone	C ₄ H ₈ O	8.68	5.66-7.12	3.17-6.56
Butyraldehyde	C ₄ H ₈ O	8.92	0.55-1.46	<D.L.-0.21
Pentanal	C ₅ H ₁₀ O	9.38	1.10-3.65	<D.L.-4.23
n-pentanone	C ₅ H ₁₀ O	9.48	0.73-1.46	<D.L.-0.85
Hexanal	C ₆ H ₁₂ O	10.77	0.44-0.18	<D.L.-0.06
Heptanal	C ₇ H ₁₄ O	16.06	<D.L.-0.55	<D.L.-0.21
<u>Aromatic carbonilic compounds</u>				
Furfural peak1	C ₅ H ₄ O ₂	12.35	<D.L.-0.18	<D.L.-0.08
Furfural peak2	C ₅ H ₄ O ₂	12.6	<D.L.-0.18	<D.L.
Benzaldehyde	C ₅ H ₆ O	14.62	<D.L.-1.46	<D.L.-1.48
Tolualdehyde	C ₈ H ₈ O	15.81	2.19-6.94	<D.L.-2.96
Coniferyl aldehyde	C ₁₀ H ₁₀ O ₃	23.09	<D.L.-0.04	<D.L.
<u>Dicarbonilic compounds</u>				
Glyoxal peak1	C ₂ H ₂ O ₂	17.08	0.01-0.04	0.01-0.02
Glyoxal peak2	C ₂ H ₂ O ₂	17.17	0.02-0.04	0.01-0.02
Methylglyoxal	C ₃ H ₄ O ₂	17.44	0.01-0.09	0.01-0.02
<u>Acid compounds</u>				
<u>Alkanoic compounds</u>				
Nonanoic acid	C ₉ H ₁₈ O ₂	11.11	1.64-4.20	1.06-4.44
Dodecanoic acid	C ₁₂ H ₂₄ O ₂	14.17	0.73-0.91	<D.L.
Myristic acid	C ₁₄ H ₂₈ O ₂	16.28	0.05-0.18	0.13-0.21
Palmitic acid*	C ₁₆ H ₃₂ O ₂	18.23	0.18-1.10	0.63-2.75
<u>Dicarboxilic compounds</u>				
Malonic acid	C ₃ H ₄ O ₄	8.77	<D.L.-0.07	<D.L.-0.04
Maleic acid	C ₄ H ₄ O ₄	10.35	0.07-0.73	<D.L.-0.13
Glutaric acid	C ₅ H ₈ O ₄	12.38	0.18-5.48	<D.L.
Pimelic acid	C ₇ H ₁₂ O ₄	16.4	0.05-0.18	<D.L.-0.11
<u>Unsaturated carboxilic compounds</u>				
Undecenoic acid		17.55	0.02-6.39	<D.L.-6.35
Heptadecenoic acid		21.26	<D.L.-0.55	<D.L.-0.21
<u>Biomarkers acids compounds</u>				
Vanillic acid*	C ₈ H ₈ O ₄	15.41	<D.L.-0.07	<D.L.-0.63
Syringic acid*	C ₉ H ₁₀ O ₅	16.82	<D.L.-0.37	<D.L.-0.42
Dehydroabietic acid*	C ₂₀ H ₂₈ O ₂	21.76	0.09-0.18	<D.L.-0.21
<u>Alcohol compounds</u>				

<u>Phenil compounds</u>				
Phenols	C ₆ H ₆ O	6.76	115.01-494.34	<D.L.-18.40
Catechol*	C ₆ H ₆ O ₂	9.95	0.07-0.91	<D.L.-0.21
Resorcinol	C ₆ H ₆ O ₂	10.82	0.05-0.18	<D.L.-0.02
Hydroquinone	C ₆ H ₆ O ₂	11.07	<D.L.-0.09	<D.L.-0.04
Methylcatechol	C ₇ H ₈ O ₂	11.64	0.01-0.09	<D.L.
1-Naphthol	C ₁₀ H ₈ O	12.55	1.64-20.99	<D.L.
2-Naphthol	C ₁₀ H ₈ O	12.7	7.048-104-96	<D.L.
Trimethylcatechol	C ₉ H ₁₂ O ₂	13.12	<D.L.-0.37	<D.L.
<u>Methoxy Phenol compounds</u>				
Guaiacol	C ₇ H ₈ O ₂	9.59	0.07-0.55	<D.L.-0.08
3-Methoxyphenol	C ₇ H ₈ O ₂	9.65	0.18-0.55	0.15-1.06
Mequinol	C ₇ H ₈ O ₂	9.69	0.18-0.55	<D.L.-0.11
Methylguaiacol isomer1	C ₈ H ₁₀ O ₂	10.64	0.018-0.05	<D.L.-0.11
Methylguaiacol isomer2	C ₈ H ₁₀ O ₂	10.69	<D.L.-0.05	<D.L.
Methylguaiacol isomer3	C ₈ H ₁₀ O ₂	10.74	0.09-1.09	<D.L.-0.42
Ethylguaiacol	C ₉ H ₁₂ O ₂	11.24	<D.L.-0.13	<D.L.
Ethylguaiacol	C ₉ H ₁₂ O ₂	11.41	<D.L.-0.18	<D.L.
Syringol	C ₈ H ₁₀ O ₃	12.13	<D.L.-3.10	<D.L.-0.42
Methylsyringol	C ₉ H ₁₂ O ₃	12.22	<D.L.-1.28	<D.L.-0.17
<u>Biomarkers alcohol compounds</u>				
Galactosan	C ₆ H ₁₀ O ₅	14.13	<D.L.-2.74	<D.L.
isomer monosacarde	C ₆ H ₁₀ O ₅	14.27	1.64-2.01	<D.L.-5.28
Mannosan	C ₆ H ₁₀ O ₅	14.39	<D.L.-0.91	<D.L.
Levogluosan*	C ₆ H ₁₀ O ₅	14.62	3.65-68.64	<D.L.-42.52
β-sitosterol*	C ₂₉ H ₅₀ O	36.31	<D.L.-0.04	<D.L.

rt: time retention, <D.L.: Bellow the detection limit

* Compounds proposed as particle tracers for cellulose in biomass burning (Simoneit et al., 1999).

Table A3. Volatile Organic Compounds Emitted in Ayoraburning experiments. (part 1)

	rt (min)	Mr	Range $\mu\text{g m}^{-3}$	Range EF (mg kg^{-1} dry mater)		rt (min)	Mr	Range $\mu\text{g m}^{-3}$	Range EF (mg kg^{-1} dry mater)
Alkanes					Aldehydes				
Octane	5.12	114	2.17-4.36	2.86-3.47	4-oxo-2-pentanal	12.57	98	4.53-7.89	2.97-12.60
Nonane	8.01	128	1.77-4.83	2.84-3.17	Acetaldehyde	5.58	44	144.86-294.65	193.31-231.48
Decane	11.19	142	2.67-8.33	4.27-5.46	Acrolein	6.55	56	6.66-24.29	10.64-15.94
Undecane	14.27	156	3.21-8.68	5.13-5.70	Benzaldehyde	9.69	106	18.56-84.69	29.66-55.56
Dodecane	17.20	170	4.86-11.92	7.76-7.82	Butendial	11.14	84	<D.L.-20.15	<D.L.-32.21
Tridecane	20.11	184	5.52-9.31	6.11-8.83	Crotonaldehyde	7.8	70	13.99-55.85	22.35-36.64
Total			20.2-47.43	28.71-34.45	Ethylglyoxal	11.64	86	5.18-21.20	8.27-13.91
Monocyclic and bicyclic arenes					Formaldehyde	4.58	30	107.00 -145.56	95.49-171.02
Toluene	4.31	92	10.89-20.78	13.63-17.40	Glutaraldehyde	11.87	100	1.15-2.87	0.75-4.58
Ethyl-Benzene	6.81	106	4.19-7.31	4.80-6.70	Glycolaldehyde	1.94	60	20.70-50.14	32.89-33.08
m+p Xylenes	7.06	106	7.63-15.89	10.42-12.20	Glyoxal	10.66	58	64.94-99.16	42.60-158.48
Styrene	7.70	104	10.15-16.11	10.57-16.22	Heptanal	11.6	114	0.82-3.19	1.31-2.09
o-Xylene	7.76	106	2.80-6.53	4.28-4.47	Hexanal	10.86	100	2.38-3.20	1.56-5.11
Cumene	8.77	120	0.43-0.67	0.44-0.69	Metacrolein	8.2	70	<D.L.-1.83	<D.L.-2.92
n-propyl-Benzene	9.69	120	1.51-3.80	2.42-2.50	Methylglyoxal	11.47	72	88.21-91.38	57.87-146.04
m+p ethyl-Toluene	9.96	120	3.56-9.69	5.69-6.36	Nonanal	12.41	142	2.19-4.07	2.67-3.50
Mesitylene	10.14	120	3.84-4.59	3.01-6.14	Octanal	12.01	128	0.37-1.34	0.58-0.88
Pseudocumene	10.93	120	2.65-7.65	4.23-5.02	o-Tolualdehyde	10.89	120	1.95-14.23	3.11-9.34
Hemimellitene	11.81	120	2.08-5.51	3.33-3.62	Propionaldehyde	6.94	58	13.40-21.16	8.79-33.82
Naphthalene	16.66	128	12.77-22.22	14.58-20.41	Total			496.89-946.75	514.82-969.20
Total			62.50-120.75	77.40-101.73	Ketones				
Isoprenoids					2,3-butanedione	12.01	86	18.47-96.34	29.52-63.21
α -Pinene	9.03	136	16.34-26.19	10.72-41.85	Acetophenone	10.88	120	<D.L.-82.41	<D.L.-131.71
β -Pinene	10.37	136	0.56-3.02	0.37-4.83	Acetone	6.82	58	21.50-34.71	22.77-34.36
Limonene	12.03	136	9.87-27.39	15.77-17.97	Ciclohexanone	10.54	98	<D.L.-1.11	<D.L.-1.77
Total			26.77-56.60	26.86-64.65	Cyclopentanone	9.7	84	7.61-16.55	10.86-12.16
					Cyclobutanone	8	70	4.11-11.29	6.57-7.41
					Hexanone	10.99	100	<D.L.-11.44	<D.L.-7.51
					MEK	8.72	72	2.93-5.26	3.45-4.68
					Total			54.62-259.12	73.17-262.81

Table A3. Volatile Organic Compounds Emitted in Ayoraburning experiments. (part 2)

	tr (min)	Mr	Range $\mu\text{g m}^{-3}$	Range EF (mg kg^{-1} dry mater)		tr (min)	Mr	Range $\mu\text{g m}^{-3}$	Range EF (mg kg^{-1} dry mater)
Heptanol	8.46	116	40.66-377.19	64.99-1196.06	Glyoxylic acid	3.14	74	4.76-4.92	3.23-7.60
Catechol	10.3	110	4.90-31.08	7.83-93.46	Pyruvic acid	7.39	88	45.26-71.31	72.34-171.55
Decanol	10.92	158	147.40-1100.98	235.59-4755.18	Benzoic acid	9.12	122	<D.L.-10.79	<D.L.-17.24
Methylcatechol	11.26	124	3.63-11.02	5.81-37.35	Nonanoic acid	11.47	158	114.32-359.49	182.72-1552.63
Undecanol	11.37	172	99.72-232.81	159.39-1094.62	Glutaric acid	12.7	132	32.39-88.46	51.77-319.20
Syringol	11.59	154	9.32-22.90	14.89-96.40	Vanillic acid	15.19	168	7.83-13.09	12.51-60.11
Vinylguaiacol	12.05	150	4.19-18.26	6.70-74.87	Syringic acid	16.64	270	<D.L.-24.66	<D.L.-39.42
Ethylguaiacol	12.22	152	4.80-27.15	7.68-112.83	Palmitic acid	18.64	256	4.21-24.10	6.73-168.69
Propylguaiacol	12.33	166	4.99-27.21	7.98-123.49	Dehydroabietic acid	22.35	300	15.69-51.22	25.08-420.05
4-methylsyringol	12.6	168	7.53-17.30	12.03-79.47	Total			224.46-648.04	354.38-2756.49
Ethylsyringol	13.39	182	5.93-17.19	9.48-85.52					
Galactosan	14.65	162	72.77-113.10	116.31-500.85					
Mannosan	14.78	162	115.04-493.99	183.86-2187.59					
Levogluosan	15	162	795.94-1076.50	1272.14-4767.15					
Total			1316.82-3566.68	2104.68-15204.84					

rt: time retention ; Mr molecular mass; <D.L.: Bellow the detection limit