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Article

Characterization of PAHs Trapped in the Soot from the Combustion of Various Mediterranean Species

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Abstract: Climate change causes more frequent and destructive wildfires even transforming them into megafire. Moreover, all biomass fires produce emissions of carbon compounds in the form of soot to the atmosphere with a significant impact on the environment and human health. Indeed, the soot is causing the formation of PAHs from (a) the high temperature thermal alteration of natural product precursors in the source organic matter and (b) the recombination of molecular fragments in the smoke. However, these molecules are known to have carcinogenic effects on human health. It is therefore interesting to quantify the 16 PAHs concentration extracted from soot emitted in open diffusion flame of biomass combustion. To achieve this objective, an analytical method developed for the study of kerosene combustion has been adapted for soot from biomass. This new method allowed to quantify the 16 PAHs defined as priority pollutants by the US EPA for their carcinogenic mutagenic effect and on human health.

Keywords: soot; PAHs; health risk; wildfire



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1. Introduction

Climate change is increasing the risk of wildfires in temperate biomes, with more extreme landscape drying combined with extreme weather events leading to increased occurrence of destructive fires [1]. In European countries bordering the Mediterranean Basin, over 40,000 fires per year were reported between 2010 and 2016 [2]. The impact of Mediterranean wildfires involves several sectors entailing environmental, human, and economic losses.

Wildfires emit carbon dioxide and other greenhouse gases that will contribute to warm the planet well into the future. They damage forests that would otherwise remove CO₂ from the air and they inject soot and other aerosols into the atmosphere, with complex effects on warming and cooling. On a global scale, wildfires emit approximately 34% of total atmospheric soot mass [3] and the carbon released from fires during combustion alters the global carbon balance [4]. For example, black carbon strongly absorbs solar radiation and atmospheric particulate matter (PM) also acts as cloud condensation nuclei (CCN), which are important for the radiation balance and the hydrological cycle [5].

With the impact on the environment, the other worrying aspect related to wildfires is the adverse effect on health caused by the exposure to biomass combustion emission [6,7]. It is well known that wildfires can produce substantial increases in the concentration of gaseous pollutants such as carbon monoxide (CO), nitrogen oxides (NO_x), ozone (O₃), and volatile organic compounds (VOCs) [8–10] as well as particulate matter (PM) [11,12] and particular carbon nanoparticles, namely soot. Soot is an important component of very fine suspended dust, often referred to in the literature as elemental carbon (EC); alternative names are black carbon (BC) or black smoke. This waste of combustion process consists of compounds including amorphous carbon, graphite-like connections, fullerenes, ashes, and metal compounds. Epidemiological studies have shown that inhalation of soot particles can cause pulmonary disease, cardiovascular damage and mortality [12]. Despite

the cause and effect relationship, the mechanism(s) by which this occurs is yet unclear. One hypothesis is that these ultra-fine particles exert toxicity by generating reactive oxygen species, OH^* , in a reaction analogous to the Fenton reaction [13]. The reactivity of soot in radical formation processes could be highly dependent upon its nanostructure. Additionally, a possible explanation of the hazardous health effects of soot is their association with Polycyclic Aromatic Hydrocarbons (PAHs). Although detailed mechanisms are not well understood, PAHs formed in combustion processes are thought to be precursors of soot [14]. Among these PAHs, the International Agency for Research on Cancer (IARC) has determined the Benzo[a]pyrene as carcinogenic and Dibenzo[a,h]anthracene as probably carcinogenic to humans. The following PAHs: benz[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, and indeno[1,2,3-cd]pyrene are possibly carcinogenic to humans; while acenaphthene, fluorene, phenanthrene, anthracene, fluorethene, pyrene, and benzo[ghi]perylene are not classifiable as to their carcinogenicity to humans. This list is quite similar to the 16 priority PAHs listed by the Environmental Protection Agency of United States (US EPA). Acenaphthylene has not been classified for carcinogenic effects by the IARC or US EPA. Moreover, it has been observed that the total PAH content is higher for combustion particles from wood smoke as compared to vehicle exhaust [15].

Aware of the impact on the environment and the health of populations of the combustion of biomass, some authors have focused on the regulatory aspect in terms of health and safety at work. So, they are turned towards the domestic use of wood as a heating system [16] with experiments carried out in a combustion chamber under perfectly controlled conditions. Other authors have already identified and quantified PAHs emitted during forest fires. These previous papers dealing with the smoke emissions of prescribed fire plumes [17–20] are focused on particulate matters such as PM 2.5 or PM 10.

However, to our knowledge, no study has proposed to quantify the PAHs extracted from the soot obtained as close as possible to the flames. However, it seems important to us to get closer to the real working conditions of firefighters because they present a significant risk of inhalation of soot.

In this context, the objective of this study is to characterize the PAHs contained in the soot emitted in wildland fires conditions. To achieve this goal, laboratory experiments were carried out in order to be as close as possible to the source and to ensure a good collection of the soot. The samples studied were representative of the Mediterranean shrublands and it was characterized by the presence of the following dominant species: rockrose, rosemary, strawberry tree, lentisk, and pine. The 16 PAHs which are a priority for the US EPA based on concerns that they cause or might cause cancer in humans were quantified using a multi-step analytical method requiring extraction, purification, and quantification by HPLC of the target molecules.

2. Materials

2.1. Fuels

Plant material was collected from a natural Mediterranean ecosystem located at 450 m height above sea level and situated far away from urban areas (near the little town of Corte in Corsica) in order to prevent any pollution on the samples. The selected plants: rockrose (*Cistus monspeliensis*: CM), rosemary (*Rosmarinus officinalis*: RO), strawberry tree (*Arbutus unedo*: AU), lentisk (*Pistacia lentiscus*: PL), and pine (*Pinus pinaster*: PP) are representative species of the Mediterranean vegetation concerned with wildland fires. Aerial parts of each plant were collected at the beginning of April. For each species, a bulk sample from six individual plants was collected in order to minimize interspecies differences. Current year mature leaves were selected, excluding newly developed tissues at the top of the twigs. To characterize the fuels, elemental analysis was performed according to the standard EN ISO 16,948 and results are presented in Table 1.

Table 1. Elemental composition of the biomass fuels.

Specie	C (%)	H (%)	O (%)	N and Minerals (%)
Pinus Pinaster-PP	50.64	6.71	41.53	1.12
Arbutus Unedo-AU	48.24	6.15	40.33	5.28
Cistus Monspeliensis-CM	46.58	6.22	37.68	9.52
Pistacia Lentiscus-PL	51.43	6.35	38.69	3.53
Rosmarinus Officinalis-RO	50.73	6.64	40.81	1.82

2.2. Soot Production (Combustion Process)

Samples were previously dried in an oven at 60 °C for 24 h before experimental burning in order to get closer to summer conditions. Then, 20 g of plants were subjected to an external radiative heat flux and burned as open diffusion flame, under the hood, such as they are burned in the field. Using radiant panels, the fuels were submitted to a heat flux of 20 kW·m⁻² (843 K), selected to be in the temperature range producing soot. The soot produced, including PAHs, was collected on a stainless steel grid of 0.5 mm diameter holes placed inside an aspiration hood. The size of the pores of the grid has been determined to collect a maximum of soot [21]. After sample collection, the soot was weighted using an analytical balance with a resolution of 0.01 mg, and placed in borosilicate glass test tubes and stored at 4 °C until analysis. Three events of combustion were carried out for each of the five biomass fuels in the same experimental conditions.

2.3. PAHs

PAHs are ubiquitous pollutants, comprising hundreds of lipophilic compounds with fused aromatic rings. They may have natural or anthropogenic origins, existing in many commonly used goods. In the pyrolysis phase of the combustion process, PAHs compounds are formed by complex mechanisms involving cyclization and aromatization of carbonaceous matter at temperatures typically higher than 673 K [22,23]. The United States Environmental Protection Agency (US EPA) listed 16 PAHs compounds as priority pollutants for environmental risk assessment due to their toxic effects [24]. Table 2 presents the US EPA 16 PAHs list and the acronyms used in this work. PAHs can be divided into two classes: Low Molecular Weight PAHs (LPAHs) with two and three benzenoid rings (Nap, Acy, Ace, Flu, Phe, and Ant), and High Molecular Weight PAHs (HPAHs) with four or more benzenoid rings (Flt, Pyr, BaA, Chry, BbF, BkF, BaP, DahA, BghiP, and IcdP).

Table 2. List of Polycyclic Aromatic Hydrocarbons (PAHs), carcinogenicity classification, and toxicity factors.

	Compound	Abbreviation	Number Rings	IARC ^a [25]	RPF US-EPA ^b [26]	TEF N&L ^c [27]
LPAHs	Naphtalene	Nap	2	2B	-	0.001
	Acenaphtylene	Acy	3	-	-	0.001
	Acenaphtene	Ace	3	3	-	0.001
	Fluorene	Flu	3	3	-	0.001
	Phenanthrene	Phe	3	3	-	0.001
	Anthracene	Ant	3	3	-	0.01
HPAHs	Fluoranthene	Flt	4	3	-	0.001
	Pyrene	Pyr	4	3	-	0.001
	Benzo[a]anthracene	BaA	4	2B	0.1	0.1
	Chrysene	Chry	4	2B	0.001	0.01
	Benzo[b]fluoranthene	BbF	5	2B	0.1	0.1
	Benzo[k]fluoranthene	BkF	5	2B	0.01	0.1
	Benzo[a]pyrene	BaP	5	1	1	1
	Dibenzo[a,h]anthracene	DahA	5	2A	1	5
	Benzo[ghi]perylene	BghiP	6	3	-	0.01
	Indeno[1,2,3-cd]pyrene	IcdP	6	2B	0.1	0.1

Notes: ^a IARC classification: 1-Carcinogenic, 2 A-Probably carcinogenic, 2B-Possibly carcinogenic, 3-Not classifiable as carcinogenicity,

^b Relative Potency Factors for Carcinogenic Polycyclic Aromatic Hydrocarbons of the US EPA, ^c Toxic Equivalent Factor.

The International Agency for Research on Cancer (IARC) classifies PAHs into different categories, according to carcinogenic potency (Table 1); BaP is classified in group 1—Carcinogenic to humans, and the others are 2 A and 2 B. For almost 30 years, correlations of PAHs toxicities with the most toxic BaP have been pursued [26,27]. The US EPA Provisional Guidance for Quantitative Risk Assessment of Polycyclic Aromatic Hydrocarbons (EPA/600/R-93/089, July 1993), recommends that Relative Potency Factors (RPF) be used to convert concentrations of carcinogenic PAHs to an equivalent concentration of benzo[a]pyrene when assessing the cancer risks posed by these substances from oral exposures [26]. Nisbet and Lagoy (N&L) proposed to consider a Toxic Equivalent Factor (TEF) presented in Table 2 [27]. While the US EPA considers DahA as carcinogenic as BaP, Nisbet and Lagoy attributed a factor of five to DahA, for its carcinogenicity proved to be higher than BaP in low doses. Other equivalence systems are used worldwide and still no consensus exists. However, in the EU also [28] the priority is given to these 16 PAHs, this is the reason this study is focused on these 16 compounds.

3. Analytical Method

3.1. Ultrasonic Extraction

For PAH extraction from soot samples, an ultrasound bath was used. Various solvents such as dichloromethane, acetone, and acetonitrile were tested. Dichloromethane and acetone require the use of an ice bath to condense the emitted vapors. So, acetonitrile was selected for its higher boiling temperature which prevents any loss of the lightest PAHs (i.e., naphthalene, acenaphthylene, acenaphthene). The time of extraction was 30 min with the use of 20 mL of acetonitrile as extraction solvent. Then, 0.45 µm filters (Acrodisc[®], Merck KGaA, Darmstadt, Germany) with glass syringes of 5 mL (Fortuna Optima[®], Poulten & Graf GmbH, Wertheim, Germany) were used for filtering soot samples before SPE extraction.

3.2. Solid Phase Extraction-SPE

One of the main difficulties of the clean-up step is the selection of the appropriate solid phase. To find the best adsorbent phase, we were guided by the literature and the work of Andrade et al. [29], who have worked on particularly sullied soot samples from the combustion of kerosene. The authors have shown that only silica-C18 is able to retain PAHs strongly enough to avoid losses during the clean-up procedure. On another hand, glass columns must be employed instead of polymer cartridges in order to avoid any interaction with acetonitrile. So silica-C18 bulk from Supelco was used for filling the clean-up glass columns. A vacuum manifold SPE 12-G from Baker allowed the conditioning of the SPE column and the elution of compounds.

3.2.1. Conditioning of the Cleaning Column

The column should be conditioned with an organic solvent with a polarity similar to that of the sample. This is a necessary step since the column, frit, and adsorbent may contain impurities that can interfere with the analysis, especially at low concentrations [30]. In addition, this process activates the octadecyl chains in the column which facilitates the retention of polarisable molecules (i.e., PAHs). The conditioning was carried out with 2 mL of acetonitrile and 2 mL of methanol.

3.2.2. Loading and Drying

In this step, 2 mL of sample were passed through the column by gravity. Then the drying is performed under a slight vacuum (900 mbar) for 30 min to avoid a loss of light PAHs. This step allows the use of solvents not miscible with acetonitrile or methanol, such as hexane, in the next elution step. Furthermore, this process facilitates the elution of the analytes of interest.

3.2.3. Elution of PAHs

As a result of multiple tests, we found that the best results were obtained using hexane as the elution solvent as its toxicity is lower than that of other possible organic solvents, such as toluene. The elution was carried out under vacuum (600 mbar) with 4 mL of hexane.

3.3. High Pressure Liquid Chromatography—HPLC

Chromatographic experiments were performed by using an HPLC system Flexar from Perkin Elmer®. The instrument integrates a UV/Vis photodiode array detector and a spectrofluorimetric detector. A pre-column SUPELCO LC-18 (5 µm, 200 mm length × 4 mm ID, Supelco, Bellefonte, PA, USA) was positioned before the analytical column a SUPELCOSIL LC-PAH (5 µm, 250 mm length × 4.6 mm ID, Supelco, Bellefonte, PA, USA). Acetonitrile and water were used as eluent components at a flow rate of 1 mL/min. The program started with 60% acetonitrile for 10 min. Linear gradient elution from 60% to 100% acetonitrile during 30 min was applied, followed by isocratic elution with acetonitrile for 12 min to rinse the column. To remove possible contaminants left behind, each run was concluded with a conditioning step (60% Acetonitrile/40%water) for 3 min. Then, 20 µL of the eluates were injected onto the column, utilizing the sample injector. The oven temperature was maintained at 30 °C throughout the analysis. The fluorescence excitation and emission wavelengths were changed during the chromatographic separation to have the highest fluorescence intensity. The programmed wavelengths were determined using an important concentrate standard of 16 PAHs at 10 ppm to estimate the retention time of each PAH. Using these preliminary results, the wavelengths settings were determined and presented in Appendix A. For the quantification, a mixture of 16 PAHs at 10 µg/mL of each component in acetonitrile (Supelco, Bellefonte, PA, USA) from Sigma Aldrich was used for preparing standards by dilution. Components in the mixture were: acenaphthene, acenaphthylene, anthracene, benz(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(ghi)perylene, benzo(a)pyrene, chrysene, dibenzo(ah)anthracene, fluoranthene, fluorene, indeno(1,2,3-cd)pyrene, naphthalene, phenanthrene, and pyrene. The calibration range was carried out using five known standards with concentrations between 5 to 50 ppb. Limits of detection (LOD) were calculated using a signal-to-noise ratio of 3 are shown in Table 3.

Table 3. Detection limits, linear range, and calibration of the quantification of PAHs.

Compound	LOD (µg/mL)	Calibration Curves	Correlation Coefficient R ²
Naphtalene	0.056	58.920x + 6.5 × 10 ³	0.9918
Acenaphthylene	0.078	1648x − 1.6 × 10 ¹	0.9999
Acenaphthene	0.090	46.566x + 4.6 × 10 ²	0.9980
Fluorene	0.149	565.075x + 5 × 10 ⁶	0.9832
Phenanthrene	0.087	247.308x + 5.5 × 10 ¹	0.9960
Anthracene	0.101	378.993x + 9.8 × 10 ²	0.9929
Fluoranthene	0.078	104.600x + 3.5 × 10 ²	0.9933
Pyrene	0.083	402.918x + 1 × 10 ⁶	0.9965
Benzo[a]anthracene	0.075	331.175x + 1 × 10 ⁶	0.9927
Chrysene	0.041	477.291x + 2 × 10 ⁶	0.9932
Benzo[b]fluoranthene	0.063	168.046x + 9.5 × 10 ²	0.9950
Benzo[k]fluoranthene	0.056	918.249x + 4 × 10 ⁶	0.9981
Benzo[a]pyrene	0.045	403.282x + 1 × 10 ⁶	0.9963
Dibenzo[a,h]anthracene	0.073	259.042x + 8.6 × 10 ²	0.9959
Benzo[ghi]perylene	0.049	254.493x + 5.4 × 10 ²	0.9948
Indeno[1,2,3-cd]pyrene	0.088	59.974x − 9.3 × 10 ¹	0.9870

For the whole procedure of extraction and analysis, standard deviations within the range of 3–7% were measured. To give a whole overview of the analytical method, Figure 1 summarizes the main experimental conditions of the four steps.

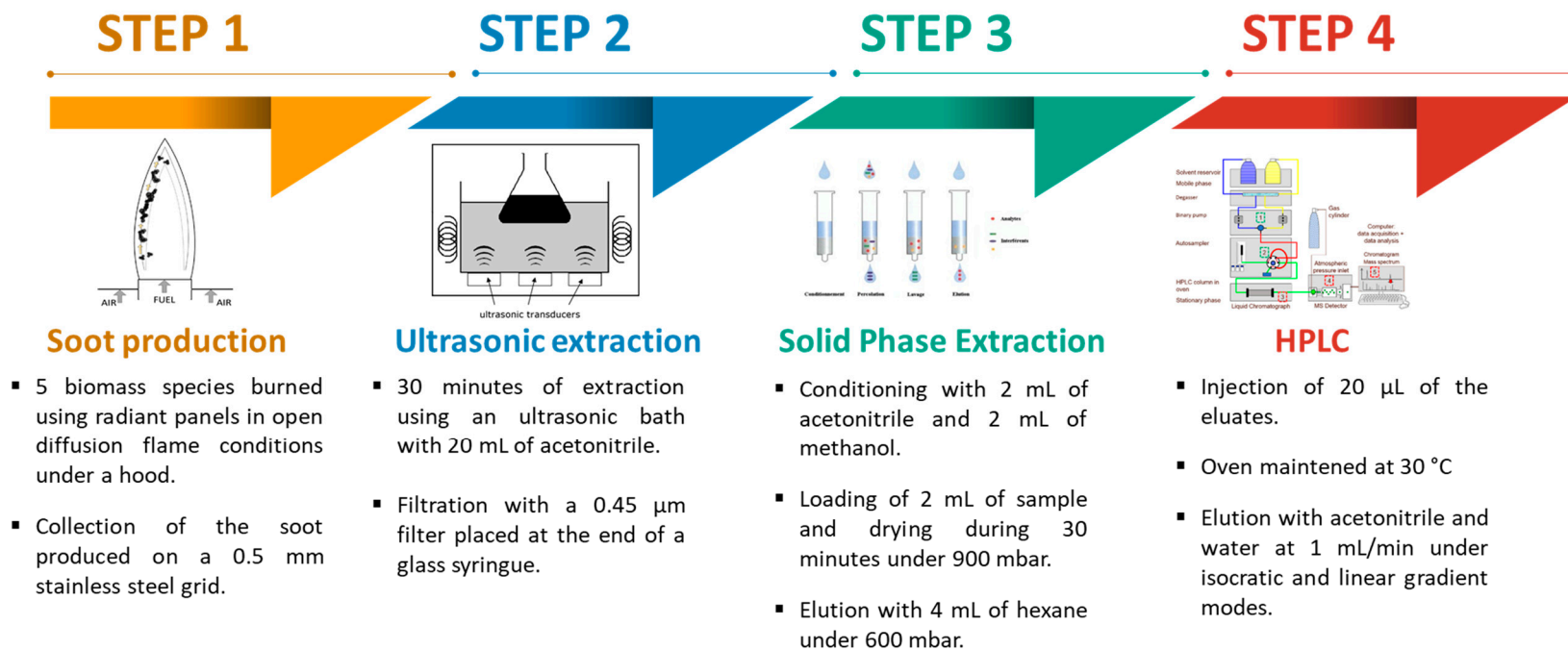


Figure 1. Overview of the analytical method.

4. Results

4.1. Soot and PAH Production

For the first time, the rate of production of soot of each fuel was estimated and compared to the rate of production of all the PAHs in order to quantify the rate of PAHs trapped in the soot. Figure 2 presents the rate of soot and PAH production of the five biomass fuels.

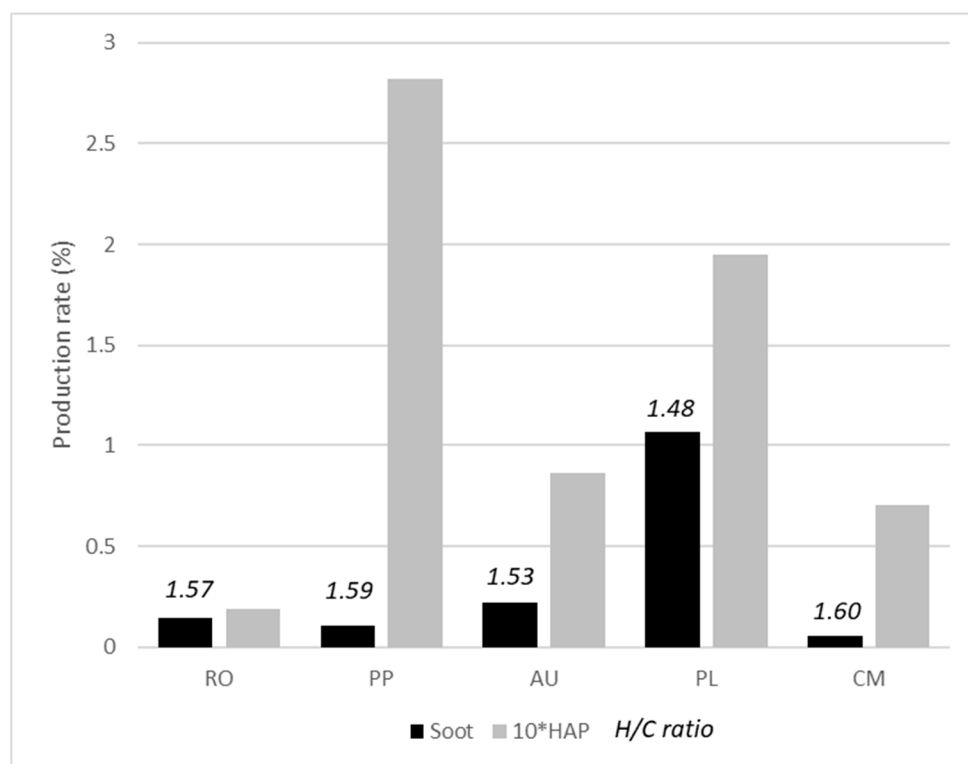


Figure 2. Rate of production of soot and PAHs compared to the H/C ratio.

Figure 1 highlights that the *Pistacias Lentiscus* is the species that produces the most significant amount of soot with more than 1% of its dry mass. On the other hand is the *Pinus Pinaster*, although emitting small quantities of soot, it contains higher amounts of PAHs than the *Pistacias Lentiscus*. For *Rosmarinus officinalis*, 74% of its soot contains the 16 PAHs; whereas for *Pinus Pinaster*, the total amount of the PAHs only represents 4% of the soot. There appears to be no correlation between the amount of soot produced and the content of PAHs trapped inside. In addition, the molar H/C ratio was calculated in order to correlate the soot production with the combustion process. As expected, the higher the ratio, the better the combustion and, therefore, the soot production is lower. The identification and abundances of the 16 PAHs of interest extracted from the various biomass soots are given in Table 4.

The biomass soot was dominated by low molecular weight. For all species, the major PAH are acenaphthylene, acenaphthene, and phenanthrene followed by benzo[a]anthracene, chrysene and pyrene in lesser amounts. It is important to note that benzo[a]anthracene which exhibits mutagenic and genotoxic potential is present in significant quantities. The formation mechanisms of PAHs during the combustion of biofuels are not fully understood, but fluorene and phenanthrene are the most abundant PAHs from cellulose pyrolysis [22], which explains the high phenanthrene fractions of the particle phase PAHs observed in this study. Oros and Simoneit [31] also found a large amount of phenanthrene when studying samples from burning pine. Alvès et al. [19] reported a significant concentration of phenanthrene and pyrene when they analyzed PAH content in particulate matters emitted during prescribed wildfires. The same predominant compounds have been found by Lee

et al. [32] when they quantified PAHs in organic carbon extracted from particles obtained from prescribed burning. Nevertheless, the concentrations are less important probably due to the collection of particles being carried out a few meters from the burning site. Looking at a similar study performed with boilers, Szatylowcz and Skoczko [16] found a total production of the 16 PAHs of 230.44 mg/kg (equivalent to ng/mg) for mixed firewood, whereas 285.75 ng/mg were found for *Pinus Pinaster*, the more productive species. Thus, even under different experimental conditions, the rate of PAHs trapped in soot are in the same range. In order to appreciate the variability of the PAH composition according to the different plant species, Figure 3 represents the percentage of PAHs according to the number of rings for each biomass fuel.

Table 4. Concentration of PAHs in biomass soot (ng/mg of soot).

Compound	Biomass Fuel				
	RO	PP	AU	PL	CM
Naphtalene	0.39	9.81	2.53	0.81	14.76
Acenaphtylene	3.93	62.34	20.07	6.39	41.89
Acenaphtene	1.39	15.60	4.81	5.26	19.52
Fluorene	0.47	3.49	1.04	0.36	1.91
Phenanthrene	3.11	70.74	4.19	1.88	7.32
Anthracene	0.75	15.72	0.30	0.22	1.14
Fluoranthene	0.96	18.35	1.65	0.98	1.29
Pyrene	0.89	16.73	1.33	0.76	1.18
Benzo[a]anthracene	0.15	33.22	2.40	2.03	17.07
Chrysene	0.90	16.01	2.57	0.13	6.83
Benzo[b]fluoranthene	0.33	6.27	0.11	0.07	3.46
Benzo[k]fluoranthene	0.20	2.90	0.04	0.08	1.70
Benzo[a]pyrene	0.40	8.51	0.03	0.07	5.19
Dibenzo[a,h]anthracene	0.17	0.93	0.00	0.06	1.17
Benzo[ghi]perylene	0.29	3.08	0.10	0.09	1.36
Indeno[1,2,3-cd]pyrene	0.00	2.04	0.00	0.02	1.21
Σ 16 PAHs	14.35	285.75	41.17	19.20	127.00
Σ LPAHs	10.04	177.71	32.95	14.92	86.53
Σ HPAHs	4.30	108.04	8.22	4.29	40.47

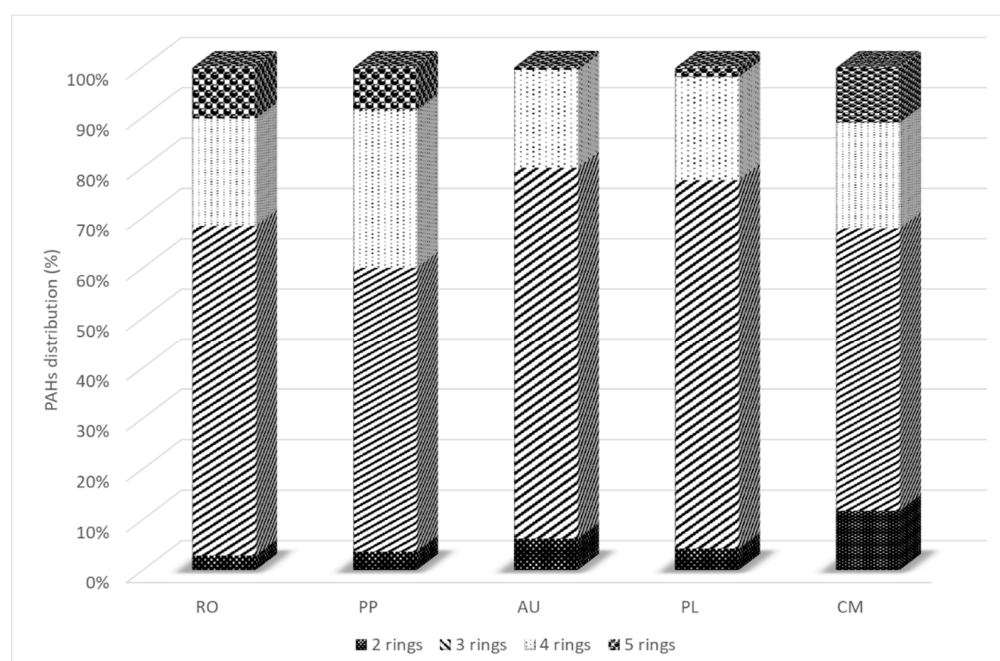


Figure 3. PAHs distribution for the 5 biomass fuels.

According to this graphic, one can note that the PAH composition is dominated by the three-ring PAHs. On the other hand, although the two rings only represent naphthalene, it is well-present compared to the five-ring group. In general, it would seem that the influence of interspecificity on the distribution of PAHs in the soot is less. Similar results have been found by Struppe et al. [33] when desorbing pyrolysis wood samples. They obtained a maximal concentration of two rings compared to the PAHs between 2 to 4 rings.

4.2. Diagnostic Ratios

PAHs in biomass burning emissions are generally the same as those from other anthropogenic combustion emissions. The diagnostic ratios for PAHs were used to investigate PAH origin in the atmosphere [19,34]. The ratios of phenanthrene to phenanthrene plus anthracene (Phe/(Phe + Ant)), fluoranthene to fluoranthene plus pyrene (Flu/(Flu + Pyr)), indeno[1,2,3-cd]pyrene to indeno[1,2,3-cd]pyrene plus benzo[ghi]perylene (IcdP/(IcdP + BghiP)), and benzo[b]fluoranthene plus benzo[k]fluoranthene to benzo[ghi]perylene (BFs/BghiP) were calculated, listed in Table 5, and compared with other sources.

Table 5. PAHs diagnostic ratios for different biomass fuels.

Diagnostic Ratio	Biomass Fuel					Average
	RO	PP	AU	PL	CM	
Flu/(Flu + Pyr)	0.52	0.52	0.55	0.56	0.52	0.53
Phe/(Phe + Ant)	0.80	0.82	0.93	0.77	0.68	0.80
IcdP/(IcdP + BghiP)	-	0.40	-	-	0.43	-
BFs/BghiP	1.81	2.97	1.50	3.13	2.92	2.47

The ratio of Phe/(Phe + Ant) ranges from 0.68 to 0.82 in agreement with other works on shrubs [20,34,35] except for AU, which presents a very high ratio of 0.93 as also found by Vicente when studying particulate matters emitted from wildfires [36]. The Flu/(Flu + Pyr) ratios exhibit an average of 0.53 in the same way as other studies on wood combustion [19,34,35]. For IcdP/(IcdP + BghiP) for some fuels, this ratio could not be estimated due to the absence of indeno[1,2,3-cd]pyrene. This is the reason why the average was not calculated. In the other case, the results present a ratio of around 0.4 specific to lignite combustion emissions [35]. The ratio BFs/BghiP varies from species to species but the same diversity of results has been reported by Vicente et al.

5. Conclusions

Polycyclic Aromatic Hydrocarbons (PAHs) are associated with health hazardous effects, and wildfires are major sources of their presence in atmospheric aerosols and especially in soot. This work reports on the chemical characterization of PAHs trapped in the soot released by five biomass species under diffusion flame combustion. An analytical method developed for kerosene pool fire was adapted to biomass soot emission. This method includes three steps: ultrasonic extraction, solid phase extraction, and HPLC quantification with reproducible results. When quantifying the 16 PAHs present in biomass soot, an important variability of concentrations was observed depending on the species ranging from 285.75 ng/mg of soot for *Pinus Pinaster* to 14.35 ng/mg for *Rosmarinus Officinalis*. Even if the concentrations are very disparate, it appears that PAHs with three rings contributed largely to the total concentration of the 16 PAHs. Various diagnostic ratios have been determined and compared with those of similar studies looking at the toxicological impact of wildfires. The obtained results are in agreement with these previous ones. After this chemical characterization of PAHs, it would be interesting to carry out further investigations to evaluate the health risk for firefighters.

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Conflicts of Interest: The authors declare no conflict of interest.

Appendix A. Wavelengths Programm

Time (min)	$\lambda_{\text{excitation}}$ (nm)	$\lambda_{\text{emission}}$ (nm)
0	280	330
28	250	310
29.5	254	370
33.4	280	450
34.8	240	390
38	265	385
42	395	422
44.2	295	422
51.5	300	500

References

- Jia, G.; Shevliakova, E.; Artaxo, P.; De Noblet-Ducoudré, N.; Houghton, R.; House, J.; Kitajima, K.; Lennard, C.; Popp, A.; Sirin, A.; et al. Land-Climate Interactions. In *Climate Change and Land: An IPCC Special Report on Climate Change, Desertification, Land Degradation, Sustainable Land Management, Food Security, and Greenhouse Gas Fluxes in Terrestrial Ecosystems*; IPCC: Geneva, Switzerland, 2019; pp. 131–247.
- European Commission. *Forest Fires—Sparkling Firesmart Policies in the EU*; European Union: Brussels, Belgium, 2018.
- Chakrabarty, R.K.; Beres, N.D.; Moosmüller, H.; China, S.; Mazzoleni, C.; Dubey, M.K.; Liu, L.; Mishchenko, M.I. Soot Superaggregates from Flaming Wildfires and Their Direct Radiative Forcing. *Sci. Rep.* **2014**, *4*, 5508. [[CrossRef](#)]
- Van der Werf, G.R.; Randerson, J.T.; Giglio, L.; Collatz, G.J.; Mu, M.; Kasibhatla, P.S.; Morton, D.C.; DeFries, R.S.; Jin, Y.; van Leeuwen, T.T. Global Fire Emissions and the Contribution of Deforestation, Savanna, Forest, Agricultural, and Peat Fires (1997–2009). *Atmos. Chem. Phys.* **2010**, *10*, 11707–11735. [[CrossRef](#)]
- Martins, J.V.; Artaxo, P.; Liousse, C.; Reid, J.S.; Hobbs, P.V.; Kaufman, Y.J. Effects of Black Carbon Content, Particle Size, and Mixing on Light Absorption by Aerosols from Biomass Burning in Brazil. *J. Geophys. Res.* **1998**, *103*, 32041–32050. [[CrossRef](#)]
- Reid, C.E.; Consideine, E.M.; Watson, G.L.; Telesca, D.; Pfister, G.G.; Jerrett, M. Associations between Respiratory Health and Ozone and Fine Particulate Matter during a Wildfire Event. *Environ. Int.* **2019**, *129*, 291–298. [[CrossRef](#)]
- Aguilera, R.; Corringham, T.; Gershunov, A.; Benmarhnia, T. Wildfire Smoke Impacts Respiratory Health More than Fine Particles from Other Sources: Observational Evidence from Southern California. *Nat. Commun.* **2021**, *12*, 1493. [[CrossRef](#)] [[PubMed](#)]
- Crutzen, P.J.; Heidt, L.E.; Krasnec, J.P.; Pollock, W.H.; Seiler, W. Biomass Burning as a Source of Atmospheric Gases CO, H₂, N₂O, NO, CH₃Cl and COS. *Nature* **1979**, *282*, 253–256. [[CrossRef](#)]
- Crutzen, P.J.; Andreae, M.O. Biomass Burning in the Tropics: Impact on Atmospheric Chemistry and Biogeochemical Cycles. *Science* **1990**, *250*, 1669–1678. [[CrossRef](#)]
- Phuleria, H.C. Air Quality Impacts of the October 2003 Southern California Wildfires. *J. Geophys. Res.* **2005**, *110*. [[CrossRef](#)]
- Dennis, A.; Fraser, M.; Anderson, S.; Allen, D. Air Pollutant Emissions Associated with Forest, Grassland, and Agricultural Burning in Texas. *Atmos. Environ.* **2002**, *36*, 3779–3792. [[CrossRef](#)]
- Lighty, J.S.; Veranth, J.M.; Sarofim, A.F. Combustion Aerosols: Factors Governing Their Size and Composition and Implications to Human Health. *J. Air Waste Manag. Assoc.* **2000**, *50*, 1565–1618. [[CrossRef](#)] [[PubMed](#)]
- Kennedy, I.M. The Health Effects of Combustion-Generated Aerosols. *Proc. Combust. Inst.* **2007**, *31*, 2757–2770. [[CrossRef](#)]
- Richter, H.; Howard, J.B. Formation of Polycyclic Aromatic Hydrocarbons and Their Growth to Soot—A Review of Chemical Reaction Pathways. *Prog. Energy Combust. Sci.* **2000**, *26*, 565–608. [[CrossRef](#)]
- Kocbach, A.; Li, Y.; Yttri, K.E.; Cassee, F.R.; Schwarze, P.E.; Namor, E. Physicochemical Characterisation of Combustion Particles from Vehicle Exhaust and Residential Wood Smoke. *Part. Fibre Toxicol.* **2006**, *3*, 1–10. [[CrossRef](#)]
- Szatylowicz, E.; Skoczko, I. Evaluation of the PAH Content in Soot from Solid Fuels Combustion in Low Power Boilers. *Energies* **2019**, *12*, 4254. [[CrossRef](#)]
- Alves, C.A.; Vicente, A.; Monteiro, C.; Gonçalves, C.; Evtyugina, M.; Pio, C. Emission of Trace Gases and Organic Components in Smoke Particles from a Wildfire in a Mixed-Evergreen Forest in Portugal. *Sci. Total Environ.* **2011**, *409*, 1466–1475. [[CrossRef](#)] [[PubMed](#)]

18. Miranda, A.I.; Ferreira, J.; Valente, J.; Santos, P.; Amorim, J.H.; Borrego, C. Smoke Measurements during Gestosa-2002 Experimental Field Fires. *Int. J. Wildland Fire* **2005**, *14*, 107–116. [[CrossRef](#)]
19. Alves, C.A.; Gonçalves, C.; Evtugina, M.; Pio, C.A.; Mirante, F.; Puxbaum, H. Particulate Organic Compounds Emitted from Experimental Wildland Fires in a Mediterranean Ecosystem. *Atmos. Environ.* **2010**, *44*, 2750–2759. [[CrossRef](#)]
20. Alves, C.A.; Gonçalves, C.; Pio, C.A.; Mirante, F.; Caseiro, A.; Tarelho, L.; Freitas, M.C.; Viegas, D.X. Smoke Emissions from Biomass Burning in a Mediterranean Shrubland. *Atmos. Environ.* **2010**, *44*, 3024–3033. [[CrossRef](#)]
21. Cachier, H.; Aulagnier, F.; Sarda, R.; Gautier, F.; Masclat, P.; Besombes, J.-L.; Marchand, N.; Despiou, S.; Croci, D.; Mallet, M.; et al. Aerosol Studies during the ESCOMPTE Experiment: An Overview. *Atmos. Res.* **2005**, *74*, 547–563. [[CrossRef](#)]
22. McGrath, T.E.; Chan, W.G.; Hajaligol, M.R. Low Temperature Mechanism for the Formation of Polycyclic Aromatic Hydrocarbons from the Pyrolysis of Cellulose. *J. Anal. Appl. Pyrolysis* **2003**, *66*, 51–70. [[CrossRef](#)]
23. Lima, A.L.C.; Farrington, J.W.; Reddy, C.M. Combustion-Derived Polycyclic Aromatic Hydrocarbons in the Environment—A Review. *Environ. Forensics* **2005**, *6*, 109–131. [[CrossRef](#)]
24. United States Environmental Protection Agency. *Guidelines for Carcinogen Risk Assessment*; United States Environmental Protection Agency: Washington, DC, USA, 2005; p. 166.
25. International Agency for Research on Cancer. *Agents Classified by the IARC Monographs*; International Agency for Research on Cancer: Lyon, France; Volume 1–125, Available online: <https://monographs.iarc.who.int/agents-classified-by-the-iarc/> (accessed on 30 June 2021).
26. United States Environmental Protection Agency. *Provisional Guidance for Quantitative Risk Assessment of Polycyclic Aromatic Hydrocarbons*; United States Environmental Protection Agency: Washington, DC, USA, 1993; pp. 1–20.
27. Nisbet, I.C.T.; LaGoy, C.K. Toxic Equivalency Factors (TEFs) for Polycyclic Aromatic Hydrocarbons (PAHs). *Regul. Toxicol. Pharmacol.* **1992**, *16*, 290–300. [[CrossRef](#)]
28. Working Group on Polycyclic Aromatic Hydrocarbons. *Ambient Air Pollution by Polycyclic Aromatic Hydrocarbons (PAH)*; Office for Official Publications of the European Communities: Luxembourg, 2011; ISBN 92-894-2057-X.
29. Andrade-Eiroa, A.; Leroy, V.; Dagaut, P.; Bedjanian, Y. Determination of Polycyclic Aromatic Hydrocarbons in Kerosene and Bio-Kerosene Soot. *Chemosphere* **2010**, *78*, 1342–1349. [[CrossRef](#)]
30. Kiss, G.; Varga-Puchony, Z.; Hlavay, J. Determination of Polycyclic Aromatic Hydrocarbons in Precipitation Using Solid-Phase Extraction and Column Liquid Chromatography. *J. Chromatogr. A* **1996**, *725*, 261–272. [[CrossRef](#)]
31. Oros, D.R.; Simoneit, B.R.T. Identification and Emission Factors of Molecular Tracers in Organic Aerosols from Biomass Burning Part 1. Temperate Climate Conifers. *Appl. Geochem.* **2001**, *16*, 1513–1544. [[CrossRef](#)]
32. Lee, S.; Baumann, K.; Schauer, J.J.; Sheesley, R.J.; Naeher, L.P.; Meinardi, S.; Blake, D.R.; Edgerton, E.S.; Russell, A.G.; Clements, M. Gaseous and Particulate Emissions from Prescribed Burning in Georgia. *Environ. Sci. Technol.* **2005**, *39*, 9049–9056. [[CrossRef](#)] [[PubMed](#)]
33. Struppe, H.G.; Franke, F.; Hofmann, J.; Ondruschka, B. Coupling of Thermal Desorption in Modified Closeable Sampling Columns with Wide-Bore Capillary Gas Chromatography and Mass Spectrometric Detection. *J. Chromatogr. A* **1996**, *750*, 239–244. [[CrossRef](#)]
34. Wang, Z.; Bi, X.; Sheng, G.; Fu, J. Characterization of Organic Compounds and Molecular Tracers from Biomass Burning Smoke in South China I: Broad-Leaf Trees and Shrubs. *Atmos. Environ.* **2009**, *43*, 3096–3102. [[CrossRef](#)]
35. Mara dos Santos Barbosa, J.; Ré-Poppi, N.; Santiago-Silva, M. Polycyclic Aromatic Hydrocarbons from Wood Pyrolysis in Charcoal Production Furnaces. *Environ. Res.* **2006**, *101*, 304–311. [[CrossRef](#)]
36. Vicente, A.; Alves, C.; Monteiro, C.; Nunes, T.; Mirante, F.; Cerqueira, M.; Calvo, A.; Pio, C. Organic Speciation of Aerosols from Wildfires in Central Portugal during Summer 2009. *Atmos. Environ.* **2012**, *57*, 186–196. [[CrossRef](#)]