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Comprehensive assessment of PM_{10} from home heating using different appliances and biomass fuels: Chemical composition, oxidative potential, and ecotoxicity

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HIGHLIGHTS

- Indoor PM_{10} was higher during briquette and firewood combustion.
- I/O ratios >1 for room equipped with wood stove indicate dominant indoor PM_{10} sources.
- Pellet stove use led to lower PM_{10}, OP, toxicity and PM_{10}-bound elements.
- All PM_{10} samples from the wood stove room was classified as “very toxic”.
- PAHs, quinones and phenolic proved redox-active in OP assays from wood stove PM_{10}.

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ABSTRACT

The European Union has implemented policies to promote renewable energy, with an emphasis on biomass for heat generation. However, residential biomass combustion is a major source of particulate matter (PM_{10}), and its chemical constituents pose health concerns worldwide. This study characterised the organic and inorganic composition, oxidative potential (OP), and ecotoxicity of PM_{10} indoors and outdoors during the operation of two heating appliances fuelled with different types of biomasses: a modern hydronic stove and a traditional wood stove. PM_{10} concentrations were higher in the room equipped with the traditional system during the combustion of briquettes (95.9 ± 74.9 μg m^{-3}) and firewood (50.1 ± 25.6 μg m^{-3}), compared to the modern stove using pellets (27.1 ± 11.8 μg m^{-3}) and olive stone (23.0 ± 4.5 μg m^{-3}). While element oxides accounted for similar PM_{10} mass fractions (7 %), the wood stove produced higher levels of organic constituents, including carbonaceous fractions, polycyclic aromatic hydrocarbons (PAHs), quinones and saccharides. Significant correlations between OP assays and concentrations of PAHs, quinones and phenolic compounds were found in the room equipped with wood stove, with indoor to outdoor (I/O) ratios higher than 1. In contrast, I/O ratios below 1 were observed for OP in PM_{10} samples collected during hydronic stove operation. Ecotoxicity assays using *Aliivibrio fischeri* classified indoor PM_{10} from the wood stove as ’very toxic’, whereas samples from the hydronic stove exhibited lower toxicity and OP levels. These findings highlight the need to reconcile renewable energy goals with air quality and public health.

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1. Introduction

The transition toward a low-carbon economy is a central component of the European Union's (EU) strategy to address climate change and reduce energy dependency (Li et al., 2023). To this end, the EU has implemented policies and instruments promoting renewable energy sources (RES), with specific targets set under the Renewable Energy Directives (RED I and RED II) (Magni et al., 2024). These directives mandate increasing the share of RES in gross final energy consumption to 32 % by 2030, while emphasising the sustainable and efficient use of biomass fuels for electricity and heat generation. This shift is expected to contribute significantly to reducing greenhouse gas (GHG) emissions and enhancing energy security (Colocci et al., 2023; Pastore et al., 2022).

Within the framework of RES deployment, solid biomass, particularly wood-based fuels, has emerged as a critical resource for residential heating systems across Europe (Olsen et al., 2020). National incentives, such as subsidies and tax reductions, have further encouraged the adoption or change of biomass-based energy modern systems. In contrast to fossil fuels, wood burning is often considered a "clean" or "green" energy source (Dale et al., 2017; Richter et al., 2009) due to climate policies promoting use of energy from renewable sources (Directive, 2009/28/EC). In European Union countries, from 2007 to 2017, the quantity of renewable energy increased by 64 %, with solid fuels accounting for 43 % of primary production (Eurostat, 2019).As a result, residential wood combustion is one of the main sources of airborne particulate matter (PM) in Europe (Brandt et al., 2013; Denier Van Der Gon et al., 2015), surpassing contributions from the industry and transport sectors (EEA, 2020). This has raised concerns about the environmental and public health impacts of residential wood combustion. A critical issue in this context is the wide variability in the technologies employed for domestic heating across European countries. Many households continue to use outdated and inefficient heating devices, such as traditional wood stoves or open fireplaces, which lack modern certifications ensuring lower emissions (Vicente et al., 2020a).

Among the various air pollutants, PM is particularly concerning due to its significant impacts on both climate (Fuzzi et al., 2015; Kanakidou et al., 2005) and human health (Brook et al., 2010; Ghosh et al., 2021). PM concentrations are commonly used as a marker of air pollution (Daellenbach et al., 2020; Martins and Carrilho da Graça, 2018; Rovira et al., 2020; Tan et al., 2021), with scientific evidence suggesting that the chemical characterisation of PM offers deeper insights into the factors driving its harmful effects (Alves et al., 2018; de Miranda et al., 2018; Perrone et al., 2016; Pio et al., 2020; Zong et al., 2018). The assessment and management of ambient concentration levels are well-documented, supported by national air quality networks in fixed monitoring stations and legally stipulated limit values for air pollutants. However, fixed monitoring stations may misrepresent the population's real exposure, given the high spatial variability of PM concentrations in urban centres (Bereitschaft, 2015; Cipoli et al., 2022; Qiu et al., 2017; Rabie et al., 2024) and by residents spending more than 90 % of their time indoors (Deng and Deng, 2018; Leech et al., 2002). Several studies have reported higher levels of PM in indoor environments than outdoors (e.g. (Cheung and Jim, 2019; Furst et al., 2025; Vicente et al., 2021),), highlighting that the chemical composition can differ significantly between these environments. In general, indoor PM concentrations are related to human activities, such as cooking (Canha et al., 2018), smoking (Canha et al., 2019), particle resuspension (Charres et al., 2024; Cipoli et al., 2023a) and heating systems (Stabile et al., 2018; Vicente et al., 2020b). A review by Sigsgaard et al. (2015) concluded that anthropogenic biomass burning emissions are increasing in the last years in Europe in contrast to emissions from other sources. In addition, in response to fuel poverty, wood-based fuel is often considered a cheap energy source, especially when gathered locally, which contributes to elevated particulate matter concentrations in winter. A recent study in Portugal found nighttime PM levels to increase by up to 20 %, showing strong correlations with wood combustion tracers, particularly levoglucosan and potassium (K) (Cipoli et al., 2023b). Moreover, these nocturnal PM increases may partly result from dark oxidation processes that enhance the secondary formation of organic aerosols, particularly under high relative humidity conditions (Jorga et al., 2021; Kodros et al., 2022)).

Research has increasingly emphasised that the type of combustion appliance plays a pivotal role in determining the toxicological profile of PM emissions (e.g. (Canha et al., 2016; Corsini et al., 2017; Tapanainen et al., 2011; Uski et al., 2015),). Beyond the appliance, the type of fuel used and combustion conditions have also been identified as critical factors (Canha et al., 2018; Uski et al., 2015; Vicente and Alves, 2018; Vu et al., 2012). Despite this growing body of research, PM generated by residential biomass combustion exhibits distinct physicochemical characteristics based on fuel type, combustion technology, and household behaviour (e.g. (Lamberg et al., 2011),). These characteristics are closely linked to varying biological responses, such as inflammation, cytotoxicity, genotoxicity, and oxidative stress (Claxton et al., 2004; Figueiredo et al., 2023; Happo et al., 2013; Kocbach Bølling et al., 2009).

Although numerous studies have reported PM levels from wood-based fuels in various regions, including Spain (Castro et al., 2018), Italy (de Gennaro et al., 2015), Portugal (Canha et al., 2018; Vicente et al., 2020a), and China (Tang and Wang, 2018), most have not incorporated ecotoxicological assessments and oxidative potential assays. Given the limited information on residential microenvironments, the proposed methodology seeks to provide detailed insights into PM_{10}-bound constituents by two different heating appliances, including both a traditional manually fed unit and a modern automatically fed system, operated by households under real-world conditions rather than by researchers in controlled settings. The samples were collected for four wood-based fuels (pellets, olive stone, briquettes and firewood), and characterised for their ionic, elemental, and carbonaceous composition. PM_{10} ecotoxicity was assessed using the *Aliivibrio fischeri* bioluminescence inhibition bioassay, while the oxidative potential was measured with acellular methods (dithiothreitol and ascorbic acid). Thus, this work is expected to contribute to a better understanding of the adverse effects caused by emissions from different biomass combustion technologies, helping to align renewable energy goals with public health objectives.

2. Material and methods

2.1. Study area and monitoring sites

The indoor/outdoor sampling campaign was conducted in two dwellings (Fig. 1) located in the city of Bragança. The city, with a population of approximately 35,000 inhabitants (Pordata and PORDATA, 2021), is characterised by a temperate climate (Csa classification in the Köppen-Geiger system), marked by high thermal amplitude, with hot and dry summers, and cold and rainy winters. The urban area spans approximately 10 km^2 and is surrounded by farmlands and small rural settlements, contributing to a diverse economic structure dominated by commercial and agricultural activities. Furthermore, Bragança is characterised by its reliance on traditional methods for residential heating during winter, often using older appliances and various biomass fuels. This practice, while economically accessible and deeply rooted in local culture, poses challenges to air quality. A previous study identified biomass burning as one of the major sources of PM_{10} in Bragança, emphasing its toxic potential and the harmful effects on human health (Cipoli et al., 2023b). As reported by Cipoli et al. (2023b), mean PM_{10} concentrations reached 44.5 ± 23.6 μg m^{-3}, with exceedances of the EU daily limit of 50 μg m^{-3} (in force at that time) recorded on 22 days during the campaign (January 14th to March 17th, 2021), mainly associated with residential biomass combustion."

Due to the lack of a local database on the types of residential heating appliances and fuels used in the city, a questionnaire (Table S1) was

administered to gather contextual insights. This reconnaissance initiative aimed to capture diverse and representative areas of the city through fully anonymous online questions. In total, 173 responses were collected, covering approximately 25 different areas within the city. Additionally, recognising that many residents are elderly and may lack access to online questionnaires, several dozen door-to-door surveys were conducted to address gaps and ensure coverage of underrepresented areas.

Based on the questionnaire responses, two distinct residential heating devices were selected: a pellet stove (hydronic stove) and an outdated wood stove (Fig. S1). The intention was to characterise PM_{10} emissions of different fuels using devices with significant technological differences: the pellet stove (hydronic stove) is an automatic system, whereas the wood stove is entirely manual. In addition, the residences were selected in collaboration with the volunteers, taking into account daily wood-fuel use, ventilation settings (i.e., all doors and windows remained closed) and the absence of smokers. Due to the technical challenges involved in operationalising the monitoring campaign, particularly the disruptive noise from the equipment and the researcher's daily presence to change filters, the target homes were selected from among residents who volunteered to participate in the study under these conditions. Volunteers were requested to carry out their activities under normal conditions, including the typical types of fuels used and the usual operational settings of their heating devices. The only requirement was to burn every day the specified wood-based fuel each day for a consecutive week. Descriptive characteristics and configurations of the environments are described in Table 1.

Dwelling A is located in a three-story building with external insulation, which enhances its thermal retention properties. The duplex apartment spans two levels. The lower level includes the living room, kitchen, and bedrooms. The upper level, which is used less frequently, consists of three separate areas divided by walls and doors, and features a balcony that is accessible during the summer months. Upon entering the apartment, occupants remove their footwear. Cleaning is carried out using both robotic and manual vacuum cleaners. All windows and exterior-facing doors are equipped with double glazing.

Table 1
Characteristics of each residential site.

	Dwelling A	Dwelling B
Type	Apartment in a building (3rd floor)	Detached house
Floors	2	1
Microenvironment with heating device	Upper floor attic room	Living room
Volume of the microenvironment (m^3)	35.8	90
Balcony orientation	Open green space	Street
Number of windows	1	2
Ventilation settings[a]	CD/CW	CD/CW
Occupants	3	3
Pets	1 cat	none
Heating system	Hydronic stove	Wood stove
Fuel types	Pellets and olive stones	Briquettes and firewood
Combustion time	6 p.m.–6 a.m.	6 p.m.–9 p.m.

[a] CD – closed doors; CW – closed windows.

In contrast, dwelling B lacks external insulation and shows clear signs of structural ageing, including cracks and mould patches on the walls. Electric heaters are used intermittently in bedrooms before bedtime, while cleaning is performed weekly using traditional methods, such as brooms and damp mops. During winter, residents predominantly occupy the living room, where the heating system is located. The dwelling was recently upgraded with double-glazed windows and doors. Its outdoor balcony faces a low-density traffic street in a student neighbourhood.

2.2. Heating appliances and biomass fuels

2.2.1. Hydronic stove

The hydronic stove (Hidrocopper 18, Ecoforest) used in dwelling A was designed to heat spaces via a water radiator network, with an 18 kW

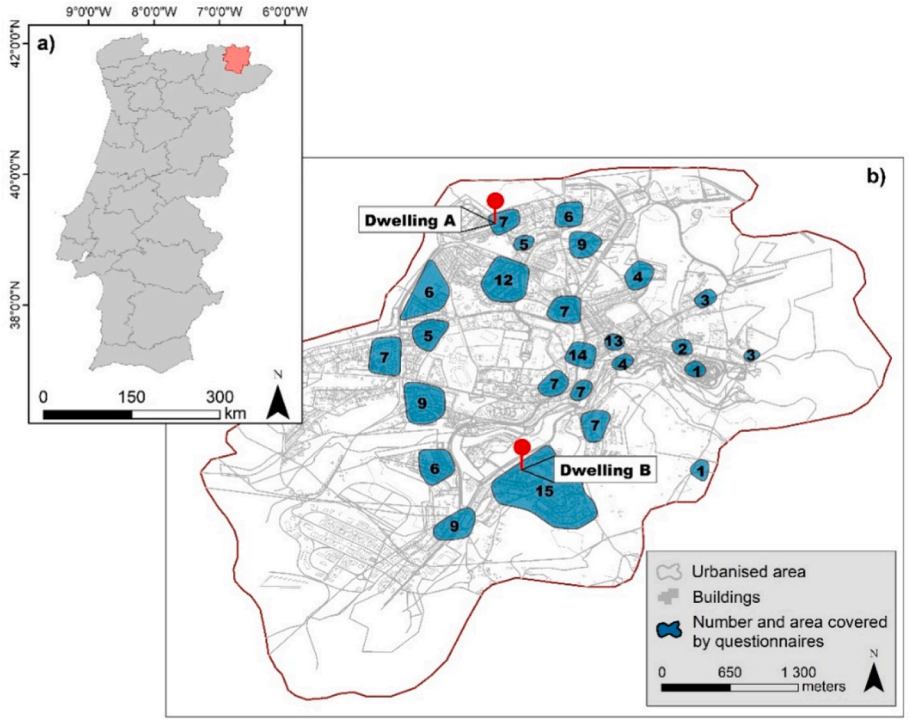

Fig. 1. Geographical location of Bragança (a), with sampling sites marked in red and the total number and area covered by the applied questionnaires shown in blue (b). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

(15.5 kW is transferred to the water circuit and 2.5 kW to the environment) capacity and a thermal efficiency of 95 %. This device features automatic control of combustion air, fuel supply, and recirculating pump flow. The flow can be regulated, and the temperature stabilises without the need for an anti-condensation valve. Additionally, it supports multi-fuel use, accommodating wood pellets and olive stones. The unit is equipped with a vacuum cleaning system, multiple safety features, a cast-iron hearth, and a burning pot made of cast iron and stainless steel. It also includes an integrated circulation pump, an expansion tank, and a safety valve. The hopper holds 36 kg of fuel (pellets), providing an autonomy of 9–18 h depending on consumption levels.

The hydronic stove was operated using two types of fuels: ENplus A1 pellets and olive stones. The pellets are certified to meet strict specifications, ensuring low ash and moisture content, high calorific value and minimal emissions during combustion. The specific characteristics provided by the manufacture were as follows: 100 % natural wood, moisture content $\leq$10 %, ash content $\leq$0.7 %, lower heating power $\geq$16.6 MJ kg^{-1}, diameter of 6 $\pm$ 1 mm, and density ranging from 600 to 750 kg m^{-3}. These pellets are particularly well-suited for optimal performance in modern combustion systems. Olive pits, a by-product of olive oil production, are typically prepared for burning through processes such as drying, oil removal, size reduction, cleaning of non-combustible impurities, and sieving to separate uniformly sized particles, facilitating efficient feeding and combustion. However, the local producer lacks technical specifications for the product, as it is part of the informal market.

2.2.2. Wood stove

A traditional wood stove device was used for space heating in dwelling B. This equipment is installed within the cavity of an old open fireplace, with an exhaust system (stainless steel pipes) connected to the chimney. This system is characterised by its age, with evident accumulation of ash and soot residues. It is a versatile burner, capable of accepting a wide range of combustible materials. However, its most common fuels are firewood and briquettes. The system was installed for local heating, lacking integration with broader heating networks. Moreover, the wood stove is manually fuelled from the top of the drum, where a manual air control mechanism is also located, enabling users to regulate the airflow entering the combustion chamber. This design provides very limited control over the combustion process.

The wood stove was fuelled with briquettes and cork oak firewood. Briquettes (Ecologic briquettes, JAF group) are manufactured from compacted pine wood residues and offer higher energy density and lower moisture content compared to traditional firewood. The technical specifications provided by the manufacturer indicate a moisture content between 5 % and 7 %, higher heating value of 20.1 MJ kg^{-1}, 3 % residue after combustion, and 100 % vegetable pressed wood. The cork oak firewood was sourced from local producers and lacked formal specifications, leading to more variable combustion characteristics typical of natural, untreated wood.

2.3. PM_{10} sampling setup

Gravimetric and continuous PM_{10} measurements were conducted over a four-week winter monitoring period, covering two weeks in each dwelling. During this timeframe, specific fuel types were assessed on a weekly basis as follows: pellets (November 30 to December 6, 2022), olive stones (December 12 to December 18, 2022), briquettes (December 19 to December 25, 2022), and firewood (December 26, 2022, to January 1, 2023). For the indoor microenvironments, the experimental setup consisted of one photometric and two gravimetric devices, while the outdoor setup was composed of two gravimetric devices. Additionally, indoor real time measurements of CO_2 were provided by WolfSense probes (Gray Wolf®, Roswell, GA, USA, IQ-610). Continuous monitoring of PM_{10} was performed with an optical particle sizer spectrometer (OPS 3330, TSI Inc., Shoreview, MN, USA). The real-time monitor operated with a 1-min time resolution and was previously calibrated by the manufacturer before the sampling campaign. Additionally, a weekly maintenance routine included zero checks, inlet cleaning, and greasing of the impactors. Gravimetric collection of PM_{10} took place every 24 h using low-volume samplers (Echo Tecora, Italy) at a flow rate of 2.3 m^3 h^{-1}. The PM_{10} fraction was selected through an impactor inlet (Echo Tecora, Italy) compliant with the EN12341:2014 standard for reference gravimetric measurements. One sampler was equipped with quartz fibre filters (2.0 μm pore size, Pallflex®) and the other with Teflon membrane filters (Pall Corporation), both 47 mm in diameter and pre-weighed. The indoor devices were placed near the heating system, at least 1 m from the walls, with inlets positioned 1.5 m above the ground, which corresponds approximately to the breathing zone. The outdoor gravimetric samplers were placed on the balcony of the residences, maintaining the same distance and height conditions as mentioned above.

2.4. Analytical determinations

2.4.1. Thermochemical characterisation of biomass fuels

The thermochemical (lower and higher heating value) properties, humidity, ash, carbon, hydrogen, nitrogen and sulphur contents of the wood-based fuels are displayed in Table 2. The analyses were performed using standardised methodologies in accordance with UNE-EN ISO for solid biofuels: sample preparation (UNE-EN 14780), ash content (UNE-EN ISO, 18122), carbon, nitrogen and hydrogen content (UNE-EN ISO 16948), sulphur content (UNE-EN ISO 16994), and heating value (UNE-EN ISO, 18125). Representative samples of each wood-fuel were used, with two or three replicates performed for each analysis. Further details regarding the methods and equipment are provided in Monedero et al. (2016).

2.4.2. PM_{10} -carbon components

A thermo-optical transmission technique was employed to determine the carbonaceous fraction of PM_{10} samples, following the EUSAAR-2 protocol. Two replicate analysis of circular punches of 9 mm of the quartz filters were submitted to sequential heating under controlled conditions. Initially, organic carbon (OC) is volatilised in an inert nitrogen atmosphere, and subsequently, elemental carbon (EC) is oxidised in a mixture of 4 % oxygen and 96 % nitrogen. The carbon released during these steps is quantified as CO_2 using a non-dispersive infrared gas analyser (NDIR). A laser beam and photodetector system measure light transmittance, enabling the differentiation of EC formed during the pyrolysis of OC from the EC initially present in the sample. Each sample was analysed in duplicate, and results were averaged when the relative deviation between replicates was below 5 %. When this threshold was exceeded, a third replicate analysis was performed, and the two closest values were retained for averaging. The details of this methodology are described elsewhere (Alves et al., 2011; Pio et al., 2011).

2.4.3. PM_{10} -bound metals

Half of each Teflon filter was used to determine elements with Z > 10 (Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Br, Rb, Sr, Y, Zr, Mo, Ba, Pb) by particle-induced X-ray emission (PIXE), following the methodology detailed by Lucarelli et al. (2018). Samples were irradiated with a 3.2 MeV proton beam (2 mm^2 spot, 5–50 nA) for approximately 5 min, and the deposited area was scanned prior to analysis. Elemental concentrations were calculated using the GUPIX software, calibrated with thin standards of known areal density (Micromatter Inc.). Quality control included re-measurement of selected samples and routine analysis of reference material (NIST SRM2783), ensuring agreement with certified values. The method detection limit (3 σ) ranged from 0.5 ng m^{-3} (Se) to 11.6 ng m^{-3} (Ba).

Table 2
Physicochemical characteristics of biomass samples.

	Pellets		Olive stones		Briquettes		Firewood	
	dry basis	wet basis	dry basis	wet basis	dry basis	wet basis	dry basis	wet basis
[1]Humidity (%)		4.09		14.3		3.86		36.4
[2]Ash (%)	0.46	0.44	0.46	0.39	0.38	0.37	2.39	1.52
[3]Carbon (%)	50.7	48.6	51.4	44.0	51.6	49.6	50.9	32.4
[4]Hydrogen (%)	6.24	6.44	5.89	6.65	6.22	6.41	6.32	8.09
[5]Nitrogen (%)	0.16	0.15	0.15	0.13	0.13	0.13	0.43	0.28
[6]Sulphur (%)	0.02	0.02	0.02	0.02	0.03	0.03	0.03	0.02
[7]Higher heating value (MJ kg^{-1})	19.9	19.1	20	17.2	20.2	19.4	19.3	12.3
[8]Lower heating value (MJ kg^{-1})	18.6	17.7	18.7	15.7	18.9	18.1	17.9	10.5

The references for standard methods can be found in the supplementary material: [1]UNE-EN ISO 18134-2, [2] UNE-EN ISO 18122, [3,4] UNE-EN ISO 16948, [5] UNE-EN ISO 16994 and [6,7] UNE-EN 14918.

2.4.4. PM_{10} -organic and ionic speciation

To quantify polycyclic aromatic hydrocarbons (PAHs), half of each Teflon filter previously used for PIXE analysis, was extracted by sonication for 10 min with two aliquots (20 mL each) of dichloromethane/acetonitrile (50:50 v/v), with a 5-min stop between them. The same halves of the filters were then extracted with methanol under the same conditions for determination of organic oxygenated compounds. The organic extracts were filtered and concentrated using a Turbo Vap® II system (Biotage) and dried under a nitrogen stream. The analytical quantification of organic compounds was performed by gas chromatography – mass spectrometry (GC-MS). Prior to chromatographic analysis, polar organic compounds were derivatised to trimethylsilyl ethers. More methodological details can be consulted in Alves et al. (2011). The other half of the Teflon filter was water-extracted to analyse anhydrosugars and polyols by high-performance anion-exchange chromatography with pulsed amperometric detection (HPAE-PAD), as well as cations (Li^+, Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}) and anions (SO_4^{2-}, Cl^-, PO_4^{3-}, NO^{2-}, NO^{3-}, F^-, Br^-) by ion chromatography (Gonçalves et al., 2021). Detection limits for chromatographic parameters of the GC–MS method, water soluble ions and anhydrosugars and polyols are provided in the supplementary material (Table S3–S5).

2.4.5. Oxidative potential of PM_{10}

The oxidative potential (OP) was assessed using dithiothreitol (DTT) and ascorbic acid (AA) assays to measure antioxidant depletion rates. Aqueous extracts from a quarter of each quartz filter were prepared by ultrasonic extraction with high-purity Mili-Q water and filtered to remove solids. The reactions were conducted at 37 °C, with spectrophotometric measurements performed at 412 nm (DTT assay) and 265 nm (AA assay), following the experimental procedure described in (Clemente et al., 2023) and (Gómez-Sánchez et al., 2024). Briefly, in the DTT assay, 60 μL of 1 mM DTT solution was added to the sample, and its depletion was measured via reaction with 5,5-dithio-bis-(2-nitrobenzoic acid (DTNB), forming a measurable product. For the AA assay, 150 μL of 2 mM AA solution was added, and its depletion was directly monitored by absorbance. Antioxidant depletion rates (nmol min^{-1}) were calculated as the slope of the concentration versus time curve, with measurements taken at five (for DTT) and six (for AA) time points of known concentrations of both reagents at different times (Visentin et al., 2016). Blank filter responses were subtracted from samples and results were normalised to both air volumes collected (OP_v, nmol min^{-1} m^{-3}) and PM_{10} mass (OP_m, nmol min^{-1} μg^{-1}). Both assays demonstrated high reproducibility, with $r^2 \geq 0.98$ for linear fits.

2.4.6. Ecotoxicity assay of PM_{10}

The ecotoxicity assessment of PM_{10} samples was conducted using the bioluminescence inhibition assay with the bacterium *Aliivibrio fischeri* (NRRL-B-11177 strain), following the guidelines of ISO 21338:2010, which standardises procedures for measuring light emission inhibition due to sediment and particle-bound toxic substances. In order to ensure the direct contact between PM_{10} samples and the test bacteria, the quartz filter was punched, and the portion was ground in an agate mortar. It was then rinsed with 2 ml high-purity Mili-Q water and mixed with Vortex following the protocol developed by Kováts et al. (2012). Rehydration of lyophilised *A. fischeri* cells was performed using a sodium chloride-buffered solution (2 % NaCl), followed by stabilisation at 12 °C for 30 min. For each sample, dilutions ranging from 0.1 % to 100 % were prepared in 96-well microplates to evaluate the dose-response relationship. Bioluminescence measurements were carried out using a Luminoskan™ Microplate Luminometer (Thermo Scientific™), with luminescence inhibition recorded after 30 min of exposure. More methodological details can be consulted in Vicente et al. (2021). The EC_{50} values, representing the concentration required to reduce bioluminescence output by 50 % compared to the control under the specified experimental conditions, were derived from dose-response curves generated for the serial dilutions of the extracts. These calculations were performed using the Ascent software supplied by Aboatox Co., Finland. The EC_{50} values were then used to calculate Toxicity Units (TU, unitless) as $TU = 100/EC_{50}$. Samples were categorised into toxicity classes based on their TU values, as proposed by (Romano et al., 2020): non-toxic ($TU < 1$), toxic ($1 \leq TU < 10$), very toxic ($10 \leq TU < 100$), and extremely toxic ($TU > 100$). Procedural blanks consisting of clean quartz filters processed identically to the samples (ground and extracted) were included to confirm that the filter material itself had no effect on *A. fischeri*. No measurable luminescence inhibition was observed in these blanks, and all responses were corrected accordingly. The bacterial strain exhibits oxidative stress responses and membrane interaction mechanisms that are functionally analogous to those observed in higher organisms, allowing it to serve as a sensitive proxy for potential cytotoxic and pro-oxidant effects of PM-bound compounds.

2.5. Enrichment factor

To evaluate the degree of enrichment of PM_{10}-bound elements relative to their natural crustal abundances, the enrichment factor (EF) was calculated as follows:

$$EF = \frac{\frac{Cs}{Cref} \rightarrow PM_{10}\ sampled}{\frac{Cs}{Cref} \rightarrow Crustal\ concentration} \quad (1)$$

This approach involves comparing the concentration of a specific element sampled in PM_{10} (Cs) to its typical crustal concentration, normalised by a reference element (Cref). The calculation was based on the natural abundance values (Clarke values) for elements in the upper continental crust (Hans Wedepohl, 1995). Aluminium (Al) was selected as the reference element due to its high natural abundance in the crust and its widespread application in EF assessments of environmental samples (Chatoutsidou and Lazaridis, 2022). EF values greater than 10 are typically indicative of significant enrichment from human activities (Nayebare et al., 2018).

2.6. Data quality assurance

Quality assurance and control procedures included the analysis of field blanks and regular operational checks and calibrations. Moreover, it is widely reported that photometric devices, such as the OPS, provide valuable information with high time resolution for PM data, but their accuracy can be influenced by aerosol properties, leading to underestimation of PM concentrations (Wallace et al., 2010). Intercomparisons were performed using gravimetric samples compliant with the EN12341:2014 standard. Comparisons between daily filter-based PM_{10} concentrations and readings from the photometric device showed strong linearity (r^2: 0.93–0.97), with slopes from 0.14 to 0.96 and offsets from 6.94 to −11.9. Final PM_{10} values from OPS were rectified using calibration equations for each week.

2.7. Statistical analyses

Statistical analyses were performed using IBM SPSS software (version 25) to evaluate PM_{10} concentrations and their constituents. Nonparametric methods, including the Mann-Whitney test, were applied to assess differences between indoor and outdoor measurements, while Spearman correlations were employed to examine relationships between PM_{10}-bound constituents. All statistical tests were conducted at a 95 % confidence level ($p < 0.05$). Data curation and visualisation was performed using MATLAB 2018a (The MathWorks Inc., Natick, MA, USA). Pearson's correlations were used to establish linear relationships between gravimetric and light-scattering measurements.

3. Results and discussion

3.1. Indoor and outdoor PM_{10} mass concentrations

Indoors, PM_{10} mass concentrations were 27.1 ± 11.8 μg m^{-3}, 23.0 ± 4.5 μg m^{-3}, 95.9 ± 74.9 μg m^{-3} and 50.1 ± 25.6 μg m^{-3} for pellets, olive stone, briquettes and firewood, respectively (Table 3). PM_{10} levels for firewood were higher primarily due to its elevated ash and moisture contents compared to the other fuels. High ash content indicates a greater presence of inorganic material, which can contribute directly to particulate emissions during combustion. Additionally, higher moisture content in firewood leads to less efficient combustion, promoting incomplete burning and increased formation of fine particles. These factors combined result in higher PM_{10} emissions compared to drier, more processed fuels like pellets, olive stones, or briquettes, which generally burn more completely and cleanly. Indoor to outdoor (I/O) concentration ratios ranged from 0.73 to 0.74 for dwelling A, indicating higher PM_{10} concentrations outdoors. The opposite trend was observed for dwelling B, where the 24-h guideline value of 45 μg m^{-3} recommended by WHO was exceeded on 60 % of days. Despite the higher indoor concentrations in dwelling B, it is worth noting that during the sampling period, the cumulative precipitation reached approximately 130 mm, and a significant negative correlation was found between PM_{10} and relative humidity ($r^2 = 0.81$).

The comparison between dwellings A and B should be considered with caution, as the sampling campaigns were conducted in different periods and under distinct meteorological conditions. In particular, the campaign in dwelling B coincided with higher precipitation, which likely contributed to lower outdoor PM_{10} concentrations. Consequently, the calculated I/O ratios reflect two specific scenarios rather than directly comparable conditions. As rainfall efficiently removes atmospheric particles, any indoor emissions become more evident during wet periods. Although the absence of an air quality monitoring station in Bragança prevents comparison with representative outdoor PM_{10} levels for the heating period, the observed I/O ratios still provide valuable insight into the relative influence of indoor and outdoor sources under the measured conditions.

During the sampling campaign, daily outdoor temperatures ranged from −2.42 °C to 12.1 °C and rainfall (defined as > 0 mm) was recorded on approximately 65 % of the sampling days at both sites. However, the sampling period in dwelling B experienced up to 8 times higher cumulative precipitation than in dwelling A (15.7 mm), which likely enhanced wet deposition of PM_{10} and contributed to lower outdoor concentrations.

The daily PM_{10} cycles (Fig. 2) exhibited distinct modal patterns, with peak concentrations coinciding with the refuelling and burning period. For the hydronic stove, the average indoor PM_{10} concentration did not show statistically significant differences between burning and non-burning days. In contrast, for the wood stove, PM_{10} concentrations were up to four times higher on burning days compared to days without burning. This finding highlights the substantial impact of the older wood stove on PM_{10} levels within the microenvironment.

The wood stove showed the highest concentrations of PM_{10}, particularly when using briquettes, with hourly peaks reaching 225 μg m^{-3}. In contrast, the analysis of PM_{10} concentrations and the logbook notes revealed slight increases for pellets and olive stones, which were linked to activities such as the maid's cleaning tasks and the emptying of the ash tray of the combustion equipment. Similarly, when briquettes and firewood were burned in the old stove, PM_{10} concentration peaks were also registered. These coincided with activities before burning (cooking: fried and grilled), as well as with the startup phase and feeding of the combustion chamber, as recognised by previous studies (Canha et al., 2016, 2018; Vicente et al., 2022). The lower PM_{10} concentrations observed in the room with hydronic stove may be attributed to reduced air permeability, which limits or even prevents the exfiltration of particles from the stove to the indoor environment (Stabile et al., 2018). In perfectly sealed hydronic stoves, this effect would be more pronounced, resulting in negligible particle release to indoor air. Conversely, the lack of proper sealing and uncontrolled combustion in the wood stove contributed significantly to indoor emissions, with notes reporting smell and the presence of smoke at the start and during the burning process. Furthermore, the low efficiency of the equipment did not result in a significant increase in indoor temperature. For example, during combustion in the wood stove, a maximum increase of only 3 °C was observed, with a temperature difference of just 6 °C compared to the outdoor temperature. In contrast, the hydronic stove was designed to maintain a consistent internal temperature range of 25–30 °C, which was reliably preserved throughout the period of use.

3.2. PM_{10} chemical composition

Among the concentrations of PM_{10} constituents (Table 4), OC and EC exhibited high fluctuations for both the wood and hydronic stoves,

Table 3
Statistical summary of indoor and outdoor PM_{10} 24-h measurements.

ID	Fuels	Indoor PM_{10} (μg m^{-3})				Outdoor PM_{10} (μg m^{-3})				
		Mean	SD	Max	Min	Mean	SD	Max	Min	I/O ratio
Dwelling A	Pellets	27.1	11.8	53.1	16.5	38.1	7.59	51.9	28.4	0.74
	Olive stone	23.0	4.53	29.3	15.6	32.8	8.86	47.5	23.3	0.73
Dwelling B	Briquettes	95.9	74.9	259	23.9	25.5	13.3	47.7	12.2	4.53
	Firewood	50.1	25.6	91.5	17.3	8.41	7.19	25.0	2.11	10.7

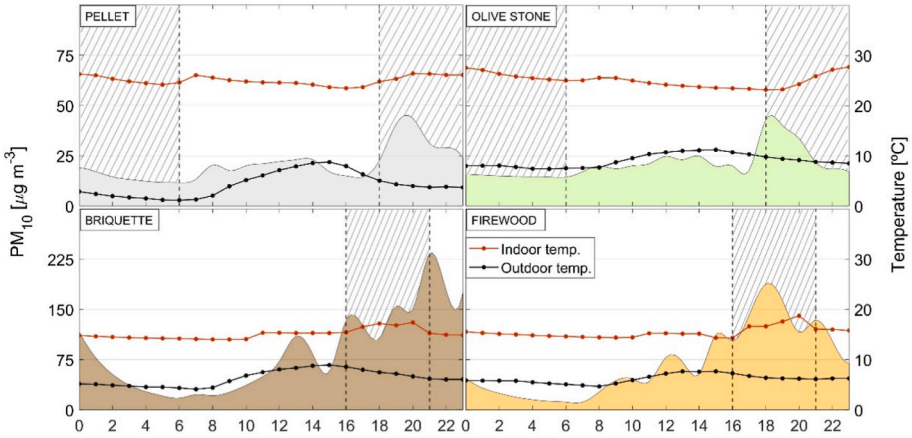

Fig. 2. Diurnal cycle of PM_{10} concentration over a one-week measurement period (shaded area), along with mean indoor (red) and outdoor (black) temperatures. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Table 4
Indoor and outdoor mean concentrations of PM_{10}-bound elements for each biofuel.

[μg m^{-3}]	Pellets		Olive stone		Briquettes		Firewood	
	in	out	in	out	in	out	in	out
OC	5.09	7.13	5.32	6.69	32.5	8.10	22.7	2.79
EC	1.79	2.22	1.58	3.07	3.88	1.94	3.31	0.64
SO_4^{2-}	0.12	1.67	0.14	0.83	0.64	0.48	0.30	0.15
Cl^-	0.16	0.37	0.08	1.09	1.92	1.06	1.12	0.35
PO_4^{3-}	0.02	0.03	0.01	0.04	0.06	0.01	0.07	0.02
NO_3^-	0.05	1.13	0.05	0.89	1.37	0.93	0.91	0.19
F^-	0.02	0.08	n.d.	0.04	0.12	0.06	0.08	n.d.
K^+	0.19	1.98	0.19	2.08	0.81	0.32	0.45	0.11
Na^+	0.09	0.12	n.d.	0.37	0.23	0.59	0.24	0.25
Li^+	0.16	0.13	n.d.	n.d.	0.07	0.06	0.05	0.02
Mg^{2+}	0.04	0.05	0.02	0.06	0.03	0.08	0.02	0.03
Ca^{2+}	0.12	0.14	0.10	0.08	0.15	0.12	0.14	0.04
NH_4^+	0.04	0.21	n.d.	n.d.	0.84	0.30	0.50	0.09
[ng m^{-3}]								
Na	30.3	220	50.9	450	90.6	520	200	300
Mg	60.4	80.2	40.2	80.3	40.3	120	70.2	50.2
Al	40.2	40.8	60.1	20.2	40.2	60.3	40.3	20.8
Si	190	110	190.2	60.5	160	200	170	70.6
P	20.8	30.6	20.4	30.8	60.1	10.4	50.4	10.4
S	110	810	100	330	300	240	180	190
Cl	30.6	520	120	1220	1640	1120	1280	650
K	240	2440	260	2200	700	410	490	370
Ca	130	230	180	160	100	110	130	50.3
Fe	70.3	70.8	60.5	40.4	80.2	140	150	70.2
Ti	4.65	2.10	8.64	1.33	1.88	4.52	2.54	n.d.
V	n.d.	n.d.	0.54	n.d.	n.d.	0.42	n.d.	n.d.
Cr	0.95	1.10	0.55	1.22	1.10	0.91	2.22	3.15
Mn	6.89	13.2	3.98	2.82	2.23	4.23	0.62	2.54
Ni	0.44	0.31	0.22	0.27	0.45	0.49	0.43	0.33
Cu	13.1	2.98	16.0	2.46	21.7	2.68	23.1	8.23
Zn	10.4	43.2	8.25	13.9	22.5	13.6	13.8	9.86
As	0.44	1.33	0.24	0.55	3.46	1.46	2.32	n.d.
Se	n.d.	0.44	0.11	0.14	0.16	n.d.	n.d.	n.d.
Br	1.02	3.55	1.41	4.64	5.36	3.96	5.44	3.45
Rb	0.47	5.28	0.44	1.98	1.14	1.74	n.d.	n.d.
Sr	n.d.	0.78	0.75	0.52	n.d.	n.d.	n.d.	n.d.

*n.d. – not detected.

ranging from 8.76 to 86.7 μg m^{-3} and from 0.87 to 9.59 μg m^{-3}, respectively. Indoor concentrations of OC and EC were not significantly correlated ($p > 0.05$) for any of the fuels, except for firewood. Total carbon (TC = OC + EC) accounted for 27–31 % and 54–58 % of the PM_{10} mass indoors, and 25–28 % and 35–39 % outdoors, for dwelling A and dwelling B, respectively. In general, the I/O ratio was lower than 1 for both OC and EC in samples from the room where pellets (0.71 ± 0.36 and 0.84 ± 0.32) and olive stones (0.85 ± 0.52 and 0.43 ± 0.21) where combusted, indicating the presence of active sources outdoors. However, much higher ratios were observed for both carbon fractions when using the wood stove appliance, with increases of up to six- and three-fold for OC and EC, respectively, suggesting the presence of a predominant indoor source.

Indoor PM_{10} OC/EC ratios varied significantly depending on the type of fuel combusted: 2.84 (pellets), 3.32 (olive stone), 8.38 (briquettes) and 6.85 (firewood). In a review paper, Vicente and Alves (2018) reported that OC/EC ratios in PM_{10} samples vary according to factors such as combustion equipment efficiency, burning rates, and fuel moisture content. These authors also noted that newer and more efficient appliances tend to result in lower OC/EC ratios compared to older combustion appliances. OC/EC ratios obtained in this study are in the range of values reported (Vicente and Alves, 2018) for the combustion of different types of biomass, and are comparable to those obtained in indoor samples by Vicente et al. (2020b) in living rooms equipped with a fireplace (7.5) or a woodstove (5.3). Pio et al. (2011) reported that OC/EC ratios are typically lower than 1 for fossil fuel combustion and generally higher for biomass burning.

Indoors, element oxides accounted for similar PM_{10} mass fraction (wt %) of 7.24 ± 2.14 %, regardless of biofuels. Outdoors, the elemental content was approximately three times higher than that recorded in the rooms (21.1 ± 7.5 %). Higher mass fractions of Ti and Mn were found in the room equipped with the automatic combustion appliance fuelled by pellets or olive stone, revealing substantial differences compared to the manual system, in which briquettes and firewood were burned. The presence of Ti and Mn in pellets and olive pits may be attributed to contamination during processing or handling, and/or to additives or residues from fertilisers, pesticides, or machinery. Automatic stoves operate at higher and more consistent combustion temperatures, which can enhance the volatilisation of these elements and their subsequent condensation into particulate form. However, notable differences were also observed when comparing the most abundant metal(loid)s in indoor PM_{10} samples between the wood stove and the hydronic stove. PM_{10} collected in the room where briquettes and firewood were burned, displayed higher particulate mass fractions for Na, Si, S, Cl, K, Ca, and Fe. The enrichment of Na, Si, Ca and Fe (EF < 10) suggests that these elements are mainly associated with dust resuspension. In contrast, S, Cl, and K exhibited EF values up to three times higher than 10, indicating significant anthropogenic contributions from biomass burning.

The elevated mass fractions of Na, Si, S, Cl, K, Ca and Fe observed in the room where briquettes and firewood were burned can be rationalised by the chemical composition of the fuel and by the behaviour of metals during combustion. The fate of a given metal in combustion emissions (remaining in coarse ash vs. partitioning to finer aerosol) is

strongly influenced by its associated counter-ions and by the overall ash chemistry: alkali metals (K, Na), alkaline earths (Ca), halides (Cl^-) and sulphates promote the formation of low-volatility salts or condensable species that enrich either the particulate or the ash fraction depending on combustion temperature and oxygenation (Jenkins et al., 1998; Knudsen et al., 2004). Several combustion studies have reported that biomass fuels with higher ash contents or distinct inorganic composition (for example, agricultural residues or olive-derived fuels) produce particulate matter with systematically different inorganic fingerprints compared with typical firewood (Kortelainen et al., 2015; Obernberger et al., 2006; Puri et al., 2024). For instance, studies of pellets and other biofuels show enrichment in K, Ca, Na and other crustal elements as part of the inorganic fraction, while comparative work on olive pruning/pomace-based fuels reports notable differences in both organic emissions and ash-forming elements relative to common woody fuels (Boman et al., 2003; Kougioumtzis et al., 2021; Palma et al., 2023; Vicente and Alves, 2018). These differences likely explain the enriched Na, K, Cl and Ca in our samples from the room where briquettes/olive-derived fuels were used. We therefore interpret the measured elemental pattern as the combined result of (i) fuel composition (ash and mineral content), (ii) combustion conditions in the appliance, and (iii) partitioning reactions controlled by counter-ions (e.g., formation of K–Cl, Ca–sulphate phases).

The particulate matter organic extracts encompassed, among others, several polycyclic aromatic hydrocarbons (PAHs), quinones, phenolic compounds, and saccharides (Table 5). Biomass burning has been identified in several studies as a major source associated with PM_{10}-bound constituents, including OC, levoglucosan, K, Cl, SO_4^{2-}, NO_3^- and NH_4^+ (Bhattarai et al., 2019; Brown et al., 2016; Saggu and Mittal, 2020; Thepnuan et al., 2019; Vicente and Alves, 2018). Despite the varying contributions to outdoor PM_{10}, the results of this study reveal significant correlations between PM_{10} mass concentrations and these specific constituents in outdoor samples. Notably, K and Cl exhibited strong correlations with levoglucosan, suggesting that these elements are primarily associated with biomass burning emissions in the ambient air. In contrast, indoor PM_{10} measurements from the room equipped with the stove showed no significant correlations between PM_{10} and biomass burning tracers, with the exception of OC. This absence of correlation aligns with the lack of detectable levoglucosan in the indoor samples, which can be attributed to the high combustion efficiency of modern automatic-fed appliances. Hydronic stoves operate at elevated and stable combustion temperatures, typically above 800 °C, with optimised air-to-fuel ratios, promoting complete combustion and minimising the formation of pyrolysis products such as levoglucosan. On the other hand, indoor PM_{10} mass concentrations obtained during briquette and firewood burning depicted strong and significant correlations with OC, EC, Cl, levoglucosan, SO_4^{2-}, NO_3^- and NH_4^+.

The levoglucosan to mannosan (L/M) ratios can be employed to

Table 5
Indoor and outdoor mean concentrations of PM_{10}-bound organic compounds for each fuel.

[ng m^{-3}]	Pellets		Olive Stone		Briquettes		Firewood	
Polyaromatic and alkyl-aromatic compounds	in	out	in	out	in	out	in	out
Naphthalene	0.81	2.24	0.04	0.94	2.57	2.46	4.58	0.46
Phenanthrene	<LD	0.34	<LD	<LD	<LD	0.27	<LD	<LD
Anthracene	<LD	0.04	<LD	<LD	<LD	<LD	<LD	<LD
Fluoranthene	<LD	0.16	<LD	0.09	0.71	0.04	0.04	<LD
Pyrene	<LD	0.21	<LD	0.12	0.84	0.04	0.18	<LD
Benzo[e]pyrene	0.11	1.05	0.04	1.53	2.06	3.33	2.39	0.30
Benzo[a]pyrene	0.05	0.94	<LD	1.28	2.26	2.62	3.88	0.18
Benzo[a]anthracene	<LD	0.72	<LD	0.77	1.62	0.59	1.90	0.11
Chrysene	0.02	1.25	<LD	1.16	2.14	0.94	2.25	0.21
Benzo[b]fluoranthene	0.25	1.45	0.11	2.17	2.90	4.26	3.19	0.42
Benzo[k]fluoranthene	0.10	1.22	<LD	1.99	2.75	3.64	4.10	0.28
Perylene	0.06	0.28	0.04	0.33	0.52	0.18	0.88	0.05
Indeno[1,2,3-cd]pyrene	0.20	1.13	0.19	2.02	2.46	0.83	3.78	0.37
Benzo[g,h,i]perylene	0.17	1.03	0.19	1.76	2.31	0.70	2.98	0.32
Dibenzo[a,h]anthracene	<LD	0.21	<LD	0.34	0.48	0.15	0.70	0.06
Picene	<LD	<LD	<LD	0.14	0.23	0.10	0.36	0.04
Coronene	0.06	0.40	0.03	0.73	0.89	0.24	1.37	0.08
Methylnaphthalene	<LD	<LD	<LD	<LD	0.59	<LD	0.18	<LD
2-Methylanthracene	<LD	<LD	<LD	0.06	0.30	0.14	0.03	<LD
Retene	<LD	0.22	<LD	0.08	1.57	0.16	0.17	0.02
1-Methylpyrene	<LD	0.03	<LD	0.03	0.17	0.03	<LD	<LD
Quinones and oxy-aromatic compounds								
2,6-Di-tert-butyl-1,4-benzoquinone	0.87	1.46	0.14	0.51	1.43	0.25	1.36	<LD
9-Fluorenone	<LD	0.08	<LD	<LD	<LD	<LD	<LD	<LD
Xanthone	0.11	0.04	0.05	<LD	0.43	<LD	0.06	0.31
Acenaphthenequinone	<LD	<LD	0.05	0.06	0.10	<LD	<LD	<LD
9,10-Phenanthrenequinone	0.83	3.15	0.43	1.39	10.23	3.23	7.51	1.24
Benzo[a]anthracene-7,12-dione	0.05	0.47	0.02	0.40	0.79	1.22	0.57	0.08
5,12-Naphthacenequinone	0.02	0.17	<LD	0.19	0.48	0.92	0.47	0.04
Phenolic compounds								
3-Hydroxybenzoic acid	0.36	0.09	0.07	0.04	0.03	<LD	<LD	<LD
4-Hydroxybenzoic acid	1.90	1.13	0.51	0.80	1.20	1.07	1.23	0.35
Saccharides [µg m^{-3}]								
Levoglucosan	n.d.	19.2	n.d.	1.92	19.6	21.0	44.7	n.d.
Mannosan	n.d.	0.97	n.d.	0.15	3.93	1.87	3.50	n.d.
Galactosan	n.d.	2.65	n.d.	1.74	3.83	2.10	3.28	0.59
Arabinose	3.48	1.48	1.75	n.d.	11.9	1.43	11.3	0.92
Glucose	n.d.	1.00	0.41	1.82	0.95	0.59	1.00	0.17
Mannose + Xylose	n.d.	n.d.	n.d.	0.06	0.22	0.11	0.12	n.d.
Fructose	0.25	0.49	0.69	n.d.	n.d.	0.37	n.d.	n.d.
Sucrose	0.92	n.d.	1.87	0.92	4.79	n.d.	3.66	n.d.

*LD – Limit of detection.
*n.d. non-detected in any samples.

distinguish biomass categories. The average L/M ratio for indoor PM_{10} during briquette (4.98) and firewood (12.8) combustion showed similar values than those reported in previous studies (Caseiro et al., 2009; Cordell et al., 2016; Engling et al., 2009; Schmidl et al., 2008, 2011) for softwood (2.6–6.9) and hardwood (13–24) combustion, respectively. In addition to the type of wood, variations in L/M ratios may also be influenced by operational parameters, such as fluctuating temperatures and oxygen availability during combustion (Schmidl et al., 2008). Outdoors, the L/M ratio was higher than 11, indicating a prevalence of hardwood combustion. Unlike hydronic stoves, which maintain consistent, well-controlled combustion, traditional stoves operate with intermittent fuel feeding and undergo smouldering, oxygen-limited phases that favor the formation of pyrolysis products such as levoglucosan.

Among the 16 priority PAHs stipulated by the U.S. EPA, acenaphthylene, acenaphthene, and fluorene, were not detected in any of the samples. Overall, the highest indoor concentrations of total PM_{10}-bound PAHs were observed in samples during briquette and firewood combustion, with benzo[a]pyrene (BaP) reaching mean values of 3.88 ng m^{-3} and 2.26 ng m^{-3}, respectively. These compounds are of particular concern due to their carcinogenic and mutagenic potential. Jakovljević et al. (2023) found that BaP alone accounted for more than 60 % of the total toxic equivalent concentration (BaPeq) of PAHs associated with PM_{10}, underscoring its significant contribution to the overall carcinogenic potential. Additionally, genotoxicity studies conducted by Mourón et al. (2006) demonstrated that BaP induces DNA strand breaks and significantly increases sister chromatid exchanges in human lung fibroblast cells, confirming its high genotoxicity even at low concentrations.

Naphthalene was the most abundant PAH detected in PM_{10} samples across all scenarios, with the highest indoor mean concentration observed during firewood combustion (4.58 ng m^{-3}). This suggests that naphthalene is a common product of incomplete combustion, occurring under both traditional manually operated systems and modern automatic appliances. Despite differences in combustion efficiency and control, its consistent presence in PM_{10} indicates that naphthalene plays a significant role as a dominant PAH associated with biomass burning emissions, including pellets, olive stone, firewood, and briquettes. Phenanthrene, anthracene, and fluoranthene were not detected in the PM_{10} samples. This absence may be attributed to multiple factors, including combustion conditions, compound volatility, and the physicochemical properties of the fuels. High combustion efficiency and stable temperatures, particularly in modern hydronic stoves, can promote the complete thermal degradation of PAHs typically associated with smouldering and oxygen-limited phases (Priestley et al., 2023).

Low-molecular-weight (LMW) PAHs, such as naphthalene and phenanthrene, were more prevalent in PM_{10} from the room equipped with the automatic combustion appliance, whereas high-molecular-weight (HMW) PAHs, including chrysene, benzo[b]fluoranthene, and indeno[1,2,3-cd]pyrene, predominated in PM_{10} samples from the room with the traditional system. These findings are consistent with previous studies indicating that the incomplete combustion of firewood and briquettes leads to significant emissions of HMW PAHs. Zhang et al. (2022) emphasised that biomass rich in volatiles and lignin tends to produce higher amounts of phenyl radicals during combustion, which are key intermediates in the formation of HMW PAHs. Furthermore, PM_{10} samples collected during firewood combustion exhibited the highest total PAH concentration ($\sum$PAHs = 32.9 ± 1.6) exceeding the levels observed for briquettes, olive stones, and pellets by factors of 1.2, 51, and 18, respectively. The thermochemical properties of the specific fuels used in this study (Table 2) help to explain these observations. Firewood presented notably higher moisture content on a wet basis compared to pellets and olive stone (4.09 % and 14.3 %), which likely contributed to less efficient combustion. Additionally, firewood had the highest ash content (1.52 %) and the lowest lower heating value (10.5 MJ kg^{-1}), further indicating suboptimal combustion performance. In contrast, pellets, with their low moisture and ash contents and higher energy density (lower heating value of 17.9 MJ kg^{-1}), promote more complete and stable combustion. These physical and chemical differences are critical, as low-density and high-moisture fuels are known to favor smouldering phases and oxygen-limited conditions during combustion. The lower bulk density of such fuels reduces packing efficiency and airflow, while high moisture content consumes part of the released heat for water evaporation, thereby lowering combustion temperature and delaying ignition. These processes inhibit complete flaming oxidation and promote incomplete combustion, typically associated with higher emissions of high-molecular-weight PAHs (Shen et al., 2012; Vicente et al., 2015).

Several quinones and other oxygenated aromatic compounds were identified in the PM_{10} samples, with particularly elevated concentrations of 9,10-phenanthrenequinone detected indoors during briquette (10.2 ng m^{-3}) and firewood (7.51 ng m^{-3}) combustion. This compound has been strongly associated with oxidative stress and cytotoxic effects (Kim et al., 2022; Yang et al., 2018). Notably, 2,6-di-tert-butyl-1,4-benzoquinone (DTBB), a synthetic antioxidant degradation product, was detected in PM_{10} from all combustion conditions, with higher levels recorded during briquette and firewood burning. The detection of 2, 6-di-tert-butyl-1,4-benzoquinone in all PM_{10} samples could be due to several factors. This quinone can form as a byproduct through oxidative degradation of organic matter, particularly under high-temperature or inefficient combustion conditions. The presence of tert-butyl groups in the quinone structure suggests that the combustion of certain fuels or additives might involve organic compounds with tert-butyl groups (Liu et al., 2017). Moreover, DTBB is recognised as a degradation product of antioxidants used in plastics, such as butylated hydroxytoluene (BHT), possibly related to additive use or plastic contamination in the fuel matrix (Kato and Conte-Junior, 2021). DTBB levels in indoor PM_{10} samples from briquette and firewood combustion (1.43 ng m^{-3} and 1.36 ng m^{-3}, respectively) were notably lower than those documented for outdoor $PM_{2.5}$ samples collected near a chemical industrial complex (115 ng m^{-3}) (Alves et al., 2023). However, its concentrations were higher than those previously reported for an University cafeteria (0.44 ng m^{-3}) and residential environments using vacuum cleaners (1.34 ng m^{-3}) (Alves et al., 2020; Vicente et al., 2020c). Experimental studies have shown that DTBB can induce cleavage of supercoiled DNA at low concentrations, indicating its potential for genotoxicity and greater toxicity compared to its precursor compounds, such as butylated hydroxytoluene (BHT) (Liu and Mabury, 2020; Nagai et al., 1993).

Alongside DTBB, bis(2-ethylhexyl) phthalate emerged as one of the most prominante plasticisers detected in the PM_{10} samples. Notably high indoor concentrations were observed during briquette (31.5 ng m^{-3}) and firewood (25.6 ng m^{-3}) combustion (Table S2). Plasticisers, such as phthalates, are extensively used in a variety of applications, including fuel packaging and building materials, and personal care products (Vogelsang et al., 2020).

3.3. Oxidative potential

The oxidative potential of PM_{10} samples collected during biomass combustion was evaluated using two complementary acellular assays: dithiothreitol (DTT) and ascorbic acid (AA). OP values were normalised by the volume of sampled air (OPv^{DTT} and OPv^{AA}), providing an inhalation-based exposure metric. As shown in Table 6, OPv^{DTT} and OPv^{AA} varied significantly across fuel types. PM_{10} collected in the room during firewood and briquette combustion exhibited the highest OP responses, reflecting an enhanced capacity to generate reactive oxygen species (ROS). This elevated OP is consistent with the chemical profiles of these samples, which included higher concentrations of redox-active compounds such as quinones, PAHs, and higher levels of elemental carbon acting as a carrier for these reactive species. (Farahani et al., 2022). Conversely, indoor PM_{10} samples associated with pellet and olive stone combustion, demonstrated lower depletion rates in both assays, suggesting a lower oxidative burden. Interestingly, while both OP assays

Table 6
Values of DTT and AA normalised by the sample volume for each sampled fuel.

Sampling fuel		OPv^{AA} (pmol min^{-1} m^{-3})			OPv^{DTT} (pmol min^{-1} m^{-3})		
		min	max	mean ± SD	min	max	mean ± SD
Pellets	in	45.2	280	207 ± 71	142	320	237 ± 99
	out	187	1340	667 ± 386	1228	1870	1464 ± 196
Olive stone	in	29.1	195	168 ± 47	102	383	209 ± 93
	out	65.8	785	405 ± 207	509	1595	979 ± 401
Briquettes	in	62.9	8810	2145 ± 2894	487	4762	1484 ± 1383
	out	160	1457	597 ± 400	269	1705	803 ± 475
Firewood	in	334	2380	1196 ± 747	660	1666	996 ± 321
	out	8.91	585	347 ± 210	26.1	707	261 ± 251

showed comparable response ranges for pellets and olive stone, no significant correlations were observed between OPv values and specific PM_{10}-bound elements. These OP values are in good agreement with those previously reported for residential environments without combustion sources, such as in (Cipoli et al., 2025), where values ranged from 30 to 530 pmol min^{-1} m^{-3} (OPv^{AA}) and 10–380 pmol min^{-1} m^{-3} (OPv^{DTT}). For both assays, significant differences in OP values were observed among fuel types (Mann–Whitney test, $p < 0.05$), with higher oxidative responses for PM_{10} from firewood and briquette combustion compared with pellet and olive-stone samples.

In general, the I/O ratios were below 1 for both OP assays in PM_{10} samples collected during hydronic stove operation. Nevertheless, I/O ratios higher than 1 were observed for OPv^{AA} and OPv^{DTT} in PM_{10} samples collected in the room equipped with the traditional combustion system. OP values for outdoor PM_{10} in this study were higher than those reported for a suburban site by (Pietrogrande et al., 2018), where OPv^{DTT} and OPv^{AA} reached 240 and 290 pmol min^{-1} m^{-3}, respectively. Notably, the mean PM_{10} concentration at that site (33 μg m^{-3}) was comparable to the levels observed during the pellet and olive stone combustion period in this study. This stresses that PM mass concentration alone is not a reliable indicator of aerosol toxicity, highlighting the importance of considering chemical composition and oxidative potential. In fact, for indoor samples, lower and not statistically significant correlations were found between PM_{10} concentrations and OP values (for both assays). In contrast, outdoor PM_{10} exhibited significant correlations with OP, except for the firewood burning period. Moreover, no significant correlation was found during the sampling period between OPv^{DTT} and OPv^{AA}, suggesting that the AA and DTT assays may respond to different PM_{10}-bound constituents.

Significant positive correlations were observed between oxidative potential (OPv^{AA} and OPv^{DTT}) and several PM_{10}-bound components during briquette and firewood combustion. For briquettes, OP was correlated with OC, PO_4^{3-}, NO_3^-, NH_4^+, Fe, Cu, glucose and EC, SO_4^{2-}, Cl, NH_4^+ and Rb. For firewood, significant associations were found with SO_4^{2-}, Ca^{2+}, Al, Si, Mg, Zn, Ti, Fe, Cl, mannose, EC, Cu, NH_4^+, and NO_3^-. Notably, EC, Fe, Cl, Cu, NO_3^-, SO_4^{2-}, and NH_4^+ consistently displayed positive correlations with at least one of the OP assays for PM_{10} samples collected indoors during wood stove operation, indicating they act as common redox active species.

In outdoor samples, both assays exhibited strong correlations ($r^2 > 0.8$) with levoglucosan, a tracer of biomass burning (Bhattarai et al., 2019), supporting its significant contribution to ambient PM toxicity, as previously reported for Bragança during winter (Cipoli et al., 2023c). Indoors, despite weaker correlations with levoglucosan, OPv^{AA} and OPv^{DTT} were closely associated with secondary inorganic ions (especially nitrate and sulphate), likely reflecting the role of combustion-related precursors and secondary aerosol formation in redox activity. This is in line with previous findings indicating the oxidative relevance of secondary species in biomass burning environments (Cesari et al., 2019; Fang et al., 2016; Massimi et al., 2020; Paraskevopoulou et al., 2019).

The concentrations of total PAHs in outdoor samples showed strong and statistically significant correlations with both OP assays throughout all sampling periods. Indoors this association was only evident for PM_{10} sampled in the room where briquettes and firewood were combusted, suggesting that PAHs may contribute to the oxidative potential of PM_{10} from these biomass fuels. Nonetheless, such correlations must be interpreted with caution, as previous studies have shown that individual PAH species often exhibit limited or negligible activity in ROS assays (Molina et al., 2020). Therefore, the associations observed may more accurately reflect the influence of co-emitted redox-active compounds rather than the intrinsic reactivity of PAHs themselves (Kramer et al., 2020; Pirhadi et al., 2020). This interpretation is supported by significant correlations between ∑PAHs and both ∑quinones and ∑phenolic compounds, as well as with established biomass burning markers such as levoglucosan, and key indicators like Cl and K, which have been associated with ROS formation and oxidative reactivity (Bates et al., 2019; Paraskevopoulou et al., 2019). Notably, ∑quinones and ∑phenolics showed particularly strong correlations with OPv^{AA} ($r^2 = 0.89$ and $r^2 = 0.81$, respectively), emphasising their likely role in driving oxidative potential in combustion-impacted environments. These results are consistent with seasonal observations from other studies, which report elevated oxidative activity during colder months due to increased biomass burning (Li et al., 2019; Lyu et al., 2018; Tuet et al., 2019).

It should be noted that the DTT assay is more responsive to organic redox-active species, particularly quinones and other aromatic compounds capable of electron transfer, whereas the AA assay is more sensitive to transition metals and inorganic oxidising species (Kato and Conte-Junior, 2021; Romano et al., 2020). Hence, differences between OPv^{DTT} and OPv^{AA} reflect the distinct chemical composition of PM_{10} generated during the use of each fuel. The higher OP values observed in PM_{10} from firewood and briquette combustion indicate the predominance of organic redox-active compounds and transition metals typically associated with incomplete combustion, while the lower responses recorded for pellet and olive stone samples suggest that PM_{10} are dominated by less reactive PM_{10}-bound element. These findings reinforce that the PM_{10} oxidative potential results from the combined contribution of multiple redox-active species rather than from any single compound class. Although these associations are compelling, correlation-based findings must be interpreted with caution, as they do not establish causality. The oxidative potential of PM_{10} is shaped by a complex mixture of constituents, including PM_{10}-bound elements, quinones, and possibly other unidentified compounds not measured in this study. As such, the interplay of multiple redox-active species may confound direct attribution to any single compound class.

3.4. Ecotoxicological assays

Ecotoxicity of indoor and outdoor PM_{10} was assessed using the aqueous extracts and expressed in Toxicity Units (TU). The results showed TU values ranging from 0.67 to 12.4. Among the outdoor samples, 22 % were classified as non-toxic, 75 % as toxic and one sample (3 %) as very toxic (Fig. 3). Non-toxic samples were predominantly observed outdoors during rainy periods, which likely contributed to the lower concentrations of PM_{10}-bound constituents. Indoors, PM_{10} samples collected during pellet and olive stone combustion showed no

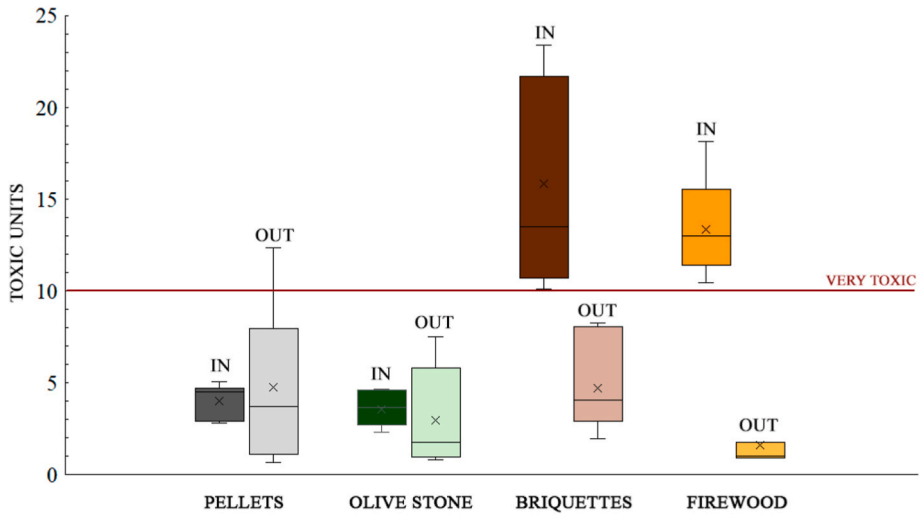

Fig. 3. Toxic units (TU) obtained for the PM_{10} samples collected during the combustion of woody-based fuels. The threshold for 'very toxic' (TU = 10) is indicated by a red line. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

significant correlation between TU and PM_{10}-bound elements. All samples were classified as toxic, with TU values ranging from 2.32 to 5.05.

All PM_{10} samples collected indoors during wood stove operation were classified as very toxic. The increased ecotoxicity can be primarily attributed to specific PM_{10}-bound constituents, with significant and strong correlations ($r^2 > 0.8$) observed in PM_{10} samples from the room where briquettes (OC, EC, Cl, PO_4^{3-}, NO_3^-, NH_4^+, Ni and Rb), and firewood (Cl, PO_4^{3-}, NO_3^-, F^-, S, Ti, Cu, Cr, Fe and Ni) were burned. Notably, PM_{10} samples from firewood burning exhibited the highest mass fractions of several redox-active elements, including Fe, Cr, Cu, and Ni, which have been previously shown to intensify toxicity over time in bioassays (Yang et al., 2016). These results are consistent with previous studies that reported increased ecotoxicity of PM from biomass combustion (Cipoli et al., 2023c; Romano et al., 2020; Sainnokhoi et al., 2022; Vicente et al., 2021). They suggest that wood stove emissions can induce ecotoxicity levels up to five times higher than those from hydronic stoves, even at lower PM_{10} mass concentrations.

In addition to inorganic constituents, organic compounds also played a central role. Strong and significant correlations were observed between TU and ∑PAHs for PM_{10} collected during briquette ($r^2 = 0.93$) and firewood combustion ($r^2 = 0.89$), indicating that polyaromatics make a substantial contribution to the overall toxicity of PM_{10}. These results align with the literature, where PAHs are recognised for their genotoxic and associated with increased toxicity in PM (Kováts et al., 2021). Therefore, correlations between TU and ∑PAHs should be interpreted as indicative rather than causal, representing the co-occurrence of PAHs with water-soluble or bioavailable compounds that are more likely to drive the observed ecotoxic responses.

Quinones, particularly 9,10-phenanthrenequinone and DTBB, also exhibited statistically significant correlations between TU and indoor PM_{10} samples during wood stove operation, indicating their contribution to bacterial luminescence inhibition. The co-occurrence of elevated mass fractions of both PAHs and quinones, and specific PM_{10}-bound elements in these samples, suggests a multifaceted mechanism of toxicity. Organic and inorganic components may act synergistically to enhance the oxidative burden, leading to increased toxic responses (Van Den Heuvel et al., 2018). In contrast, PM_{10} from pellets and olive stone combustion showed lower concentrations of these harmful constituents and correspondingly reduced TU values. This highlights the critical influence of fuel composition, combustion technology, and conditions on indoor air ecotoxicity profiles.

4. Conclusions

For the first time in Bragança, a comprehensive indoor/outdoor winter assessment of PM_{10} levels was conducted in living rooms and outdoors during the use of residential biomass-burning heating appliances, focusing on detailed characterisation, oxidative potential, and ecotoxicity. Significant differences in PM_{10} oxidative potential and ecotoxicity were observed across the monitored scenarios. In the room equipped with an automatic hydronic stove, lower PM_{10} levels were observed, along with reduced OP and ecotoxicity responses, indicating more efficient combustion. In contrast, during briquette and firewood combustion in a manually fed stove, the highest OP and ecotoxic responses were found for PM_{10}-bound constituents. The lack of correlation between OP assays and indoor PM_{10} concentrations, along with divergent assay-specific associations, highlights the need for multiple OP assays. Outdoor samples showed strong correlations with levoglucosan, confirming biomass burning as a dominant source during winter. PAHs, quinones and phenolic compounds were significantly associated with OP assays, especially under incomplete combustion conditions. Ecotoxicological trends aligned with OP, with briquette and firewood combustion presenting the most PM_{10} harmful profiles, driven by the synergistic effects of PAHs, quinones, and specific PM_{10}-bound elements.

These findings reinforce that PM_{10} mass alone is insufficient to assess aerosol toxicity. Regulatory efforts should prioritise the replacement of inefficient combustion systems and the implementation of public awareness and mitigation strategies to reduce health risks associated with residential biomass burning. Importantly, the results highlight critical trade-offs between renewable energy goals and public health, as biomass combustion, particularly in outdated systems, contributes to the formation of highly redox-active species that drive oxidative stress and adverse toxicological responses, posing significant risks to the human health.

CRediT authorship contribution statement

Yago Alonso Cipoli: Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis, Conceptualization. **Estela D. Vicente:** Writing – review & editing, Methodology. **Isabella Charres:** Methodology. **Margarita Evtyugina:** Methodology. **Marina Alfosea-Simón:** Methodology. **Franco Lucarelli:** Methodology. **Nora Kováts:** Methodology. **Jiří Ryšavý:** Methodology. **Manuel Feliciano:** Writing – review & editing, Supervision. **Célia Alves:** Writing – review

& editing, Writing – original draft, Supervision, Methodology, Funding acquisition, Conceptualization.

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.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.atmosenv.2025.121700.

Data availability

Data will be made available on request.

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