Atmospheric Research 316 (2025) 107954

Contents lists available at ScienceDirect

Atmospheric Research

journal homepage: www.elsevier.com/locate/atmosres

Particulate-bound PAHs, nitro and oxy-PAHs from small scale boilers fueled with non-woody biomass

Esperanza Monedero [a,*], Rocío Collado [a], Florentina Villanueva [b,c], Elena Borjabad [d], Raquel Ramos [d], Juan José Hernandez [a,e]

[a] Instituto de Investigación en Energías Renovables, Universidad de Castilla-La Mancha, C/ Investigación s/n, 02006 Albacete, Spain
[b] Instituto de Investigación en Combustión y Contaminación Atmosférica, Universidad de Castilla La Mancha, Camino de Moledores s/n, 13071 Ciudad Real, Spain
[c] Escuela de Ingeniería Industrial y Aeroespacial de Toledo, Avenida Carlos III s/n, 45071 Toledo, Spain
[d] CEDER-CIEMAT, Autovía A-15, salida 56, 42290 Lubia, Soria, Spain
[e] Escuela Técnica Superior de Ingeniería Industrial, Universidad de Castilla La-Mancha, Avda. Camilo José Cela s/n, 13071 Ciudad Real, Spain.

ARTICLE INFO

Keywords:
PAHs
Biomass combustion
Domestic boiler
Non-woody biomass
Particulate matter

ABSTRACT

Polycyclic Aromatic Hydrocarbons (PAHs) and their derivatives (oxy-PAHs and nitro-PAHs) are released during the biomass combustion process, both in the exhaust gas and bound to the particulate matter (PM). The composition of PAHs, including the number of carbon atoms and their molecular weight, is directly related to their toxicity. The aim of this work was to determine the PM-bound emission of the 16 EPA priority PAHs and some of their nitrated and oxygenated derivatives from the combustion of exhausted olive cake (EOC) and almond shell (AS) in a domestic boiler at two loads, nominal (55 kW) and partial (24 kW). In addition, pine pellet (P) was investigated as a reference fuel. Total PAHs emissions ranged from 1.7 to 8.4 μg/kg and from 5.7 to 357.8 μg/kg at nominal and partial load, respectively. While AS was the most PAHs-forming fuel at nominal load, EOC caused the highest emission at low load. The influence of the boiler load was quite relevant regarding the molecular weight of PAHs bound to PM. At nominal load, EOC and AS were dominated by low molecular weight compounds (LMW) and high molecular weight compounds (HHW), respectively, while at partial load medium molecular weight (MMW) PAHs gained importance for AS (59 %) and EOC PM were clearly dominated by high molecular weight PAHs (99 %). The higher unburned matter at partial load led to higher oxy and nitro-PAHs concentrations for the three biomass fuels, being in all cases 3 to 4 orders of magnitude lower than their derivative PAHs. EOC at partial load presented the highest value of KE_{sum} and therefore its use in a modular boiler is less recommended from the health risk point of view.

1. Introduction

Polycyclic Aromatic Hydrocarbons (PAHs) are a group of organic compounds with multiple fused aromatic rings. Due to their toxicological properties, high stability and hydrophobicity, PAHs are of significant environmental concern (Eisler, 2000; Lundstedt et al., 2007). The United States Environmental Protection Agency (EPA) has included sixteen basic PAHs in a priority pollutants list, because their serious threats to the environment and biota (USEPA, 2016). The composition of PAHs, including the number of carbon atoms and their molecular weight, is directly associated to their toxicity. Regarding their classification, PAHs can be divided into three categories based on their molecular weight: low molecular weight (LMW-PAHS), containing 2–3 rings, medium molecular weight PAHs (MMW-PAHs), with 4 rings, and high molecular weight PAHs (HMW-PAHs), containing 5–7 rings. As the molecular weight increases, their hydrophobicity also increases, while their water solubility and vapor pressure decreases, making the compound more recalcitrant. Additionally, the higher the molecular weight, the smaller the Henry's law constant, while the octanol-water partition coefficient (K_{ow}) increases. Consequently, LMW-PAHs tend to volatilize while HMW-PAHs are mainly adsorbed onto solid particles (Jelic et al., 2015). According to Juhasz and Naidu (2000), the presence of HMW-PAHs, such as benzo[*a*]pyrene, is particularly concerning due to their carcinogenic potential, whereas LMW compounds, such as naphthalene, are the most acutely toxic PAHs. Additionally, nitrated, and oxygenated PAHs derivatives (nitro-PAHs and oxy-PAHs, respectively) are

* Corresponding author.
E-mail address: Esperanza.Monedero@uclm.es (E. Monedero).

https://doi.org/10.1016/j.atmosres.2025.107954
Received 16 October 2024; Received in revised form 14 January 2025; Accepted 25 January 2025
Available online 29 January 2025

considered to be hazardous to human health due to their mutagenic, teratogenic and carcinogenic properties (IARC, 2012). These compounds have lower vapor pressure and higher molecular weight than their derivative PAHs, and also a higher tendency to be adsorbed onto particulate matter (PM) (Vione et al., 2004; Goldfarb and Suuberg, 2008). Several studies have shown that the concentration of some nitro-PAHs and oxy-PAH in PM is lower than that of their derivative-PAHs, but their toxicity is up to 10,000 times higher (Eiguren-Fernandez et al., 2004; Lewtas and Nishioka, 1990; Lundstedt et al., 2007; Zhang et al., 2021a, 2022. Therefore, studies about the sources of polycyclic aromatic hydrocarbons and their derivatives are necessary to reduce the air pollution and the related health risks.

Solid fuels combustion is recognized as a significant source of particles (Tissari et al., 2009; González et al., 2004). These particles contain several types of organic compounds adsorbed on them, such as aliphatic hydrocarbons, aromatic hydrocarbons, carbonyls, and PAHs (as well as their nitrated and oxygenated derivatives, nitro-PAHs and oxy-PAHs), as reported by Zhang et al. when comparing different types of coal and biomass (Zhang et al., 2021a, 2021b). PAHs are formed through complex chemical reactions during combustion. The primary formation route involves the pyrolysis and subsequent reaction of organic compounds present in the biomass feedstock (Zdeněk et al., 2016). PAHs can be released at high combustion temperatures in the gas phase, deposited and/or adsorbed in fly ash or bound to particles as the temperature decreases. Inefficient combustion results in high unburnt carbon and elevated levels of PAHs in the ash or in PM (Masto et al., 2015). PAH derivatives are emitted directly (anthropogenic emission) together with their derivative PAHs, but they are also formed as secondary pollutants by heterogeneous or homogeneous photo-oxidation reactions of PAHs with atmospheric oxidants, and the subsequent photolysis and thermal transformation (Atkinson and Arey, 2007; Walgraeve et al., 2010; Bandowe and Meusel, 2017). Despite the commented problems derived from PAHs emission, the literature on this topic is still very scarce and the existing literature is mainly focused on high-quality woody wastes and on the gas phase and ashes (Krugly et al., 2014; Lee et al., 2005; Masto et al., 2015).

PM concentration, as well as its composition, morphology and size distribution, depends on the biomass properties, combustion technology and operating conditions (Leskinen et al., 2014; Collado et al., 2024; Vicente et al., 2015). The same is true for PAHs (Jenkins et al., 1996; Ross et al., 2002). Krugly et al. (2014) reported that residues, such as rice straw and corn stover, tend to generate higher PAHs emission than woody biomass, with the two former producing 566 and 532 μg/kg, respectively, compared to 469 μg/kg for the latter. Lu et al. (2009) studied the total PAHs emissions from rice and bean straw, and they observed that the raw material moisture content has a negative effect on PAHs formation (especially on the low molecular weight compounds). They reported that, compared to dried straw, PAHs emission from burning wet bean straw (30 % moisture content) increased between 8.1 and 34.5 % for two-to three-ring PAHs, and between 34.8 and 54.1 % for five to six-ring PAHs, They also observed that an increase in the combustion temperature led to an increase of PAHs. Zhang et al., 2021c, studied the PAHs emission factor of six types of biomass (crops and wood residues) used in heated kangs (home-made brick stove which burns biomass for cooking). They obtained values in the range of 84.5–344 mg/kg with lower emission factor for biomass with greater densities (such as wood trunk). Furthermore, operating conditions such as temperature, residence time, burning rates and oxygen availability also play an important role in the PAHs emission (Johansson et al., 2004; Lamberg et al., 2011; Orasche et al., 2012). An oxygen deficient atmosphere or an increase in the combustion temperature during the combustion leads to higher PAHs formation (Lu et al., 2009; Shen et al., 2013). Leskinen et al. (2014) observed a higher PAHs amount when the combustion efficiency was lower, although they also observed that the proportion of genotoxic PAHs was higher under efficient combustion conditions.

The main objective of this work has been to analyze the emission of PM-bound PAHs from the combustion of two non-woody residues (exhausted olive cake and almond shell) in a 55-kW domestic boiler at two loads, nominal (55 kW) and partial (24 kW). The sixteen US EPA compounds and their nitrated and oxygenated derivatives have been investigated. This type of waste has a high potential as fuel for thermal applications in the southwest European countries, as previously reported by Collado et al. (2022, 2024). Although the increasingly restrictive emissions standards for small-scale biomass boilers does not consider the PM composition but the total mass, the results of this work could be used to assess environmental and human health implications related to the PM emitted when using sustainable fuels such as industrial wastes (much more eco-friendly than the widely used pine pellets).

2. Materials and method

2.1. PM sampling

Particulate matter was obtained from the combustion of two non-woody biomass, exhausted olive cake (EOC) and almond shell (AS), at two boiler loads (nominal, 55 kW, and partial, 24 kW). Pine pellets (P) were also tested as a reference and usual woody fuel. Table 1 summarizes the main properties of the fuels. As observed, and also reported in (Collado et al., 2022, 2024), the ash content of EOC was significantly higher than that of AS and pine, while AS showed the highest moisture content. A full description of the combustion installation can be found elsewhere (Serrano et al., 2013; Collado et al., 2024). Moreover, the results regarding the optimal boiler operating conditions (primary/secondary air ratio, air excess, etc.) for each fuel, as well as the corresponding performance (efficiency) and regulated emissions (CO, NOx and particles total mass) have been previously described in Collado et al. (2022). For a better understanding of the results derived from this work (PAHs determination), Table 2 shows the main findings previously obtained (Collado et al., 2022). In that table, T_{ff} is the fireplace fume temperature, which greatly affects the PAHs concentration and composition. Particulate matter was collected in quartz filters for 30 min periods according to UNE-EN 16510-1 (UNE-EN 16510-1, 2023). More

Table 1
Elemental composition (dry basis), ash, bulk density and moisture content of the fuels (wt%).

	Pine pellets (P)	Almond shells (AS)	Exhausted olive cake (EOC)	Standard
Moisture (wt%, wet basis)	8.2	13.4	8.4	ISO 18134-2
Bulk density (wt%, wet basis)	647	406	616	ISO 15103
Proximate analysis (wt%, dry basis)				
Ash	0.4 ± 0.0	1.9 ± 0.1	9.0 ± 0.4	ISO 18122
Volatiles	84.2 ± 0.7	83.4 ± 4.3	81.0 ± 4.3	ISO 18123
Fixed carbon	14.9 ± 0.7	14.7 ± 4.2	10.2 ± 3.4	By difference
Elemental composition (wt%, dry basis)				
C	50.8 ± 0.2	51.5 ± 0.3	50.7 ± 0.2	ISO 16948
H	6.0 ± 0.6	5.2 ± 0.1	5.4 ± 0.1	ISO 16948
N	0.1 ± 0.0	0.7 ± 0.2	1.3 ± 0.1	ISO 16948
S	0.0 ± 0.0	0.0 ± 0.0	0.2 ± 0.0	ISO 16994
Cl	0.0 ± 0.0	0.0 ± 0.0	0.3 ± 0.0	ISO 16994
Higher heating value, HHV (MJ/kg, dry basis)	20.5 ± 0.3	19.8 ± 0.1	20.5 ± 0.1	ISO 18125
Lower heating value, LHV (MJ/kg, dry basis)	19.1 ± 0.2	18.8 ± 0.0	19.3 ± 0.1	ISO 18125

Table 2
Results from the combustion tests.

	55 kW			24 kW		
	P	EOC	AS	P	EOC	AS
$\dot{m}_{biomass\ fueled}$ (kg/h)	8.7 ± 1.2	6.5 ± 1.1	10.3 ± 1.1	4.2 ± 0.1	3.3 ± 0.1	4.5 ± 0.1
PM (mg/Nm^3)	40.8 ± 2.1	2097.9 ± 221.2	481.8 ± 34.9	158.8 ± 20.2	733.1 ± 93.8	315.0 ± 6.4
Unburned matter in PM (C-containing compounds, wt,%)	47.6 ± 0.5	27.3 ± 0.6	45.0 ± 0.6	76.9 ± 0.6	49.3 ± 0.5	38.5 ± 0.6
CO (mg/Nm^3)	363.2 ± 377.9	5422.1 ± 1973.2	3962.9 ± 724.3	538.9 ± 125.1	17,367.2 ± 2833.2	5239.9 ± 1031.7
NOx (mg/Nm^3)	97.6 ± 8.3	419.9 ± 75.9	291.8 ± 26.6	98.5 ± 11.3	284.9 ± 59.9	185.3 ± 18.4
T_{ff} (°C)	660.9 ± 27.4	706.6 ± 57.8	540.4 ± 29.9	499.7 ± 44.0	493.1 ± 112.9	439.1 ± 33.6

detailed information about the PM filter sampling system and boiler operating conditions is available in the supplementary material document.

2.2. Reagents and materials used for GC–MS analysis

This section provides information on the reagents and materials used for the PAHs analysis by GC–MS (described in Section 2.3). A Certified Reference Material (CRM) comprising a mixture of 18 native Polycyclic Aromatic Hydrocarbons (PAHs) dissolved in a benzene/methylene chloride solution at a concentration of 2000 μg mL^{-1} was used for calibration and quality assurance/quality control (Section 2.4). This solution included naphthalene, 2-methylnaphthalene, 1-methylnaphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(*a*)anthracene, chrysene, benzo(*b*)fluoranthene, benzo(*k*)fluoranthene, benzo(*a*)pyrene, indeno (1,2,3-cd)pyrene, dibenzo (a,h)anthracene, and benzo (g,h,i)perylene. An internal standard (IS) PAH solution containing six deuterated PAHs at 2000 μg mL^{-1} in methylene chloride (1,4-dichlorobenzene-d_4, naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12} and perylene-d_{12}) was also prepared. Both native and deuterated PAHs were supplied by Supelco®. The recovery standard solution at 100 μg mL^{-1} in isooctane/toluene included fluorene-d_{10} and terphenyl-d_{14} and was supplied by Wellington Laboratories Inc. Individual certified standard oxy-PAHs (9-fluorenone, 9,10-anthraquinone, benzanthrone, benzo(*a*)anthracene-7,12-dione, 1000 μg mL^{-1} in toluene, perinaphthenone, 200 μg mL^{-1} in toluene, anthrone, benzo(*a*)fluorenone, 10 mg) and nitro-PAHs (9-nitroanthracene, 1-nitropyrene (1NP), 2-nitrofluoranthene and 3-nitrofluoranthene, 100 μg mL^{-1} in toluene) were supplied by CHIRON. Individual solutions of internal standards (IS) for oxy-PAHs (9-fluorenone-d_8 and 9,10-anthraquinone-d_8, 100 μg mL^{-1} in toluene) and nitro-PAHs (9-nitroanthracene-d_9, 3-nitrofluoranthene-d_9, 1000 μg mL^{-1} and 1-nitropyrene-d_9, 100 μg mL^{-1} in toluene) were also supplied by CHIRON.

Organic solvents like isooctane, n-hexane, and dichloromethane (of GC grade), as well as acetone, methanol, were sourced from Lab Scan. A cleaning process involving soapy water, tap water rinse, ultrapure water (from a Milli-Q system, Millipore), methanol, acetone, and dichloromethane was employed for the glassware and microwave vessels before their use.

2.3. Methodology for the GC–MS/MS analysis

For the analysis of particles-bound PAHs, nitro-PAHs and oxy-PAHs, the quartz filters were cut in quarters and each quarter was inserted into an individual Teflon extraction vessel to ensure accurate measurement. The results presented represent the average of the compound concentration determined in at least three of these filter quarter. PAHs, nitro-PAHs and oxy-PAHs were extracted with 40 mL of dichloromethane by using a microwave digestor (Ethos 1, Milestone) operating at a power of 900 W. The temperature profile consisted of a heating ramp up to 120 °C for 40 min followed by an isothermal period for 30 min following the procedure described in Lara et al. (2022, 2023).

Before extraction, the quartz filters were spiked with 100 ng of deuterated PAHs and 200 ng of deuterated oxy-PAH and nitro-PAH internal standards. The extracted samples were filtered through a PTFE membrane filter (0.45 μm), then concentrated to about 1 mL in a rotating evaporator (Hei-VAP, Heidolph) at room temperature and, finally, to a few microliters by using a gentle nitrogen stream in a concentrator (Techne, FSC400D, Dri-block DB200/3). After solvent evaporation, the solvent was changed to hexane. Prior to analysis, the different extracts were spiked with 100 ng of the deuterated recovery standards (RS).

PAHs, nitro-PAHs and oxy- PAHs were quantified by means of a gas chromatograph coupled to a triple quadrupole mass spectrometer, (GC–MS/MS, Shimadzu TQ-8030). The GC was equipped with an SLBtm-5 ms capillary column (30 m × 0.25 mm × 0.25 μ m, Supelco) and an autosampler. The quadrupole mass spectrometer was operated under electron impact ionization (EI) at 70 eV. The acquisition mode chosen for mass spectrometry analysis was MRM mode (multiple reaction monitoring). Details of the chromatographic working conditions and optimization of the MRM method for the analysis of PAH and their derivatives can be found elsewhere (Villanueva et al., 2018; Lara et al., 2022).

2.4. Quality control and quality assurance

Standard concentrations of 20, 50, 100, 200, and 400 ng/mL for each PAH and their derivatives were prepared for the calibration of the GC–MS/MS. The internal standards were set at a concentration of 100 ng/mL for PAHs, 200 ng/mL for oxy-PAH and nitro-PAH and 100 ng/mL for the recovery standards. Linearity was assessed by calculating the coefficient of determination (R^2). In our study, response factors were utilized for the quantification. Further details of the procedure are available in Lara et al. (2022).

The method's precision is usually determined by the relative standard deviation (RSD) from measuring five filter blanks spiked with known quantities of PAHs and derivatives. Five filters spiked with 100 ng and another five with 200 ng of the polycyclic compounds. The filters are subsequently extracted and analyzed in accordance with the protocol established for samples. The coefficients of variation of these repeated standards were within 12 % except for anthrone that was 23 %. The same filters utilized to determine precision are also used to assess accuracy, which is calculated in terms of recovery. The average recoveries of each polycyclic aromatic compound ranged from 77 % to 130 % for the filters spiked with 100 ng and from 84 % and 147 % for the filters spiked with 200 ng, except anthrone that was 37 %.

In addition, the precision and accuracy of the analytical method have also been assessed with the standard reference materials SRM 1649b "urban dust" and SRM 1650b "diesel particulate matter" (Lara et al., 2022, 2023). Generally, good recoveries were obtained (52–134 %), except 1-methylnaphthalene (< 50 %) and benzanthrone (248 %). There is no available standard reference material on the market for the samples being analyzed in this study.

For the calculation of PAHs and their derivatives concentrations, blank filters were analyzed simultaneously in the batches of their respective filter samples and the corresponding blank concentrations were subtracted from the masses of polyaromatic compounds. Finally,

the limits of detection (LOD) and quantification (LOQ) for the method were calculated as three and ten-fold the standard deviation of five blank samples spiked with the internal standard (100 ng for PAHs and 200 ng for oxy-PAHs and nitro-PAHs). For compounds with zero blank values, the LOD and LOQ were calculated as three and ten-fold the standard deviation of the lowest concentration of the analytical standards. These blank samples were processed, preserved, and analyzed using the identical protocol applied to the field samples. Since the biomass fueled (in kilograms) varies depending on the type of biomass and load, LOD and LOQ have been independently determined for each specific condition. The LOD ranged from 0.02 and 0.05 (acenaphthene) to 2.7 and 5.6 (2-methylnaphthalene) ng/kg for pine pellets at nominal and partial load, respectively, from 0.03 and 0.04 (acenaphthene) to 3.6 and 4.6 (2-methylnaphthalene) ng/kg for exhausted olive cake pellets at nominal and partial load, respectively, and from 0.02 and 0.05 (acenaphthene) to 2.2 and 5.2 (2-methylnaphthalene) ng/kg for almond shells at nominal and partial load, respectively, whereas the LOQ ranged from 0.14 and 0.28 (acenaphthene) to 26.9 and 56.2 (2-methylnaphthalene) ng/kg for pine pellets at nominal and partial load, respectively, from 0.18 and 0.23 (acenaphthene) to 36.1 and 46.8 (2-methylnaphthalene) ng/kg for exhausted olive cake pellets at nominal and partial load, respectively, and from 0.11 and 0.26 (acenaphthene) to 22.2 and 52.7 (2-methylnaphthalene) ng/kg for almond shells at nominal and partial load, respectively.

2.5. Emission factors and health risk assessment

Emission factors, defined as mass of PAHs bound to PM per kilogram of dry fuel, are used as representative to compare with previous results from other studies, PM concentration being normalized to a 10 % oxygen content attending to the standard UNE-EN 303-5 (UNE-EN 303-5, 2022). Since the heating value and the boiler efficiency are quite similar for the fuels tested, conclusions will be also similar when referred to energy basis (mg/kJ). EFs (μg/kg) are calculated following Eq. (1):

$$EF = \frac{Ci \times \dot{Q}_g}{\dot{m}_f} \quad (1)$$

where, C_i is the concentration of PAHs normalized to 10 % of O2 (μg m^{-3}), $\dot{Q}_g$is the dry flue gas volume flow rate at standard conditions (m^3 h^{-1}), $\dot{m}_f$is the dry fuel consumption (kg/h).

As previously stated, polycyclic aromatic hydrocarbons (PAHs) and their derivatives are carcinogenic. To assess the potential health risk of the PAHs found in PM from the different biomass fuel, the carcinogenic equivalent (KE_{sum}) was calculated. Consequently, the individual concentrations of PAH and their derivatives bound to PM in each sample (denoted as C_i, in μg/kg) are multiplied by either the potency equivalency factor (PEF) established by the Office of Environmental Health Hazard Assessment (OEHHA, 2015) or the toxicity equivalent factor (TEF) established by Nisbet and LaGoy (1992) (as shown in Eq. (2)). This calculation allows us to determine the distinct toxicity indices for each PAH (Lara et al., 2023).

$$KE_{sum} = \sum_i (C_i x\ PEF_i) \text{ or } KE_{sum} = \sum_i (C_i x\ TEF_i) \quad (2)$$

3. Results

3.1. PAHs concentration and composition

The total PAHs (∑PAHs) represent the sum of the sixteen compounds considered by the US Environmental Protection Agency (EPA). Fig. 1 shows the total PAHs concentration coming from P, EOC and AS. Values ranged between 1.7 and 8.4 μg/kg and between 5.7 and 357.8 μg/kg at nominal and partial load, respectively, were measured. While almond shell was the most PAHs-forming fuel at nominal load, exhausted olive cake caused the highest emission at low load, the contribution of the former under this latter condition being the lower. Compared to earlier studies, the values obtained for pine in the current work (1.8 and 136.7 μg/kg, at nominal and partial load, respectively) were slightly lower. Krugly et al. (2014) reported total PAHs emission of 51.1 μg/kg from the combustion of wood in a 13 kw domestic boiler at nominal load, while Lee et al. (2005) when burning hardwood in an open fire reported values around 9 μg/kg (also at nominal load). The existing literature on particles-bound PAHs emitted by non-woody biomass is really scarce, mainly when using industrial wastes as those employed in this study. This aspect difficult comparison of the results obtained, although they are in agreement with those reported by Krugly et al. (2014) for agricultural residues (straw, corn and sunflower stalks). As described in Collado et al. (2022), a lower PM emission with EOC and AS (with a significant ash content) at low load was caused by the lower air flow rate and the corresponding entrainment of particles in the flue

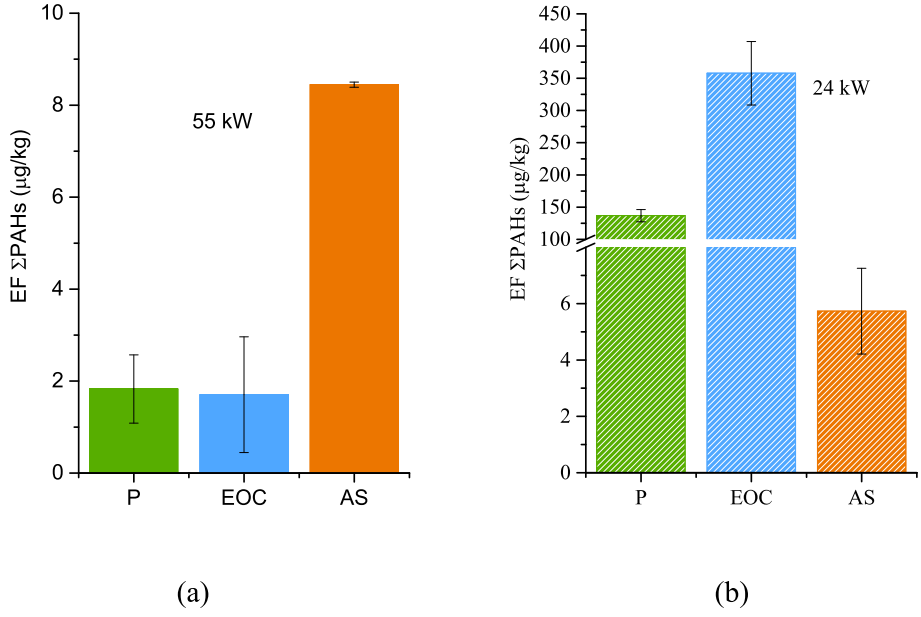

Fig. 1. Emission factors of particle bounds ∑PAHs during combustion of P, EOC and AS at nominal load (a) and partial load (b).

gas. However, the relative contribution of inorganic matter and soot (where PAHs are adsorbed) to PM was different for EOC and AS, the latter being dominated by fly ash and the former by C-containing compounds (Table 2). The insignificant content of ash in pine pellets caused the mentioned phenomena (ejection of particles with the flue gas) to be less significant when compared to the combustion detriment derived from a lower bed temperature, thus leading to an increase in PM (mainly composed by soot) for pine at low load. Attending to the previous statements, regarding the type of biomass and the boiler load, a considerable increase in the ∑PAHs content for pine and EOC at partial load was observed (which increases from 1.8 to 136.7 μg/kg and from 1.7 to 357.8 μg/kg for pine and EOC, respectively), while AS exhibited a significant decrease (from 8.4 to 5.7 μg/kg). The lower fireplace temperature with AS could also contribute to this reduction since part of the PAHs could keep retained on the bottom ash.

The ∑PAHs was divided into three groups according to their molecular weight (low, medium and high): LMW-PAHs (2–3 rings: Naphthalene, 2-methylnaphthalene, 1-methylnaphthalene, Acenaphtylene, Acenaphthene, Fluorene, Phenanthrene and Anthracene), MMW-PAHs (4–5 rings: Fluoranthene, Pyrene, Benzo(*a*)anthracene and Chrysene) and HMW-PAHs (6–7 rings: Benzo(*b*)fluoranthene, Benzo(*k*)fluoranthene, Benzo(*a*)pyrene, Indeno (1,2,3-cd)pyrene, Dibenz(*ah*)anthracene, Benzo(*ghi*)perylene). Fig. 2 shows the concentration of these compounds for the different fuels and loads. At nominal load, PM emitted from EOC was dominated by LMW compounds. In contrast, although the contribution of these lighter PAHs was important (34 %), MMW PAHs (65 %) were more abundant for pine and HHW compounds for AS (99 %). Sing et al. (2013) also revealed the predominance of 3–4 ring PAHs from wood emissions. The influence of the boiler load was quite relevant. In fact, MMW-PAHs gained importance for pine and AS (74 and 58 %, respectively), followed by LMW-PAHs (26 % and 42 %, respectively) at partial load. This was due to the deterioration of the combustion process. Particulate bound PAHs from EOC at partial load was clearly dominated by HMW-PAHs (99 %). It is worth noting that HMW PAHs, including the presence of Benzo(*a*)pyrene (the most concerning PAH due to its carcinogenic and mutagenic potential), were observed with EOC at partial load and AS at nominal load. The very significant ash content of EOC (worsening the local oxygen availability) together with the lower bed temperature at partial load (Table 2, also leading to more soot and adsorbed hydrocarbons in the emitted particles), probably inhibits the formation of PAHs precursors (acetylene, ethylene) via the HACA mechanism (Wang et al., 2023). In contrast, other generation routes based on RSR (resonance-stabilized hydrocarbon-radical chain reaction) by radical-chain reactions leading to 5–6 rings PAHs are promoted (Wang et al., 2023). The results obtained for EOC were consistent with the results reported by Sing et al. (2013) for fuels with high ash content. In the case of AS at nominal load, not only the effect of the load on the bed temperature as well as on PM emission is less significant (Table 2) than in EOC test, but also its ash content is much lower. This latter aspect makes the relative concentration of soot and unburnt C-containing compounds bounded to PM (which also included ashes ejected with the flue gas) higher than that of EOC at partial load. As reported in a previous work (Collado et al., 2024), this concentration was more important for AS at nominal load because of the lower optimum primary/secondary air ratio. This greater supply of secondary air (above the bed) could maybe promote the further oxidation of the low and medium molecular weight PAHs although being less efficient regarding HMW compounds (maybe adsorbed in the particle phase prior to the supply of the commented secondary air flow).

The emission factors of the individual 16 US EPA PAHs for each biomass and load are shown in Fig. 3. In general, there was significant variations in the individual PAHs emission among fuels and loads. At nominal load, chrysene and pyrene were the most abundant for pine particles, followed by 2-methylnaphthalene and 1-methylnaphthalene. Although with a minor concentration, fluoranthene, phenanthrene, benzo(*a*)anthracene and naphthalene were also present. Similar PAHs distribution was previously determined in woody biomass (Masto et al., 2015; Krugly et al., 2014). However, non-woody biomass displayed different distribution. For EOC, 2-methylnaphthalene and 1-methylnaphthalene were the most abundant while benzo(*ghi*)perylene, indeno(1,2,3-*cd*)pyrene, and dibenz(*ah*)anthracene, benzo(*b*)fluoranthene and benzo(*a*)pyrene were detected for AS (the latter with a high carcinogenic potential (Heldeberg et al., 2002). At partial load, pyrene, phenanthrene, chrysene and benzo(*a*)anthracene were the most abundant PAHs for pine. Differences between EOC and AS were also evident at 24 kW. While AS was dominated by MMW and LMW compounds, such as chrysene (2.6 μg/kg) and naphthalene (2.06 μg/kg), HMW-PAHs, such as benzo(*ghi*)perylene, indeno(1,2,3-*cd*)pyrene, dibenz(*ah*)anthracene, followed by benzo(*b*)fluoranthene, chrysene, benzo(*a*)pyrene, benzo(*a*)anthracene, benzo(*k*)fluoranthene and pyrene, were the most significant for EOC. As explained in the next section, the individual distribution of the PAHs is related to its toxicity.

3.2. Nitro-PAHs and oxy-PAHs concentration and composition

Oxy-PAHs are formed through complex reactions between PAHs and reactive oxygen species (oxidative degradation) and NOx (nitration) (Alves et al., 2016). Particulate matter formed during the combustion process is continuously exposed to the flue gases containing both compounds. Fig. 4 shows the total PM-bound oxy-PAHs emission from the combustion of the three fuels at both loads.

In general, a much higher oxy-PAHs concentration was obtained at partial load. This was due to the higher unburned matter (and thus higher C content) at this load, which favored the PAHs adsorption (see Table 2) and their oxidation to oxy-PAHs. As indicated by Alves et al.

Fig. 2. Ratios of PAHs with different rings to total PAHs at nominal (left) and partial load (right). The ring from inside to outside represents PAHs from pine, EOC and AS, respectively.

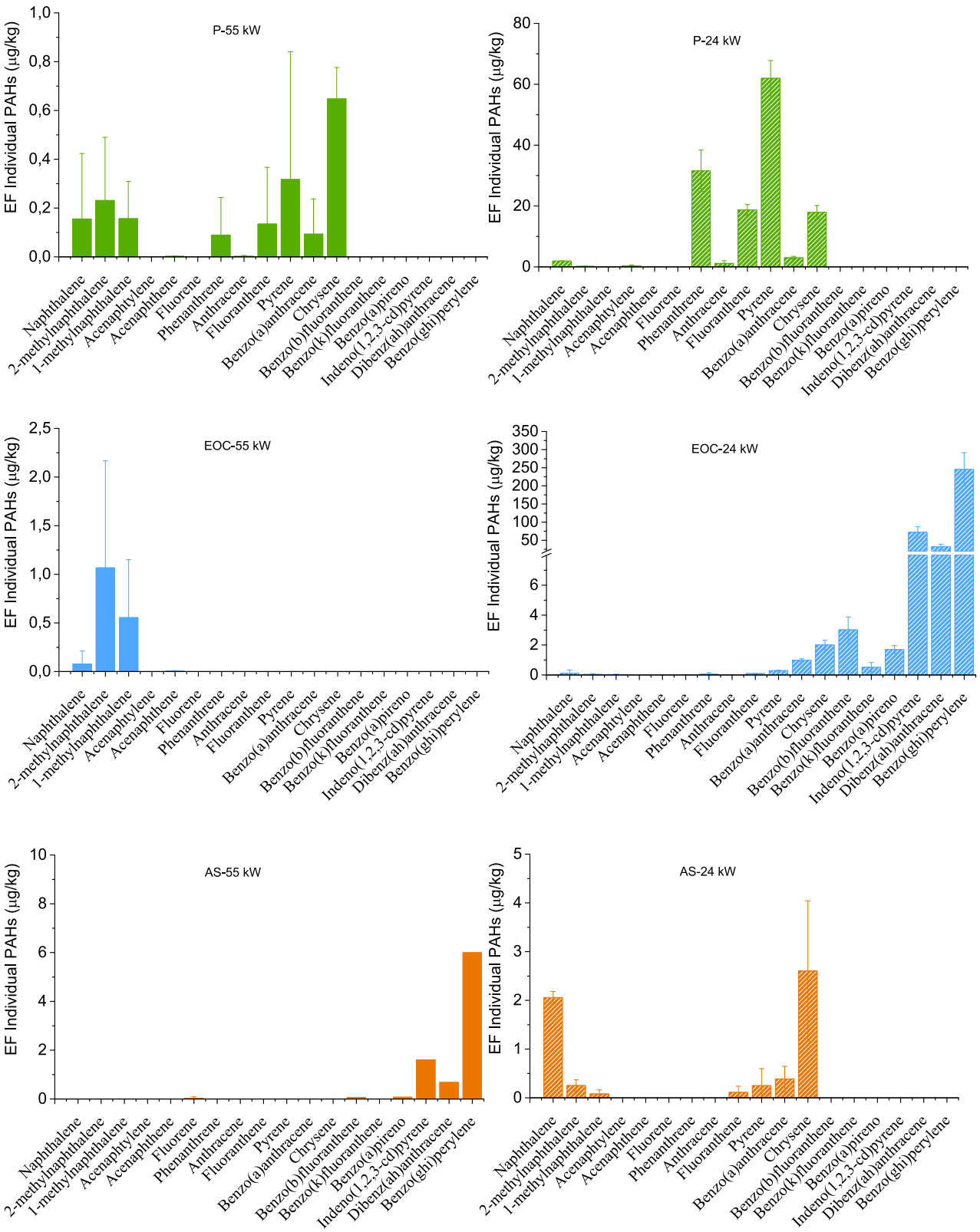

Fig. 3. Individual particulate phase PAHs emission factor profiles from combustion of P, EOC and AS at nominal (55 kW) and partial load (24 kW). No value has been assigned for those PAHs for which the determined concentration is below of the detection limit or has been non detected.

(2016), oxy-PAHs are mainly found in small size particles because of the enhanced reactivity associated to a higher surface/volume ratio. Therefore, the higher content of coarse particles (fly ash) for EOC and AS (Collado et al., 2023) resulted in a lower oxy-PAHs content when compared to pine (the latter producing mainly particles below 0.1 µm (Collado et al., 2023).

Regarding the levels of oxy-PAHs depending on the type of biomass used, while no significant differences in the oxy-PAHs distribution have

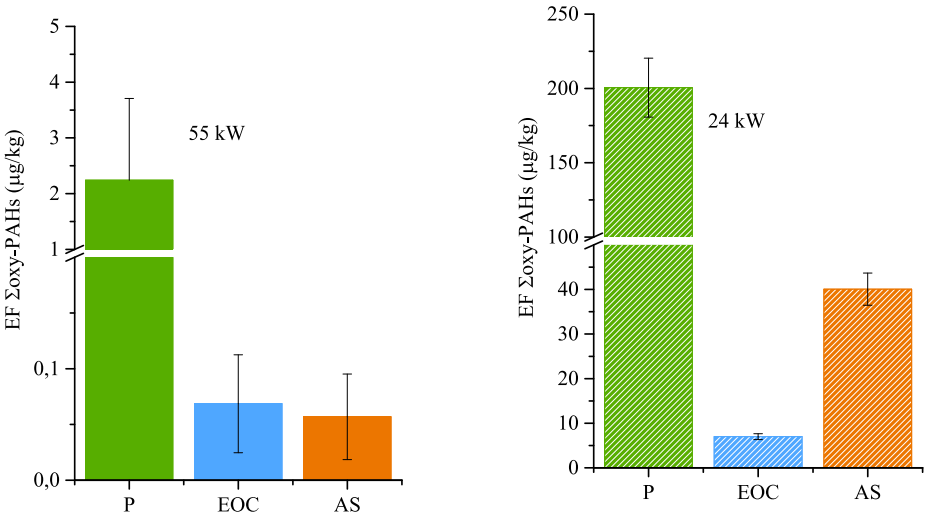

Fig. 4. Emission factors of PM-bound oxy-PAHs from P, EOC and AS at nominal and partial load.

been obtained for EOC and AS, pine led to a more significant concentration of LMW compounds. The very low PM emission of pine (because of its non significant ash content) led to a higher combustion efficiency and thus to also higher local temperatures inside the bed. These conditions could promote the formation of OH radical which favours the oxidation of the PAHs formed, which as shown in Fig. 2, are mainly composed of LMW and MMW PAHs. Among oxy-PAHs (Fig. 5), 9-fluorenone, perinaphthenone and benzanthrone, followed by 9,10-anthraquinone, benzanthraquinone and benzo(*a*)fluorenone, were the most representative compounds for pine PM at nominal load, encompassing 35 %, 19 %, 17 %, 11 %, 11 % and 6 %, respectively. The corresponding concentrations were, on average, 0.8, 0.4, 0.4, 0.3, 0.2 and 0.1 μg/Kg. Although with a higher concentration, a similar distribution was observed at partial load (107.7, 60.7, 6.4, 23.2, 0.99 and 1.29 μg/Kg, respectively). However, the effect of the load was very noticeable for AS and EOC. In fact, nominal load led to HMW compounds (mainly benzanthrone and benzo(*a*)fluorenone 54 % and 29 % for EOC and 90 % and 10 % for AS, and also 17 % benzanthraquinone only for EOC) whereas partial load also promoted LMW oxy-PAHs, (20 % and 15 % of fluorenone and perinaphtenone for EOC, and 9 % and 39 %, respectively, for AS). Nevertheless, and as previously commented, the concentration of oxy-PAHs for EOC and AS was very low compared to those of pine.

Regarding nitro-PAHs, these compounds are formed from gas-phase reactions of derivative PAHs with NOx and heterogeneous reactions of particle-bound PAHs by electrophilic nitration mechanism (Dimashki et al., 2000; Feilberg et al., 2001). Table 3 shows the results obtained for these compounds only at low load, since no nitro-PAHs emissions were detected at nominal load for any biomass. The higher fireplace temperatures at nominal load could inhibit nitro-PAHs condensation/adsorption on the particles surface (see Table 2). At partial load, the high concentration of pyrene in pine (Fig. 3) promoted the formation of 1-nitropyrene (10.23 μg/kg), while 2-nitrofluoranthene were the most significant nitro-PAHs for EOC (1.23 μg/kg).

3.3. Health risk assessment

Table 4 shows the results of the KE_{sum} calculation. The KE_{sum} followed the same trend as the emission factors. Regardless of using the Nisbet and LaGoy TEFs or OEHHA PEFs, at partial load, the KE_{sum} was higher for EOC (43.61 and 85.86 μg/kg, respectively), due to the worse combustion behavior and the higher unburned matter in the particulate matter, followed by pine (0.60 and 1.50 μg/kg, respectively). In the case of AS, it showed higher KE_{sum} (0.97 and 1.86 μg/kg, respectively) at nominal load, in accordance with the EF, being attributed to the presence of Dibenz(*ah*)anthracene and Benzo(*a*)pyrene with PEFs 2.4 and 1, respectively. It is worth noting that EOC at partial load had a very high value of KE_{sum}, due to the high content of HMW PAHs, especially Dibenz(*ah*)anthracene. Use of OEHHA PEFs results in higher KE_{sum} in those biomass fuels with higher contribution of HMW PAHs, especially Dibenz(*ah*)anthracene with a PEF value much higher than the Nisbet and Lagoy TEF value (2.4 vs. 1).

4. Conclusions

In this work, the PM-bound emission of 16 EPA priority PAHs and some of their nitrated and oxygenated derivatives from the combustion of non-woody biomass (exhausted olive cake and almons shell) has been determined and compared with those from pine (the most widely used biomass for small scale thermal applications). The main conclusion can be summarized as follows:

- The total PAH content significantly depends on the type of biomass and the boiler load. In general, the PAHs level at low load (24 kW) was much higher than at nominal load (55 kW). Regarding the fuel, while the average emission for almond shells was the highest at nominal load (~8 av. μg/kg when compared to 2 av. μg/kg for pine and EOC), the corresponding value at low load was much lower (~6 av. μg/kg) than that of pine (137 av. μg/kg) and exhausted olive cake (358 av. μg/kg).
- There were significant variations in the individual PAHs emission among fuels and loads. In contrast to pine, where medium molecular weight compounds (chrysene and pyrene) were the most abundant PAHs both at nominal and partial load, LMW PAHs (2-methylnaphthalene) were the most relevant for EOC and HMW species (Indeno (1,2,3-cd) pyrene and Benzo(*ghi*)perylene) for AS at nominal load. However, at partial load, AS was dominated by medium and lower molecular weight compounds (chrysene and naphthalene), while higher molecular weight PAHs (benzo(*ghi*)perylene, indeno(1,2,3-*cd*)pyrene, dibenz(*ah*)anthracene) appeared with EOC.
- Oxy-PAHs emission was much lower for non-woody biomass than for pine, mainly under partial load conditions (~40, 7 and 200 av. μg/kg for AS, EOC and pine, respectively). No nitro-PAHs were measured for AS regardless of the load, as well as for pine and EOC at nominal load. At partial load, EOC showed a much lower emission (~1 av. μg/kg) than pine (~11 av. μg/kg), 1-nitropyrene being the most abundant for the latter (~10 av. μg/kg), and 2-nitrofluoranthene being the only nitro-PAH determined for EOC.

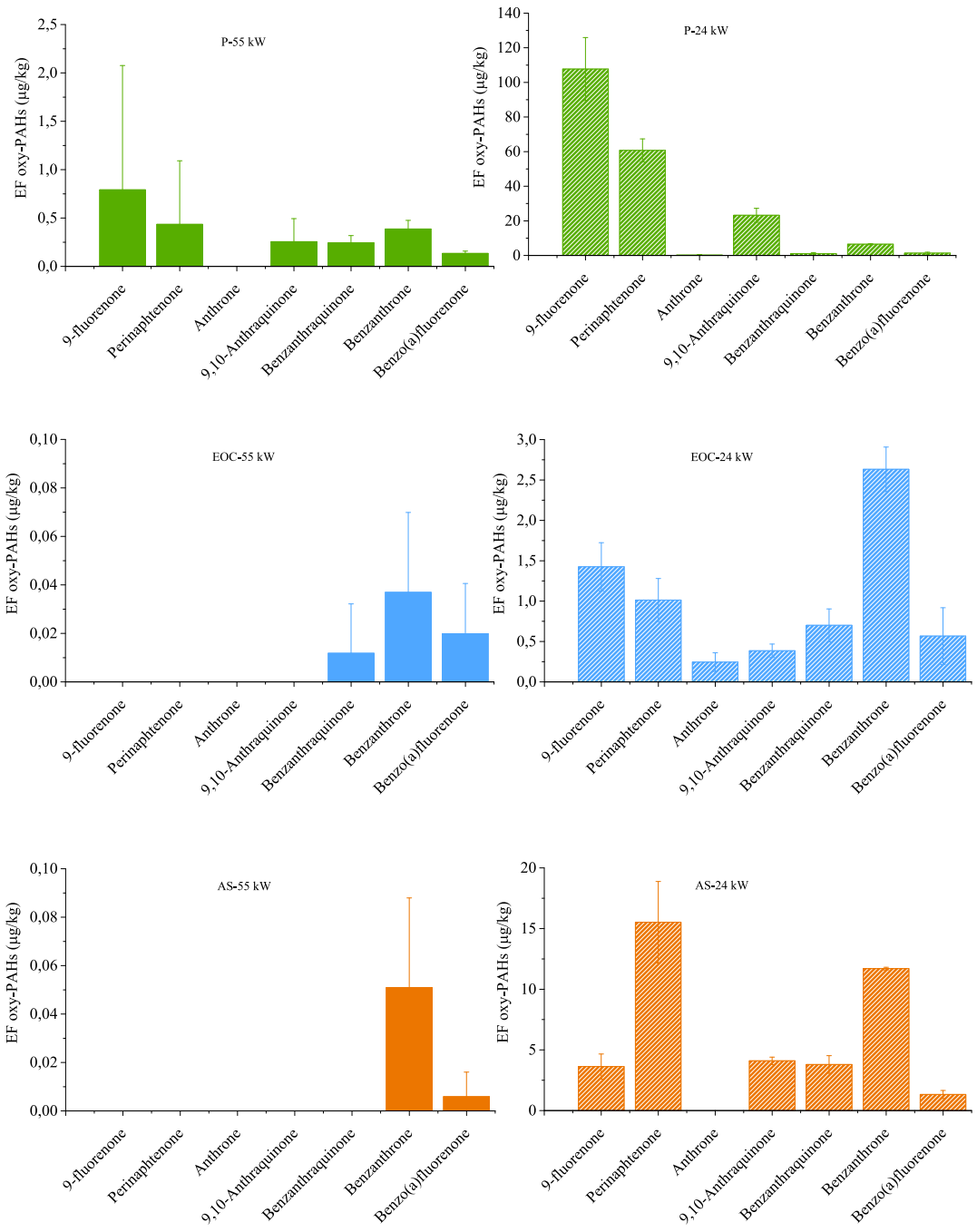

Fig. 5. Emissions of PM bound individual oxy-PAHs during combustion of P, AS and EOC.

Table 3
Nitro-PAHs content in PM from the combustion of P, EOC and AS at partial load.

	Partial load 24 kW		
	P	EOC	AS
9-nitroanthracene (µg/kg)	0.20 ± 0.34	n.d	n.d
2-nitrofluoranthene (µg/kg)	0.52 ± 0.90	1.23 ± 0.80	n.d
3-nitrofluoranthene (µg/kg)	0.32 ± 0.56	n.d	n.d
1-nitropyrene (µg/kg)	10.23 ± 17.72	n.d	n.d
6-Nitrochrysene (µg/kg)	0.00 ± 0.00	n.d	n.d
∑nitro-PAHS (µg/kg)	11.27 ± 17.76	1.23 ± 0.80	n.d

n.d Non detected.

- In general, the carcinogenic equivalent was much higher at partial load. EOC presented the highest value due to the significant content of benzo(*ghi*)perylene.

CRediT authorship contribution statement

Esperanza Monedero: Writing – original draft, Methodology, Investigation, Conceptualization. **Rocío Collado:** Writing – review & editing, Formal analysis, Data curation. **Florentina Villanueva:** Writing – review & editing, Methodology, Data curation. **Elena Borjabad:** Writing – review & editing, Methodology, Data curation, Conceptualization. **Raquel Ramos:** Writing – review & editing, Supervision, Methodology. **Juan José Hernandez:** Writing – review & editing, Supervision, Methodology, Data curation, Conceptualization.

Table 4
Carcinogenic equivalent (KE_{sum}) for P, EOC and AS at nominal and partial load.

		55 kW			24 kW			Units
		P	EOC	AS	P	EOC	AS	
TEF (Nisbet and LaGoy, 1992)	KE_{sum}	0.02 ± 0.00	0.00 ± 0.00	0.97 ± 0.00	0.60 ± 0.02	43.61 ± 0.00	0.07 ± 0.00	μg/kg
PEF (OEHHA, 2015)	KE_{sum}	0.02 ± 0.00	0.00 ± 0.00	1.86 ± 0.00	1.50 ± 0.01	85.86 ± 0.05	0.06 ± 0.00	μg/kg

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

Acknowledgement

The authors would like to thank the UCLM for financing Dra. Monedero within the UCLM's Own Research Plan.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.atmosres.2025.107954.

References

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

Atkinson, R., Arey, J., 2007. Mechanisms of the gas-phase reactions of aromatic hydrocarbons and PAHs with OH and NO3 radicals. Polycycl. Aromat. Compd. 27, 15–40. https://doi.org/10.1080/10406630601134243.

Bandowe, B.A.M., Meusel, H., 2017. Nitrated polycyclic aromatic hydrocarbons (nitro-PAHs) in the environment—a review. Sci. Total Environ. 581–582, 237–257. https://doi.org/10.1016/j.scitotenv.2016.12.115.

Collado, R., Monedero, E., Casero-Alonso, V.M., Rodríguez-Aragón, L.J., Hernández, J.J., 2022. Almond shells and exhausted olive cake as fuels for biomass domestic boilers: optimization, performance and pollutant emissions. Sustainability 2022 (14), 7271. https://doi.org/10.3390/su14127271.

Collado, R., Monedero, E., Borjabad, E., Hernandez, J.J., 2024. Size-dependent characterization of particles from domestic boilers fuelled with exhausted olive cake and almond shells. Biomass Conv. Bioref. https://doi.org/10.1007/s13399-024-05317-7.

Dimashki, M., Harrad, S., Harrison, R.M., 2000. Measurements of nitro-PAH in the atmospheres of two cities. Atmos. Environ. 34, 2459–2469. https://doi.org/10.1016/S1352-2310(99)00417-3.

Eiguren-Fernandez, A., Miguel, A.H., Froines, J.R., Thurairatnam, S., Avol, E.L., 2004. Seasonal and spatial variation of polycyclic aromatic hydrocarbons in vapor-phase and PM2.5in Southern California urban and rural communities. Aerosol Sci. Technol. 38, 447–455. https://doi.org/10.1080/02786820490449511.

Eisler, R., 2000. Polycyclic aromatic hydrocarbons. In: Handbook of Chemical Risk Assessment, Vol. 2, pp. 1343–1411. https://doi.org/10.1201/9780367801397.

Feilberg, A., Poulsen, M.W.B., Nielsen, T., Skov, H., 2001. Occurrence and sources of particulate nitro-polycyclic aromatic hydrocarbons in ambient air in Denmark. Atmos. Environ. 35, 353–366. https://doi.org/10.1016/S1352-2310(00)00142-4.

Goldfarb, J.L., Suuberg, E.M., 2008. Vapor pressures and thermodynamics of oxygen containing polycyclic aromatic hydrocarbons measured using Knudsen effusion. Environ. Toxicol. Chem. 27, 1244–1249. https://doi.org/10.1897/07-486.

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

IARC IARC (International Agency for Research on Cancer), 2012. A Review of Human Carcinogens: Some Chemicals in Industrial and Consumer Products, Food Contaminants and Flavourings, and Water Chlorination By–Products. Lyon, France.

Jelic, A., Katsou, E., Malamis, S., Bolzonella, D., Fatone, F., 2015. Occurrence, removal, and fate of PAHs and VOCs in municipal wastewater treatment plants: a literature review. In: En A. Forsgren, Wastewater treatment; Occurrence and Fate of Polycyclic Aromatic Hydrocarbons (PAHs). CRC Press (págs. 91-112).

Jenkins, B.M., Jones, A.D., Turn, S.Q., Williams, R.B., 1996. Particle concentrations, gas-particle partitioning, and species intercorrelations for polycyclic aromatic hydrocarbons (PAH) emitted during biomass burning. Atmos. Environ. 30, 3825–3835.

Johansson, L.S., Leckner, B., Gustavsson, L., Cooper, D., Tullin, C., Potter, A., 2004. Emissions characteristics of modern and old-type residential coilers fired with wood logs and wood pellets. Atmos. Environ. 38, 4183–4195. https://ui.adsabs.harvard.edu/link_gateway/2004AtmEn..38.4183J/doi:10.1016/j.atmosenv.2004.04.020.

Juhasz, A.L., Naidu, R., 2000. Bioremediation of high molecular weight polycyclic aromatic hydrocarbons: a review of the microbial degradation of benzo[a]pyrene. Int. Biodeterior. Biodegrad. 45 (1–2), 57–88. https://doi.org/10.1016/S0964-8305(00)00052-4.

Krugly, E., Martuzevicius, M., Puida, E., Buinevicius, K., Stasiulaitiene, I., Radziuniene, I., Minikauskas, A., Kliucininkas, L., 2014. Characterization of gaseous- and particle-phase emissions from the combustion of biomass-residue-derived fuels in a small residential boiler. Energy Fuel 28, 5057–5066. https://doi.org/10.1021/ef500420t.

Lamberg, H., Nuutinen, K., Tissari, J., Ruusunen, J., Yli-Pirilä, P., Sippula, O., Tapanainen, M., Jalava, P., Makkonen, U., Teinilä, K., Saarnio, K., Hillamo, R., Hirvonen, M.R., Jokiniemi, J., 2011. Physicochemical characterization of fine particles from small-scale wood combustion. Atmos. Environ. 45, 7635–7643. https://ui.adsabs.harvard.edu/link_gateway/2011AtmEn..45.7635L/doi:10.1016/j.atmosenv.2011.02.072.

Lara, S., Villanueva, F., Martín, P., Salgado, S., Moreno, A., Sánchez-Verdú, P., 2022. Investigation of PAHs, nitrated PAHs and oxygenated PAHs in PM10 urban aerosols. A comprehensive data analysis. Chemosphere 294, 133745. https://doi.org/10.1016/j.chemosphere.2022.133745.

Lara, S., Villanueva, F., Cabañas, B., Sagrario, S., Aranda, I., Soriano, J.A., Martin, P., 2023 Nov 20. Determination of policyclic aromatic compounds, (PAH, nitro-PAH and oxy-PAH) in soot collected from a diesel engine operating with different fuels. Sci. Total Environ. (900), 165755. https://doi.org/10.1016/j.scitotenv.2023.165755.

Lee, R.G.M., Coleman, P., Jones, J.L., Jones, K.C., Lohmann, R., 2005. Emission factors and importance of PCDD/Fs, PCBs, PCNs, PAHs and PM10 from the domestic burning of coal and wood in the U.K. Environ. Sci. Technol. 39 (6), 1436–1447. https://doi.org/10.1021/es048745i.

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

Lewtas, J., Nishioka, M.G., 1990. Nitroarenes: Their Detection, Mutagenicity and Occurrence in the Environment. Springer US. https://doi.org/10.1007/978-1-4615-3800-4_5.

Lu, H., Zhu, L., Zhu, N., 2009. Polycyclic aromatic hydrocarbon emission from straw burning and the influence of combustion parameters. Atmos. Environ. 43, 978–983. https://doi.org/10.1016/j.atmosenv.2008.10.022.

Lundstedt, S., White, P.A., Lemieux, C.L., Lynes, K.D., Lambert, I.B., Öberg, L., Haglund, P., Tysklind, M., 2007. Sources, fate, and toxic hazards of oxygenated polycyclic aromatic hydrocarbons (PAHs) at PAH-contaminated sites. Ambio 36 (6), 475–485.

Masto, R.E., Sarkar, E., George, J., Jyoti, K., Dutta, P., Ram, L.C., 2015. PAHs and potentially toxic elements in the fly ash and bed ash of biomass fired power plants. Fuel Process. Technol. 132, 139–152. https://doi.org/10.1016/j.fuproc.2014.12.036.

Nisbet, I.C.T., LaGoy, P.K., 1992. Toxic equivalency factors (TEFs) for polycyclic aromatic hydrocarbons (PAHs). Regul. Toxicol. Pharmacol. 16 (3), 290–300. https://doi.org/10.1016/0273-2300(92)90009-X.

OEHHA, 2015. Guidance Manual for Preparation of Health Risk Assessments, Appendix G, PAH Potency Factors and Selection of Potency Equivalency Factors (PEFs) for PAHs Based on Benzo(a)Pyrene Potency. Office of Environmental Health Hazard Assessment, California, USA. Available from: https://www.atsdr.cdc.gov/pha-guidance/resources/ATSDR-PAH-Guidance-508.pdf (Accessed June 2024).

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

Ross, A.B., Jones, J.M., Chaiklangmuang, S., Pourkashanian, M., Williams, A., Kubica, A., Andersson, J.T., Kerst, M., Danihelka, P., Bartle, K.D., 2002. Measurement and prediction of the emission of pollutants from the combustion of coal and biomass in a fixed bed furnace. Fuel 81 (5), 571–582. https://doi.org/10.1016/S0016-2361(01)00157-0.

Serrano, C., Portero, H., Monedero, E., 2013. Pine chips combustion in a 50 kW domestic biomass boiler. Fuel 111, 564–573. https://doi.org/10.1016/j.fuel.2013.02.068.

Shen, G., Xue, M., Wei, S., Chen, Y., Zhao, Q., Li, B., Wu, H., Tao, S., 2013. Influence of fuel moisture, charge size, feeding rate and air ventilation conditions on the emissions of PM, OC, EC, parent PAHs, and their derivatives from residential wood combustion. J. Environ. Sci. (China) 25 (9), 1808–1816. https://doi.org/10.1016/S1001-0742(12)60258-7.

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

UNE-EN 303-5, 2022. Heating Boilers—Part 5: Heating Boilers for Solid Fuels, Manually and Automatically Stoked, Nominal Heat Output of up to 500 kW. European Committee for Standardization, Brussels, Belgium.

UNE-EN 16510-1, 2023. Residential Solid Fuel Burning Appliances—Part 1: General Requirements and Test Methods. European Committee for Standardization, Brussels, Belgium.

USEPA, 2016. Electronic Code of Federal Regulations. Title 40 e-CFR. Chapter I. Subchapter N. Part 423: Appendix A to 40 CFR, part 423–126 Priority pollutants. Available at http://www3.epa.gov/region1/npdes/permits/generic/prioritypollutants.pdf.

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

Villanueva, F., Sevilla, G., Lara, S., Martín, P., Salgado, S., Albaladejo, J., Cabañas, B., 2018. Application of gas chromatography coupled with tandem mass spectrometry for the assessment of PAH levels in non industrial indoor air. Microchem. J. 142, 117–125. https://doi.org/10.1016/j.microc.2018.06.021.

Vione, D., Barra, S., De Gennaro, G., De Rienzo, M., Gilardoni, S., Perrone, M.G., Pozzoli, L., 2004. Polycyclic aromatic hydrocarbons in the atmosphere: monitoring, sources, sinks and fate. II: sinks and fate. Ann. Chim. 94, 257–268. https://doi.org/10.1002/adic.200490031.

Walgraeve, C., Demeestere, K., Dewulf, J., Zimmermann, R., Van, Langenhove H., 2010. Oxygenated polycyclic aromatic hydrocarbons in atmospheric particulate matter: molecular characterization and occurrence. Atmos. Environ. 44, 1831–1846. https://doi.org/10.1016/j.atmosenv.2009.12.004.

Wang, J., Jiang, H., Chen, Y., Han, Y., Cai, J., Peng, Y., Feng, Y., 2023. Emission characteristics and influencing mechanisms of PAHs and EC from the combustion of three components (cellulose, hemicellulose, lignin) of biomasses. Sci. Total Environ. 859 (Part 2), 160359. https://doi.org/10.1016/j.scitotenv.2022.160359.

Zdeněk, Košnář, Mercl, Filip, Perná, Ivana, Tlustoš, Pavel, 2016. Investigation of polycyclic aromatic hydrocarbon content in fly ash and bottom ash of biomass incineration plants in relation to the operating temperature and unburned carbon content. Sci. Total Environ. 563–564, 53–61. https://doi.org/10.1016/j.scitotenv.2016.04.059.

Zhang, B., Sun, J., Jiang, N., Zeng, Y., Zhang, Y., He, K., Xu, H., Liu, S., Ho, S.S.H., Qu, L., Cao, J., Shen, Z., 2021a. Emission factors, characteristics, and gas-particle partitioning of polycyclic aromatic hydrocarbons in PM2.5 emitted for the typical solid fuel combustions in rural Guanzhong Plain, China. Environ. Pollut. 286, 117573. https://doi.org/10.1016/j.envpol.2021.117573.

Zhang, Y., Sun, J., Zou, H., Zhang, B., Yang, D., Wang, Q., Li, J., Qu, L., Ho, S.S.H., Cao, J., Shen, Z., 2021b. Photochemical aging process on PM2.5 bound PAHs emission from solid fuel combustion in traditional and improved stoves. Atmos. Res. 263, 105807. https://doi.org/10.1016/j.atmosres.2021.105807.

Zhang, Y., Shen, Z., Sun, J., Zhang, L., Zhang, B., Zou, H., Zhang, T., Ho, S.S.H., Chang, X., Xu, H., Wang, T., Cao, J., 2021c. Parent, alkylated, oxygenated and nitrated polycyclic aromatic hydrocarbons in PM2.5 emitted from residential biomass burning and coal combustion: a novel database of 14 heating scenarios. Environ. Pollut. 268 (Part A), 115881. https://doi.org/10.1016/j.envpol.2020.115881.

Zhang, B., Wang, C., Sun, J., He, K., Zou, H., Xu, H., Li, J., Ho, K., Shen, Z., 2022. Field measurements of PM2.5 emissions from typical solid fuel combustion in rural households in Fenhe Basin, China. Environ. Res. 212 (Part C), 113361. https://doi.org/10.1016/j.envres.2022.113361.