A comprehensive assessment of emissions from prescribed fires in two Mediterranean shrublands: chemical and morphological analysis

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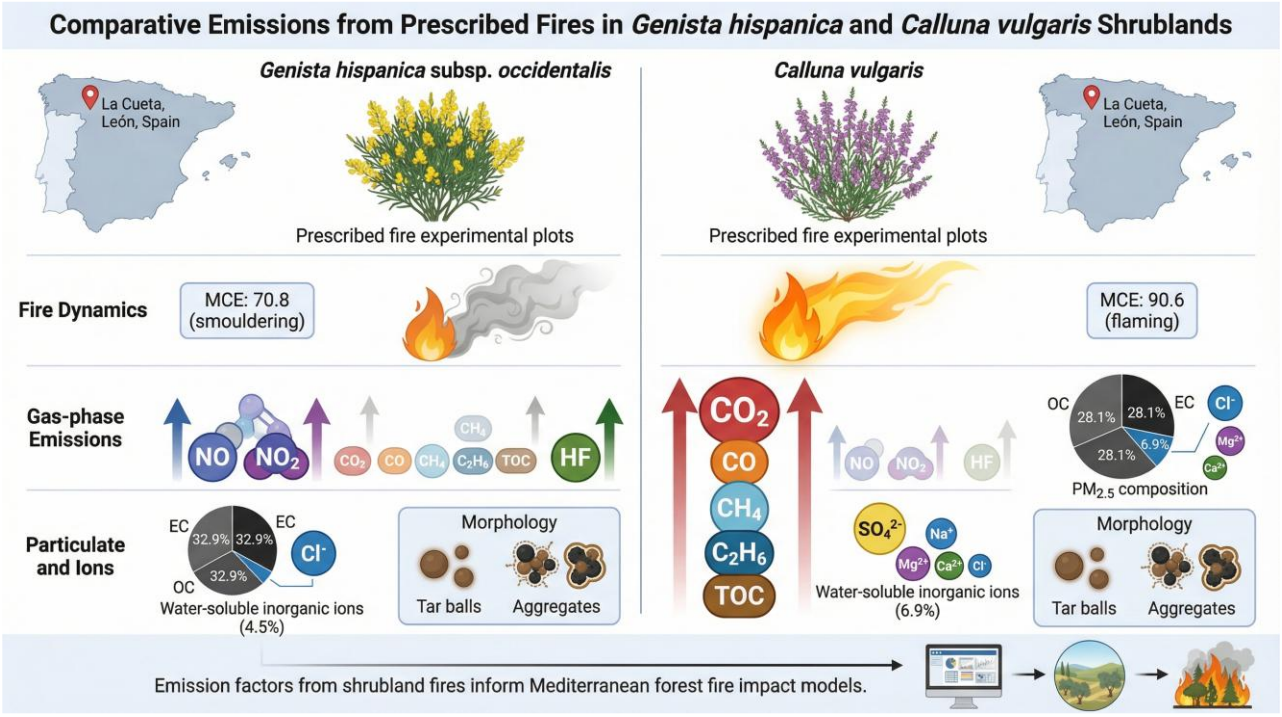
Abstract. Prescribed fires were conducted in two shrubland communities dominated by *Genista hispanica* subsp. *occidentalis* and *Calluna vulgaris* in La Cueta, León, Spain, to characterise particulate and gaseous emissions during combustion. Distinct fire dynamics were observed: *Calluna* exhibited a Modified Combustion Efficiency (MCE) of 90.6 %, indicative of flaming combustion, while *Genista* showed an MCE of 70.8 %, characteristic of smouldering conditions. Gas-phase analysis revealed notably higher concentrations of CO_2, CO, CH_4, C_2H_6, and total organic carbon (TOC) in *Calluna* compared to *Genista*, with CO_2 showing the greatest difference. Conversely, *Genista* exhibited slightly elevated NO and NO_2 levels. Most gas concentrations were higher for *Calluna*, except for hydrogen fluoride (HF), which was more abundant in *Genista*. Elemental carbon (EC) and organic carbon (OC) accounted for 28.1 % and 32.9 % of $PM_{2.5}$ mass in *Calluna* and *Genista*, respectively. Water-soluble inorganic ions contributed 6.9 % and 4.5 % to $PM_{2.5}$ mass, with most ions more abundant in *Calluna*, except chloride (Cl^-), which was higher in *Genista*. In both cases, Cl^-, SO_4^{2-}, Na^+, Mg^{2+}, and Ca^{2+} dominated the ionic composition. Morphological analysis revealed a population dominated by tar balls (submicrometer spherical particles) and aggregates with thick organic coatings. Derived emission factors are expected to provide valuable input for numerical models evaluating the impacts of prescribed and unplanned forest fires in the Mediterranean region.



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1. Introduction

In Europe, vegetation fires have increased in number and area over the last 50 years and the Mediterranean region is particularly affected. The depopulation of mountain areas has led to the uncontrolled development of shrublands, increasing the amount of fuel and the risk of fire (Elia et al., 2020). Thus, around two-thirds of forest land burned annually in the NW of
35 Spain correspond to shrublands (Vega et al., 2022). Shrubland fires release significant quantities of atmospheric carbonaceous material and greenhouse gases, with major impacts on air quality and the carbon cycle (Jacobson, 2001; Yokelson et al., 2007).

In the Mediterranean area, prescribed fire is a widely used management tool to reduce wildfire risk and to manage habitats for pastoral, hunting or nature conservation purposes. Prescribed burning is increasingly recognised as a cost-effective
40 strategy to reduce wildfire risk and is now integrated into adaptive fire management frameworks guided by seasonal forecasts (Fernandes et al., 2013; Turco et al., 2019). This is because it reduces the spread and intensity of subsequent wildfires, increasing the effectiveness and safety of fire suppression operations (Fernandes and Botelho, 2003) or decreasing impacts on ecosystems (Huffman et al., 2020; Reinhardt et al., 2008), and on people and assets (Burrows and McCaw, 2013). Furthermore, burning provides the additional benefit of ash fertilisation by quickly recycling minerals back to the soil

(McCarty, 2011) and influences the ecological aspects of the environment due to the observation of a close relationship between smoke from shrubland fires and post-fire seed germination processes after the fire (Bargmann et al., 2014). However, despite its growing use, emission factors for shrublands in Mediterranean Europe remain understudied, particularly under real field conditions.

The main disadvantage of prescribed burnings is the emission of particulate matter (PM) and gaseous pollutants, which can affect local and regional air quality and inhalation exposures. Ambient particulate matter with an aerodynamic diameter of 2.5 μm or less ($PM_{2.5}$), has been classified as a Group I carcinogen by the International Agency for Research on Cancer (Loomis et al., 2013). Combustion produces large amounts of carbonaceous material in the atmosphere, especially elemental carbon (EC) and organic carbon (OC), which alter the Earth's radiative balance (Bond et al., 2013). EC is an important absorber of solar radiation, playing an important role in climate change, while OC primarily scatters solar radiation opposing the heating effect of EC. However, biomass-burning OC can contain light-absorbing brown carbon (BrC), which absorbs radiation mainly at near-UV and short visible wavelengths and can partly offset the cooling effect of scattering organic aerosol (Saleh et al., 2015). Recent studies also show that combustion conditions such as fuel moisture, oxygen availability, and heat flux can significantly influence the emission of toxic compounds like polycyclic aromatic hydrocarbons (PAHs), offering insights into how prescribed burning might be optimized to reduce harmful byproducts (Töpperwien et al., 2025). During biomass combustion, CO_2 and water are the main products generated, mainly during the flaming phase, while CH_4, N_2O, CO and other hydrocarbons are mostly emitted during the smouldering phase (Ward and Hardy, 1991). Recent estimates indicate that global carbon emissions from biomass burning range between 2,200 and 2,700 Tg C $year^{-1}$, while fossil fuel combustion and cement production alone emitted approximately 9,839 Tg C $year^{-1}$ in 2017 (Gilfillan and Marland, 2021).

The analysis of emissions from biomass burning is important because forest ecosystems (occupying more than $4 \cdot 10^9$ ha globally) are natural carbon and nitrogen sinks that could play an important role against climate change (Evgrafova et al., 2018; Luyssaert et al., 2008). Numerous studies have assessed emission factors of gaseous and particulate constituents, such as the one by Yang et al. (2019), who have characterised air pollutants emitted by eight main tree species in subtropical China, under both smouldering and flaming stages, using a self-designed combustion system. However, studies in the Mediterranean region are scarce (Alves et al., 2010b, a; Andreae, 2019; Bertschi et al., 2003; Soares Neto et al., 2009; Yokelson et al., 2009). One of the main findings is that fire characteristics can influence emission factors of gaseous and particulate constituents. The Modified Combustion Efficiency (MCE) is often used to assess the combustion efficiency, with a strong correlation between high MCE values and a high degree of fuel packing (Soares Neto et al., 2009).

The morphology of the particles emitted during biomass burning, specifically the presence of tar balls (spherical organic particles), plays a crucial role in the optical properties of the aerosol. These particles can experience a "lensing effect" that enhances light absorption when they coat carbonaceous cores, thereby affecting radiative forcing. Likewise, the internal mixing of organic matter with inorganic salts during atmospheric aging increases the particles' hygroscopicity, facilitating their role as cloud condensation nuclei (CCN) (Bond et al., 2013; Moffet and Prather, 2009; Pósfai et al., 2004). European

heathlands dominated by the ericaceous shrub Calluna vulgaris are ecosystems of high ecological, cultural, and carbon-storage value (Fagúndez, 2013), but they are also affected by both wildfires and prescribed fires (Grau-Andrés et al., 2019; McMorrow, 2011). In a study carried out in Scotland, Grau-Andrés et al. (2019) observed that a higher fire severity improved the abundance of ericoid and graminoid species, suggesting that a specific prescribed fire condition can help achieve management objectives. Similarly, in Norway, Vandvik et al. (2014) reported that young *Calluna vulgaris* stands showed vigorous resprouting and germination after moderately severe fires. In the same way, shrublands dominated by *Genista hispanica* are also important in areas with alkaline soil reaction in Northern Spain. After a fire, this species usually regenerates by vegetative regrowth, as seed-based regeneration is very scarce. Prescribed fires and the feed by native livestock are usually necessary to avoid high fuel loads in these formations (Martín and Oria de Rueda, 2021).

The main aim of this study is to estimate particulate and gaseous emission factors, including water-soluble inorganic ions, for two shrub species: *Calluna vulgaris* and *Genista hispanica* subsp. *occidentalis*. By integrating gas analysis, $PM_{2.5}$ chemical composition, and particle morphology, this study establishes a direct link between the fire behaviour of each species and its atmospheric impact. Notably, this work is based on a field campaign rather than laboratory experiments, thereby reflecting in-situ fire conditions. Estimated emission factors will provide valuable input for numerical models evaluating the impacts of prescribed and unplanned forest fires in the Mediterranean region for a deeper understanding of fire–atmosphere interactions.

2. Material and methods

2.1. Sampling campaign

Six prescribed fires were conducted on two types of shrub species (*Genista hispanica* subsp. *occidentalis* (hereafter *Genista*) and *Calluna vulgaris* (hereafter *Calluna*)) to characterise the emissions (particulates and gases) from the burning process. Four quartz filters were sampled during *Genista* burning and two during *Calluna* burning (~1000 m^2 were burned in each plot). The fires were carried out in La Cueta, León (NW Spain), within a protected natural area ("Natural park of Babia y Luna") on October 3rd and 4th, 2016 (Figure 1). Several sampling and monitoring instruments were used: *i*) a low volume TECORA ECHOPM sampler operated at a flow rate of 38.3 L min^{-1} to collect $PM_{2.5}$ onto quartz filters; *ii*) TEDLAR bags to sample smoke for further analysis; iii) CO and CO_2 Combo IAQ Meter; and iv) a weather station Geos N11 to record meteorological variables at 1.85 m above the ground, at 10 s intervals; *v*) an infrared camera type Flir Systems to obtain the characteristics of the fires (mean rate of spread, mean temperatures and residence time). The sampling duration for each $PM_{2.5}$ filter was adjusted to the duration of the smoke plume generated by each prescribed fire and ranged from 6 to 15 min. Four $PM_{2.5}$ filter samples were collected during *Genista* burning and two during *Calluna* burning. Smoke samples for gaseous analysis were collected in TEDLAR bags during the active combustion period, avoiding the entrainment of

background air as far as possible. The $PM_{2.5}$ sampler, TEDLAR bag sampling system, CO/CO_2 monitor, meteorological station, and infrared camera were positioned at ground level approximately 10 m downwind of the fire front.

Figure 1. Location of La Cueta in northwestern Spain and surrounding areas. Site of prescribed fire experiments. Map source: ArcGIS Online © Esri and its licensors.

2.2. Chemical analysis

We conducted various chemical analyses to characterise the particulate matter and gases emitted during the burning:

i) Elemental analysis of *Calluna* and *Genista* fuel samples before burning was carried out by combustion at high temperatures, separation of the gases produced and detection by TCD (Dumas Method) with an accuracy of 0.2 %. The parameters analysed were total humidity, volatiles, ash at 550 and 815 ºC, C, H, N, and S content, Low Calorific Value (LCV), and High Calorific Value (HCV). The analysis was carried out according to the current regulations (ASTM International, 2016, 2018, 2019; UNE, 1984a, b, 1995, 2010).

ii) The quartz filters were used to quantify $PM_{2.5}$ by gravimetry (sensitivity: 0.00001 g) on an electronic semi-microbalance (Mettler Toledo, XPE105DR) and total carbon (TC) by a Thermal Optical Transmittance method. This method allows the split of TC mass into organic carbon (OC) and elemental carbon (EC). The technique and equipment used are described in Pio et al. (2011) and Castro et al. (1999).

iii) The concentration of the main water-soluble inorganic ions in Teflon filters was obtained through ion chromatography using a Thermo Scientific DionexTM ICS-5000 equipment provided with an IonPac® CS16 column (4×250 mm) for the analysis of cations (Li^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, NH_4^+) and an IonPac® AS11 column (4×250 mm) for the analysis of anions (F^-, Cl^-, SO_4^{2-}, NO_3^-, NO_2^-).

iv) Major gaseous components in the smoke samples were obtained from samples collected in TEDLAR bags, previously flushed with N_2. To avoid secondary reactions, the samples were protected from UV radiation and analysed within a few hours after sampling. Gas-phase species were quantified using a Gasmet™ DX-4000 multicomponent analyser equipped with a high-resolution Fourier transform infrared (FTIR) spectrometer. The FTIR method identifies and quantifies gases from their compound-specific infrared absorption spectra, allowing simultaneous multi-compound analysis. The analysed species included CO_2, CO, N_2O, NO, NO_2, SO_2, NH_3, CH_4, ethane (C_2H_6), propene (C_3H_6), acetylene (C_2H_2) and methanol (CH_3OH), hydrogen chloride (HCl), hydrogen fluoride (HF), and formaldehyde (CH_2O). A detailed description of the preparation of the TEDLAR bags before and after sampling and of the instrumentation procedure can be found in Alves et al. (2010b).

It should be noted that the measured concentrations may be underestimates of atmospheric concentrations, since adsorption onto the bag walls, diffusion through the polymer film, or chemical transformation during storage may have occurred. These effects are particularly relevant for reactive, soluble, or polar compounds such as NH_3 and oxygenated VOCs such as methanol, whose stability in polymer sampling bags can be affected by storage time, humidity, concentration, and bag material (Szyłak-Szydłowski, 2015). In addition, some compounds such as SO_2, NH_3, and CH_4 may have been trapped in the air sampling system. Therefore, the concentrations of NH_3, methanol, and other highly reactive or polar compounds reported here should be interpreted as conservative lower-limit estimates.

2.3. Data analysis

The parameter used to characterise combustion is Modified Combustion Efficiency (MCE). It assesses the completeness of combustion, taking into account that >90 % of the carbon combusted is emitted in the form of CO_2 and CO and <10 % of the carbon is emitted in the form of hydrocarbons and particulate carbon. The MCE, expressed as a percentage, is calculated as (1):

$$\text{MCE (\%)} = \frac{[CO_2]}{[CO_2]+[CO]} \cdot 100 \qquad (1)$$

If MCE value is higher than 90 %, it indicates that more than 50 % of the emissions were produced by flaming combustion, whereas if MCE is lower than 90 %, it suggests that more than 50 % of the emissions were caused by smouldering combustion (Ward and Hardy, 1991).

The emission factor (EF) is a parameter that relates the emission of a particular species to the amount of biomass burned. The carbon combusted during biomass burning is emitted as CO_2, CO, CH_4, non-methane hydrocarbons (NMHC), and particulate carbon (EC+OC). Therefore, the EF of a specie *n*, is estimated from the ratio of *n* mass concentration to the total carbon concentration emitted. Thus, EF is defined as the amount of a compound released per amount of dry fuel consumed, expressed in units of g kg^{-1}, where the above ratio is multiplied by the mass percentage of carbon in the fuel (Reid et al., 2005) using (2). The term NMHC is less than 2 % and includes the sum of methanol, ethane, propene and acetylene, while

the sum of CO_2 and CO is 87-92 % of the total carbon emitted (Urbanski et al., 2008). The carbon mass fraction of the dry fuel used in Eq. (2) was obtained from the elemental analysis described in Sect. 2.2 and reported in Table 2. The $\%C_{fuel}$ values were 53.3 % for *Calluna* and 53.2 % for *Genista*.

$$\mathrm{EF}_n = \frac{[n]}{[\mathrm{CO_2}]+[\mathrm{CO}]+[\mathrm{CH_4}]+[\mathrm{NMHC}]+[\mathrm{EC}]+[\mathrm{OC}]} \cdot \%C_{fuel} \qquad (2)$$

2.4. Morphological analysis

Particle morphology was analysed by scanning electron microscopy (SEM). PM_{10} polycarbonate filter membranes were mounted on aluminium SEM stubs using conductive carbon tape and sputter-coated with a 1–2 nm thick Au/Pt layer to minimize charging effects. Sampling periods for SEM analysis were kept short and adjusted according to smoke-plume intensity to minimize filter overloading and particle overlap on the substrate, which is essential for reliable single-particle SEM/EDS analysis (Mamane et al., 2001).

Observations were performed using a field-emission SEM (JEOL JSM-6335F) equipped with an Oxford Instruments X-Max energy-dispersive X-ray spectroscopy (EDS) detector at the Spanish National Center for Electron Microscopy (ICTS), Complutense University of Madrid (UCM). Multiple random SEM fields of view were inspected for each sample to ensure that the reported morphologies were representative of the overall particle population. This approach has been previously applied in similar studies (Coz et al., 2008).

3. Results and discussion

3.1. Sampling conditions

Aerosol and gas sample characteristics depend on: i) meteorological conditions, ii) biomass properties, and iii) combustion dynamics (Pio et al., 2008):

i) Calluna burnings were carried out at an altitude of 1534 m with a mean wind speed of 4.3±1.7 m s^{-1}, a mean temperature of 17.7±0.6 °C and a relative humidity (RH) of 40.1±1.1 %. Meteorological variables were similar for *Genista* burnings (at 1395 m) with a mean wind speed of 3.6±1.8 m s^{-1}, a mean temperature of 19.7±0.8 °C and a RH of 37.4±1.3 %. Meteorological conditions during the fires are therefore comparable. Table 1 summarises the recorded meteorological data.

Table 1. Summary of mean meteorological conditions in *Calluna* and *Genista* prescribed fires. Data provided by: Molina J.R, Rodríguez y Silva F., Laboratorio de Incendios Forestales. Univ. de Córdoba (Spain), LABIF-UCO (https://labif.es/).

Specie	Altitude (m)	Wind speed (m s^{-1})	Wind direction (º)	Air temperature (°C)	Dew point temperature (°C)	RH (%)
Genista	1395	4.3±1.7	158 (128-205)	17.7±0.6	4.0±0.7	40.1±1.1
Calluna	1534	3.6±1.8	180 (115-264)	19.7±0.8	4.8±0.5	37.4±1.3

ii) The vegetation cover in the *Genista* plots was dominated by *Genista hispanica* subsp. *occidentalis* (82.4 %) while the remaining area was covered by herbaceous plants. In *Calluna* plots, *Calluna vulgaris* represented a similar share of 84.7 %, with the leftover fraction of the land also occupied by herbaceous plants. The biomass fuels were subjected to elemental analysis, the results of which are presented in Table 2. The analyses show very similar values for the two species. The main difference between the two fuels is the N content (*Genista* 1.19 % vs *Calluna* 0.9 %) and the ash content at 815 ºC (*Genista* 1.58 % vs *Calluna* 1.74 %). The High Calorific Values of both species are almost identical. It should be noted that the value of humidity should be treated with caution because the samples were received some time after being cut, so they may have dried partially. The live/dead proportion in the fuel load was determined from pre-fire vegetation sampling by separating, drying, and weighing live and dead biomass fractions. The live fraction was calculated as the dry mass of live biomass divided by the total dry fuel mass. The resulting live biomass proportions were 53.5 % for *Genista* and 59.6 % for *Calluna*.

Table 2. Characteristics of the solid biomass fuels (*Calluna* and *Genista*).

SPECIES		Humidity (%)	Volatile matter (%)	Ash (815ºC) (%)	Ash (550°C) (%)	C (%)	H (%)	N (%)	S (%)	HCV** (kcal kg^{-1})	LCV** (kcal kg^{-1})
Genista	dry basis	-	80.2	1.58	1.86	53.2	6.53	1.19	0.08	5238	4882
	as received *	10.1	72.1	1.42	1.67	47.8	6.99	1.07	0.07	4710	4330
Calluna	dry basis	-	77.5	1.74	1.98	53.3	6.34	0.9	0.09	5240	4895
	as received *	9.2	70.4	1.58	1.8	48.4	6.78	0.82	0.08	4759	4391

*Sample major partially dried in field. **HCV (High Calorific Value); LCV (Low Calorific Value)

iii) Combustion efficiency was evaluated by calculating the MCE (Sect. 2.3). In the prescribed fires on the *Calluna* plots, the MCE was higher than 90 % (90.6 %), indicating that more than 50 % of the emissions were produced by flaming combustion. On the other hand, in the *Genista* plots, the MCE was lower than 90 % (70.8 %), suggesting that more than 50 % of the emissions resulted from smouldering combustion (Ward and Hardy, 1991). Differences in combustion efficiency may be related to variations in fuel humidity and fuel packing, given that it has been argued that MCE increases with decreasing biofuel packing (Soares Neto et al., 2009). The lower MCE observed for *Genista* may also be partly associated with the presence of litter and mulch beneath the shrub layer, which may favour smouldering combustion. However, because litter and mulch loads were not quantified separately, this interpretation should be considered qualitative.

Fires on the *Genista* plots were characterised by a rate of spread of 0.40 m min^{-1}, a mean maximum temperature of 454 °C at ground level and a residence time of 23.7 s, defined as the period where temperatures exceeded 300 °C (Wotton et al., 2012). *Calluna* burning was the most intense, presenting higher values of mean rate of spread (4.23 m min^{-1}), mean maximum temperature (809 °C) and residence time (103.3 s). Rate of spread and residence time describe different aspects of fire behaviour: the former represents the horizontal advance of the fire front, whereas the latter represents the duration of heating above 300 °C at the measurement point. Thus, a faster-spreading fire may also show a longer residence time when the flaming zone is broader or combustion is more intense.

3.2. Air quality: emission factors

The $PM_{2.5}$ concentrations registered in the smoke plume for the burnings of *Calluna* and *Genista* were 31.1±13.1 mg m^{-3} and 12.0±6.1 mg m^{-3}, respectively. Carbonaceous constituents (TC) accounted for 48.6 and 30.7 % of the mass of $PM_{2.5}$ from *Calluna* and *Genista* combustion. Concentrations of organic and elemental carbon during *Genista* fires were 2.05±1.51 and 0.60±0.41 mg m^{-3}, respectively, while for the *Calluna* fires the levels were 9.94±2.97 and 1.40±0.98 mg m^{-3}. It is noteworthy that the OC/EC ratio was more than twice as high for *Calluna* (8.4±3.8) compared to *Genista* (3.2±1.6). For *Calluna*, the sum EC+OC represented 28.1 % of $PM_{2.5}$, while for *Genista* it represented 32.9 %. These percentages are lower than those reported by Andreae (2019) for savanna (52.6 %) and temperate forest (61.9 %).

Net concentrations (concentrations measured in the smoke plume minus the corresponding background concentration) of gases obtained through high-resolution Fourier transform infrared (FTIR) analysis of combustion products collected from *Calluna* and *Genista* burnings are shown in Table 3. CO_2 was by far the most abundant gas emitted during combustion, with mean concentrations of 653 ppm for Calluna and 54 ppm for Genista. Of the total measured carbon emitted during combustion, carbon dioxide (CO_2) was by far the dominant component, representing 89 % in *Calluna* fires and 65 % in *Genista* fires. These results confirm that *Calluna* combustion was more efficient and dominated by flaming phases, while *Genista* fires exhibited incomplete combustion associated with smouldering conditions. The higher proportion of CO and CH_4 in Genista is consistent with lower modified combustion efficiency (MCE), as previously observed in low-intensity fires (Ward and Hardy, 1991).

Interestingly, despite its higher combustion efficiency, *Calluna* emitted more TOC than *Genista*. This may be attributed to intense flaming combustion, which enhances the volatilisation of organic compounds and the release of oxygenated hydrocarbons (Yokelson et al., 2013).

The remaining measured gaseous species—including nitrogen oxides (NO and NO_2), ethylene (C_2H_4), ethane (C_2H_6), hydrogen fluoride (HF), and formaldehyde (CH_2O)—were present at concentrations typically below 1 % of the total gas mixture. Although their contribution to total carbon emissions was minimal, these compounds are atmospherically relevant due to their roles in ozone formation, secondary aerosol production, and potential health effects (Andreae, 2019). Notably,

NO and NO_2 concentrations were slightly higher in *Genista* fires, while ethane, formaldehyde, and hexane showed significantly greater concentrations in *Calluna* fires, indicating differences in combustion conditions and fuel composition. The elevated levels of light hydrocarbons such as ethane and hexane in *Calluna* emissions point to higher pyrolysis activity and faster fuel volatilisation, typical of more intense flaming combustion (Urbanski, 2014).

Calluna/*Genista* concentration ratios were calculated for all measured gases. The largest differences were observed for CO_2 (12.1), hexane (6.7), CO (3.0), TOC (2.6), CH_4 (2.3), and ethane (2.5). These results reinforce the idea that plant species exert a strong influence on the gaseous composition of emissions, even under similar prescribed fire conditions. Such differences should be considered in emission inventories and atmospheric models for Mediterranean shrublands (Alves et al., 2010a; Andreae, 2019).

The emission factors (EF) of carbonaceous species: CO, CO_2, CH_4, C_2H_6, C_2H_4, C_3H_8, C6H14, CHOH, organic carbon (OC), elemental carbon (EC) and $PM_{2.5}$, for *Calluna* and *Genista* burning were calculated as indicated in Sect. 2.3 (Table 3). The EF_{CO2} for *Calluna* (1703 g kg^{-1}) is similar to that obtained for an Amazonian forest clearing fire and higher than that obtained for *Genista* fires (592 g kg^{-1}). Soares Neto et al. (2009) carried out a study in Mato Grosso (Brazil) in the deforestation arc and reported CO_2 EFs for different combustion stages of Amazonian Forest clearing fires: ignition (1631-1625 g kg^{-1}), flaming (1690-1741 g kg^{-1}) and smouldering (1540-1548 g kg^{-1}). (Andreae, 2019) reported an EF_{CO2} of 1660±90 g kg^{-1} for savanna and grassland.

Table 3. Concentrations and emission factors of gaseous and carbonaceous species from *Calluna* and *Genista* fires.

Specie	*Concentration (ppm)*		Ratio	*Emission factor (g/kg)*	
	Calluna	*Genista*	*Calluna/Genista*	*Calluna*	*Genista*
Water vapour H_2O	4637	441	10.5	-	-
Carbon dioxide CO_2	653	54	12.1	1700	592
Carbon monoxide CO	68.2	22.4	3.0	113.1	155.4
Nitrous oxide N_2O	0.105	0.0	-	-	-
Nitrogen oxide NO	2.47	1.50	1.6	-	-
Nitrogen dioxide NO_2	0.038	0.0	-	-	-
Sulphur dioxide SO_2	0.0	0.0	-	-	-
Ammonia NH_3	0.0	0.011	-	-	-
Hydrogen chloride HCl	0.108	0.074	1.5	-	-
Hydrogen fluoride HF	0.030	0.050	0.6	-	-
Methane CH_4	4.111	1.806	2.3	3.9	7.17
Ethane C_2H_6	1.008	0.409	2.5	1.79	3.05
Ethylene C_2H_4	2.254	1.011	2.2	3.74	7.02
Propane C_3H_8	0.0	0.0	-	0	0
Hexane C_6H_{14}	0.376	0.056	6.7	1.92	1.21
Formaldehyde CH_2O	0.193	0.091	2.1	0.37	0.72
NOx as NO_2	2.51	1.49	1.7	-	-
Total Organic Carbon TOC	6.98 (mgC Nm^{-3})	2.69 (mgC Nm^{-3})	2.6	9.27	14.97
Organic Carbon OC	9.94 (mg m^{-3})	2.05 (mg m^{-3})	4.8	13.2	11.37
Elemental Carbon EC	1.40 (mg m^{-3})	0.60 (mg m^{-3})	2.3	1.85	3.32
$PM_{2.5}$	31.1 (mg m^{-3})	12.0 (mg m^{-3})	2.6	53.5	44.7

A similar pattern between the shrubs species was obtained for the values of $EF_{PM2.5}$ and EF_{OC}. The $EF_{PM2.5}$ values obtained for *Calluna* and *Genista* were 53.5 and 44.7 g kg^{-1}, respectively. Andreae (2019) in a compilation of emission factors from 370 studies across 121 species and biomass types, reported average $EF_{PM2.5}$ values of 6.7±3.3 g $kg^{-1}$for savanna and grassland and 18.5±14.4 g $kg^{-1}$for temperate forest. In addition, contrary to what was observed by Alves et al. (2010b), whom carried out an analysis of emissions from prescribed fires in a shrub-dominated forest with some pine trees in the Lousã Mountain (Portugal) in 2008, $EF_{PM2.5}$ was higher in prescribed fires here than in wildfires reported by Alves et al. (2010b) , and EF_{CO2} was either similar (*Calluna*) or lower (*Genista*), suggesting less efficient combustion in the latter.

The pattern of EF_{CO}, EF_{CH4} and EF_{EC} is opposite to that of $EF_{PM2.5}$ (Figure 2) with higher values for *Genista* than for *Calluna*. The EF_{CO2} and EF_{CO} are explained by differences in combustion efficiencies, flaming in *Calluna* and smouldering in *Genista* fires. Typically, CO and $PM_{2.5}$ emissions increase as combustion efficiency decreases (Ward and Hardy, 1991). However, the higher $EF_{PM2.5}$ observed in *Calluna* fires (53.5 g kg^{-1}) suggests that intense flaming combustion may have enhanced the release of fine particles, possibly due to higher volatile content or fuel characteristics that promote aerosol formation during flaming. Other studies reported a clear correlation between MCE and EFs (Alves et al., 2010b; Soares Neto et al., 2009).

Regarding EF_{CO}, Bertschi et al. (2003) conducted a laboratory study to evaluate smouldering combustion of tropical wooded savanna and obtained EF_{CO} values similar to the of the present research (128-165 g kg^{-1}). Similarly, Yokelson et al. (2009) characterised emissions from deforestation and crop residue burning, reporting EF_{CO} values of 75 ± 26 g kg^{-1} and 83 ± 14 g kg^{-1}, respectively, lower than the values observed here (*Calluna*: 113 g kg^{-1}; *Genista*: 155 g kg^{-1}).

Additionally, the EF_{CO} and EF_{CH4} values for both shrubs are higher than those typically reported for savanna and grassland, and closer to those found in temperate forests. The EF_{EC} values for *Calluna* (1.85 g kg^{-1}) and *Genista* (3.32 g kg^{-1}) also exceed the averages reported for savanna and grassland (0.53 ± 0.35 g kg^{-1} and temperate forest (0.55 ± 0.36 g kg^{-1}) (Andreae, 2019).

The remaining carbonaceous species—ethane, ethylene, hexane, and formaldehyde—showed higher EFs in *Genista* than in *Calluna*, reflecting enhanced pyrolysis under smouldering conditions (Andreae, 2019; Yokelson et al., 2009). Although their absolute values were low (<7 g kg^{-1}), their atmospheric relevance lies in their contribution to ozone formation, secondary aerosol production, and toxicological impacts (Alves et al., 2010a; Bertschi et al., 2003).

A more regionally specific comparison is provided by the experimental Mediterranean shrubland wildfires reported by Garcia-Hurtado et al. (2013), who obtained emission factors of 1257 ± 40 g kg^{-1} for CO_2, 453 ± 28 g kg^{-1} for CO, 46 ± 12 g kg^{-1} for CH_4, 3.4 ± 1.39 g kg^{-1} for $PM_{2.5}$, 1.4 ± 0.34 g kg^{-1} for OC, and 0.051 ± 0.028 g kg^{-1} for EC. Compared with those values, $EFCO_2$ in the present study was higher for Calluna (1700 g kg^{-1}) and lower for Genista (592 g kg^{-1}), which is consistent with the different combustion efficiencies observed for the two fuels. In contrast, EFCO and $EFCH_4$ were substantially lower in both prescribed fires than in Garcia-Hurtado et al. (2013), consistent with the strong smouldering

contribution reported in their experiments. Conversely, $EFPM_{2.5}$, EFOC, and EFEC were markedly higher in the present study, particularly for $PM_{2.5}$ and EC. These differences highlight the influence of fuel type, combustion phase, fire behaviour, and sampling strategy on emission factors, even within Mediterranean shrubland ecosystems.

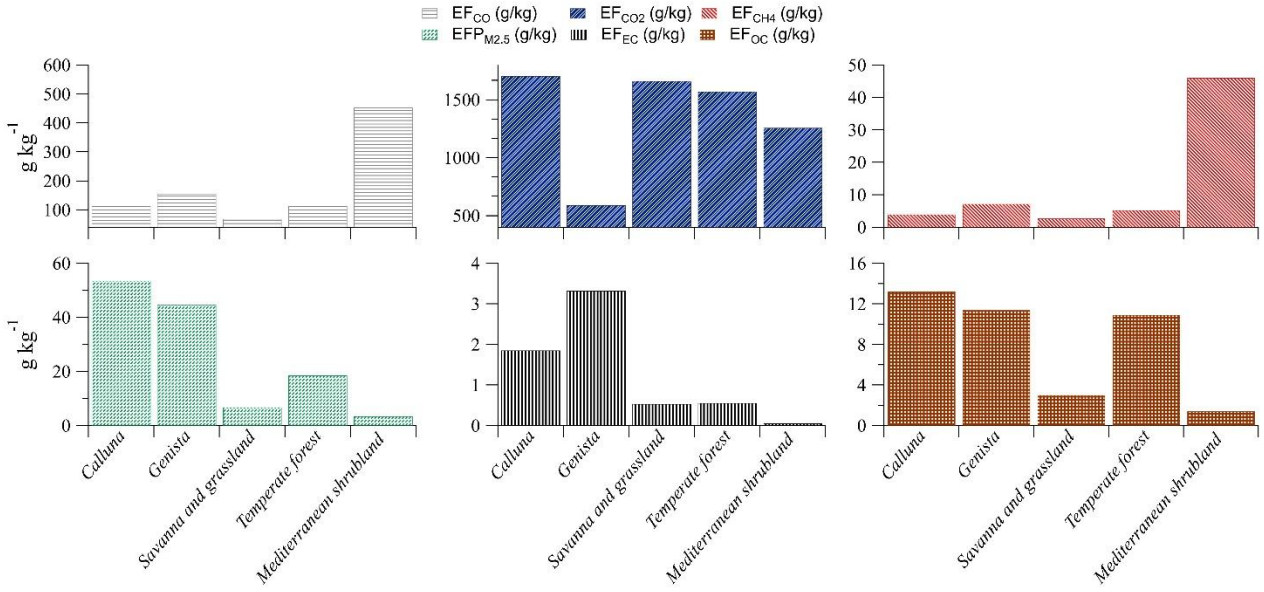

Figure 2. Comparison of emission factors (EF) for CO, CO_2, CH_4, $PM_{2.5}$, organic carbon (OC) and elemental carbon (EC) during Calluna and *Genista* prescribed fires with Mediterranean shrubland wildfire values from Garcia-Hurtado et al. (2013) and literature-average values for savannas/grasslands and temperate forests (Andreae, 2019). The Andreae (2019) values are compiled averages from multiple biomass-burning studies and represent a mixture of fire types and measurement conditions, including field and laboratory burns.

3.3. Water-soluble ions

As observed for gaseous compounds, most water-soluble ions in $PM_{2.5}$ from *Calluna* combustion—with the exception of Cl^- and Na^+—were present at higher mass fractions than those emitted by *Genista* (Figure 3). Overall, water-soluble ions represented 6.9 % of the $PM_{2.5}$ mass in *Calluna* and 4.5 % in *Genista*. The elevated ionic content in *Calluna*-derived particles may reflect a higher ash yield from this fuel. Similar proportions were reported by Alves et al. (2010b) for prescribed shrubland fires in Portugal. Although potassium (K^+) is often used as a tracer of biomass burning, no clear correlation was observed between K^+ and either organic carbon (OC) or elemental carbon (EC) in this study.

Na^+, SO_4^{2-}, Mg^{2+}, Cl^- and Ca^{2+} were the most abundant water-soluble inorganic ions emitted during the burning of *Genista*, in that order. In contrast, the same ionic species dominated *Calluna* emissions, but with a different ranking: Cl^-, Na^+, SO_4^{2-}, Mg^{2+} and Ca^{2+}. (Andreae et al., 1998) reported that Cl^-, SO_4^{2-}, K^+ and NH_4^+ were the predominant ions in savanna fires (similar to *Calluna*), while Falkovich et al. (2004) indicated that the predominant ionic species in Amazon basin fires were SO_4^{2-}, NH_4^+, K^+, NO_3^- and Cl^-.

The K^+ mass fraction (0.21±0.04 wt% for *Calluna* and 0.32±0.20 wt% for *Genista*) was very close to the values reported for fires in a Mediterranean shrubland (Alves et al., 2010b), but lower than typical values for savannas and more comparable to those observed in temperate forests. Laboratory studies have shown a wide variability in K^+ fractions, ranging from <1 % to 24 % (Andreae, 2019).

The Cl^-/EC ratios were 3.4 ± 2.0 for *Genista* and 4.2 ± 2.1 for *Calluna*, while the K^+/EC ratios were 0.104 ± 0.071 and 0.241 ± 0.045, respectively. The presence of K^+ relative to EC supports the influence of biomass combustion, as water-soluble potassium is widely used as a tracer of biomass-burning aerosol (Andreae, 2019; Yu et al., 2018). Together with the observed Cl^- levels, this suggests the possible presence of potassium-containing salts such as KCl internally mixed with carbonaceous particles. These species may act as cloud condensation nuclei (CCN), contributing to regional indirect radiative forcing in Mediterranean regions (Alves et al., 2010a; Petters et al., 2009).

However, it should be noted that comparisons across studies may be affected by multiple factors, including: i) biome characteristics of each site; ii) variability in combustion efficiencies or iii) sampling (ground-based measurements, mast, distance to the fire, PM inlets or different devices).

The ionic composition and particle-phase characteristics reported here may also support the refinement of next-generation air quality models. Recent AI-based tools for simulating $PM_{2.5}$ transport and chemical aging from prescribed fires (Liao et al., 2025) highlight the importance of comprehensive field emission datasets like those obtained in this study.

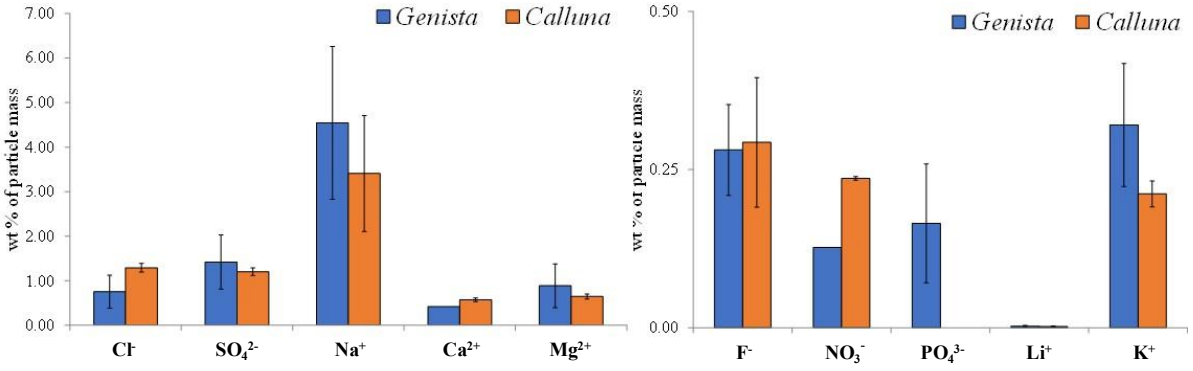

Figure 3. Water-soluble ions, expressed as wt% (mass fraction of the species times 100 of particle mass), in *Calluna* and *Genista* burnings.

3.4. Morphological analysis

Scanning electron microscopy (SEM) analysis showed that PM samples collected during prescribed burning episodes were dominated by particles with irregular morphologies and complex aggregated structures, typical of biomass burning aerosols (Figure 4). The particles shown in Figure 4 are representative of the dominant morphologies observed across the analysed samples. A minor fraction of the particulate matter could be tentatively identified as soot-like carbonaceous agglomerates; however, these structures were frequently partially or completely obscured by thick surface coatings, preventing the clear observation of their characteristic open fractal geometry when present.

The particle population was largely dominated by spherical and sub-spherical particles (Figure 4 a–g), resembling so-called tar balls (Pósfai et al., 2004), with sizes below 100 nm to several cents of nanometers. The presence of tar balls is commonly associated with the condensation of semi-volatile organic compounds and the rapid cooling of combustion vapours in fire plumes. Qualitative inspection of multiple SEM fields of view indicated that these spherical and compact morphologies accounted for most of the observed particles. These particles exhibited smooth to slightly textured surfaces and sizes predominantly in the submicrometer range. Several particles displayed hollow or shell-like morphologies (Figure 4 h–i), suggesting rapid gas-phase condensation and subsequent volatilization or restructuring, possibly during atmospheric transport; however, changes can occur during the analysis. In addition, irregularly shaped and porous aggregates were observed, likely corresponding to internally mixed particles composed of organic material, ash residues, and inorganic inclusions. These mixed particles frequently showed thick coatings and poorly defined boundaries between phases, indicating extensive internal mixing and potential atmospheric aging (Li et al., 2011).

Energy-dispersive X-ray spectroscopy (EDS) revealed a dominant contribution of carbon and oxygen, together with variable amounts of potassium, silicon, calcium, aluminium, and iron, often forming part of the coated mixed particles. The frequent presence of potassium- and calcium-containing inclusions within the aggregates further supports the strong influence of biomass combustion, as these elements are well-established tracers of wood and vegetation burning emissions. The predominance of spherical, compact, and internally mixed particles with thick organic coatings is expected to influence both the optical properties and hygroscopic behavior of the aerosol. Such coatings can modify particle refractive index and morphology, by enhancing light absorption through “lensing effects” when carbonaceous cores are present and increasing the particles' optical thickness (Bond et al., 2013; Moffet and Prather, 2009). Additionally, the internal mixing of inorganic salts (K, Ca) with organic matter suggests a transition toward higher hygroscopicity during atmospheric aging (Coz et al., 2008), by changing their effective chemical composition and surface properties, thereby promoting water uptake at elevated relative humidity and enhancing cloud condensation nuclei (CCN) activity. These effects are likely to play an important role in controlling the radiative and microphysical impacts of aerosols from biomass burning during transport and aging in the atmosphere (Carrico et al., 2010; Pósfai et al., 2004).

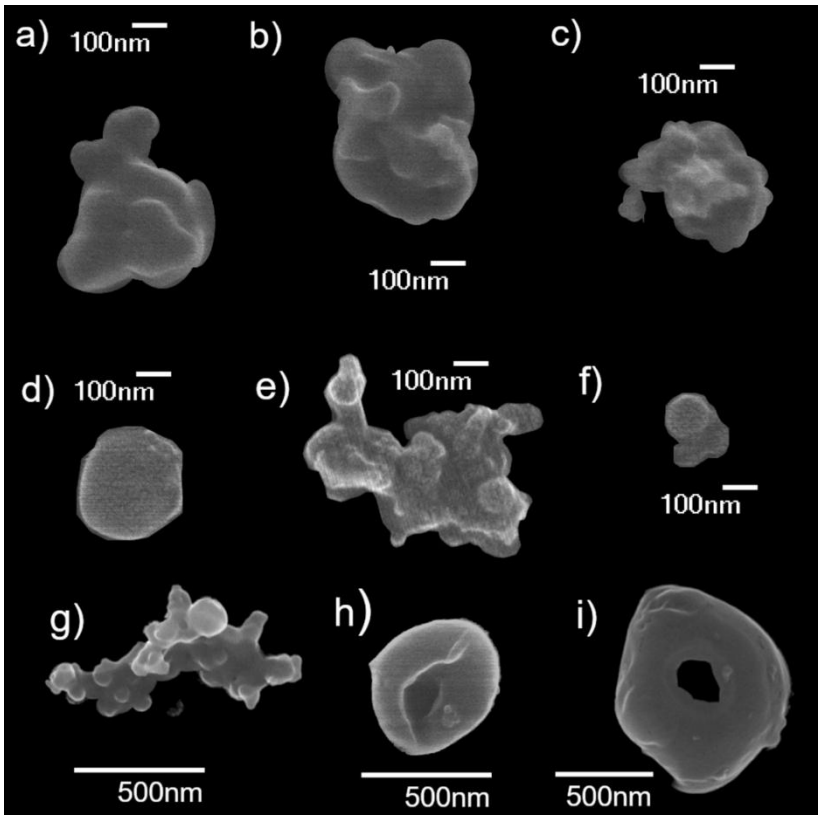

Figure 4. Representative SEM images of PM particles collected during prescribed burnings episodes: (a–g) show sub-spherical highly coated particles and aggregates, likely composed of organic material, ash residues, and inorganic inclusions; (h–i) show hollow or shell-like particles, indicative of rapid condensation and subsequent volatilization or restructuring processes. Scale bars are 100 nm (a–f) and 500 nm (g–i).

4. Conclusions

The chemical characterisation of emissions during prescribed fires of two Mediterranean shrubs (*Genista* and *Calluna*) in León, Spain, has led to the following conclusions:

- The study shows that Modified Combustion Efficiency (MCE) primarily controls emission characteristics. *Calluna* fires were more intense (MCE 90.6 %), dominated by the flaming phase, while *Genista* fires (MCE 70.8 %) were dominated by smouldering, reflecting differences in biomass structure and litter presence. These findings underscore the pivotal role of fuel characteristics in governing fire behaviour and associated emissions.
- Gas-phase concentrations were generally higher in *Calluna* than in *Genista*, especially for CO_2, CO, CH_4, and TOC. Only HF and nitrogen oxides were slightly higher in *Genista* emissions.

- For *Calluna*, carbonaceous constituents (EC+OC) represented 28.1 % of $PM_{2.5}$, while for *Genista*, they accounted for 32.9 %, both values being lower than those reported for savanna (52.6 %) and temperate forest (61.9 %).
- The $PM_{2.5}$ mass fraction of water-soluble ions in the smoke from *Calluna* burning were higher concentrations than those of *Genista* (except for Cl^-). For both species, Cl^-, SO_4^{2-}, Na, Mg^{2+} and Ca^{2+} accounted for more than 80 % of the total ion concentration emitted.
- The emission factors (EF) for $PM_{2.5}$—53.5 g kg^{-1} for *Calluna* and 44.7 g kg^{-1} for *Genista*—are substantially higher than those reported for savannas (6.7 g kg^{-1}) and temperate forests (18.5 g kg^{-1}), highlighting the significant particulate output from Mediterranean shrubland fires.
- Scanning electron microscopy revealed that emissions are dominated by submicrometer spherical particles (tar balls) with thick organic coatings. These features enhance light absorption ("lensing effect") and increase hygroscopicity, promoting cloud condensation. Such properties underline the role of fire-emitted particles in radiative forcing and cloud formation.

This is among the first field-based characterisations of prescribed fire emissions in Mediterranean shrublands dominated by *Calluna* and *Genista*. The results obtained may be useful to: i) better evaluate the impact of prescribed or non-prescribed fires in the Mediterranean region through numerical models, ii) improve emission inventories, iii) update SPECIEUROPE, the European repository of source profiles, and thus to assess more rigorously the contribution of fires to atmospheric levels when applying receptor models, and iv) contribute to decision-making.

Data availability

The data supporting the findings of this study, including those required to reproduce the figures and results, will be made publicly available in a FAIR-aligned repository upon final publication of this manuscript. During the peer-review process, the data are available to reviewers upon request from the corresponding author. Until public release, interested researchers may also request access from the corresponding author.

Author contributions

CBA: Conceptualization, Methodology, Formal analysis, Investigation, Writing – original draft preparation. AIC: Investigation, Data curation, Formal analysis, Writing – review and editing. FO: Investigation, Writing – review and editing. EC: Investigation, Investigation, Writing – review and editing. CA: Investigation, Methodology, Validation, Writing – review and editing. LV: Investigation, Writing – review and editing. RMC: Investigation, Writing – review and editing. FC: Formal analysis, Investigation, Writing – review and editing. RF: Supervision, Methodology, Writing – review and editing.

Competing interests

The authors declare that they have no conflict of interest.

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References

Alves, C. A., Gonçalves, C., Evtyugina, M., Pio, C. A., Mirante, F., and Puxbaum, H.: Particulate organic compounds emitted from experimental wildland fires in a Mediterranean ecosystem, Atmos. Environ., 44, 2750–2759, https://doi.org/10.1016/j.atmosenv.2010.04.029, 2010a.

Alves, C. A., Gonçalves, C., Pio, C. A., Mirante, F., Caseiro, A., Tarelho, L., Freitas, M. C., and Viegas, D. X.: Smoke emissions from biomass burning in a Mediterranean shrubland, Atmos. Environ., 44, 3024–3033, https://doi.org/10.1016/j.atmosenv.2010.05.010, 2010b.

Andreae, M. O.: Emission of trace gases and aerosols from biomass burning – An updated assessment, Atmospheric Chemistry and Physics, 1–27, https://doi.org/10.5194/acp-19-8523-20195, 2019.

Andreae, M. O., Andreae, T. W., Annegarn, H., Beer, J., Cachier, H., Canut, P., Elbert, W., Maenhaut, W., Salma, I., Wienhold, F. G., Zenker, T., and Planck, M.: Airbone Studies Africa: 2. Aerosol Chemical Composition, J. Geophys. Res., 103, 119–128, 1998.

ASTM International: ASTM D5373-16, Standard Test Methods for Determination of Carbon, Hydrogen and Nitrogen in Analysis Samples of Coal and Carbon in Analysis Samples of Coal and Coke, 2016.

ASTM International: ASTM D4239-18e1, Standard Test Method for Sulfur in the Analysis Sample of Coal and Coke Using High-Temperature Tube Furnace Combustion, 2018.

ASTM International: ASTM D3302 / D3302M-19, Standard Test Method for Total Moisture in Coal, , https://doi.org/10.1520/D3302_D3302M-19, 2019.

Bargmann, T., Måren, I. E., and Vandvik, V.: Life after fire: Smoke and ash as germination cues in ericads, herbs and graminoids of northern heathlands, Appl. Veg. Sci., 17, 670–679, https://doi.org/10.1111/avsc.12106, 2014.

Bertschi, I., Yokelson, R. J., Ward, D. E., Babbitt, R. E., Susott, R. A., Goode, J. G., and Hao, W. M.: Trace gas and particle emissions from fires in large diameter and belowground biomass fuels, Journal of Geophysical Research: Atmospheres, 108, https://doi.org/10.1029/2002jd002100, 2003.

Bond, T. C., Doherty, S. J., Fahey, D. W., Forster, P. M., Berntsen, T., Deangelo, B. J., Flanner, M. G., Ghan, S., Kärcher, B., Koch, D., Kinne, S., Kondo, Y., Quinn, P. K., Sarofim, M. C., Schultz, M. G., Schulz, M., Venkataraman, C., Zhang, H., Zhang, S., Bellouin, N., Guttikunda, S. K., Hopke, P. K., Jacobson, M. Z., Kaiser, J. W., Klimont, Z., Lohmann, U., Schwarz, J. P., Shindell, D., Storelvmo, T., Warren, S. G., and Zender, C. S.: Bounding the role of black carbon in the climate system: A scientific assessment, Journal of Geophysical Research Atmospheres, 118, 5380–5552, https://doi.org/10.1002/jgrd.50171, 2013.

Boreddy, S. K. R. R., Kawamura, K., Okuzawa, K., Kanaya, Y., and Wang, Z.: Temporal and diurnal variations of carbonaceous aerosols and major ions in biomass burning influenced aerosols over Mt. Tai in the North China Plain during MTX2006, Atmos. Environ., 154, 106–117, https://doi.org/10.1016/j.atmosenv.2017.01.042, 2017.

Burrows, N. and McCaw, L.: Prescribed burning in southwestern Australian forests, Front. Ecol. Environ., 11, https://doi.org/10.1890/120356, 2013.

Carrico, C. M., Petters, M. D., Kreidenweis, S. M., Sullivan, A. P., McMeeking, G. R., Levin, E. J. T., Engling, G., Malm, W. C., and Collett, J. L.: Water uptake and chemical composition of fresh aerosols generated in open burning of biomass, Atmos. Chem. Phys., 10, 5165–5178, https://doi.org/10.5194/acp-10-5165-2010, 2010.

Castro, L. M., Pio, C. A., Harrison, R. M., and Smith, D. J. T.: Carbonaceous aerosol in urban and rural European atmospheres: estimation of secondary organic carbon concentrations, Atmos. Environ., 33, 2771–2781, https://doi.org/10.1016/S1352-2310(98)00331-8, 1999.

Coz, E., Artíñano, B., Robinson, A. L., Casuccio, G. S., Lersch, T. L., and Pandis, S. N.: Individual particle morphology and acidity, Aerosol Science and Technology, 42, 224–232, https://doi.org/10.1080/02786820801958759, 2008.

Elia, M., D'Este, M., Ascoli, D., Giannico, V., Spano, G., Ganga, A., Colangelo, G., Lafortezza, R., and Sanesi, G.: Estimating the probability of wildfire occurrence in Mediterranean landscapes using Artificial Neural Networks, Environ. Impact Assess. Rev., 85, 106474, https://doi.org/10.1016/j.eiar.2020.106474, 2020.

Evgrafova, A., de la Haye, T. R., Haase, I., Shibistova, O., Guggenberger, G., Tananaev, N., Sauheitl, L., and Spielvogel, S.: Small-scale spatial patterns of soil organic carbon and nitrogen stocks in permafrost-affected soils of northern Siberia, Geoderma, 329, 91–107, https://doi.org/10.1016/j.geoderma.2018.05.014, 2018.

Fagúndez, J.: Heathlands confronting global change: Drivers of biodiversity loss from past to future scenarios, Ann. Bot., 111, 151–172, https://doi.org/10.1093/aob/mcs257, 2013.

Falkovich, A. H., Graber, E. R., Schkolnik, G., Rudich, Y., Maenhaut, W., and Artaxo, P.: Low molecular weight organic acids in aerosol particles from Rondônia, Brazil, during the biomass-burning, transition and wet periods, Atmospheric Chemistry and Physics Discussions, 4, 6867–6907, https://doi.org/10.5194/acpd-4-6867-2004, 2004.

Fernandes, P. M. and Botelho, H. S.: A review of prescribed burning effectiveness in fire hazard reduction, Int. J. Wildland Fire, 12, 117, https://doi.org/10.1071/WF02042, 2003.

Fernandes, P. M., Davies, G. M., Ascoli, D., Fernández, C., Moreira, F., Rigolot, E., Stoof, C. R., Vega, J. A., and Molina, D.: Prescribed burning in southern Europe: Developing fire management in a dynamic landscape, https://doi.org/10.1890/120298, August 2013.

Garcia-Hurtado, E., Pey, J., Baeza, M. J., Carrara, A., Llovet, J., Querol, X., Alastuey, A., and Vallejo, V. R.: Carbon emissions in Mediterranean shrubland wildfires: An experimental approach, Atmos. Environ., 69, 86–93, https://doi.org/10.1016/j.atmosenv.2012.11.063, 2013.

Ghimenti, S., Lomonaco, T., Bellagambi, F. G., Tabucchi, S., Onor, M., Trivella, M. G., Ceccarini, A., Fuoco, R., and Di Francesco, F.: Comparison of sampling bags for the analysis of volatile organic compounds in breath, J. Breath Res., 9, 047110, https://doi.org/10.1088/1752-7155/9/4/047110, 2015.

Gilfillan, D. and Marland, G.: CDIAC-FF: global and national CO_2 emissions from fossil fuel combustion and cement manufacture: 1751–2017, Earth Syst. Sci. Data, 13, 1667–1680, https://doi.org/10.5194/essd-13-1667-2021, 2021.

Grau-Andrés, R., Davies, G. M., Waldron, S., Scott, E. M., and Gray, A.: Increased fire severity alters initial vegetation regeneration across Calluna-dominated ecosystems, J. Environ. Manage., 231, 1004–1011, https://doi.org/10.1016/j.jenvman.2018.10.113, 2019.

Huffman, D. W., Roccaforte, J. P., Springer, J. D., and Crouse, J. E.: Restoration applications of resource objective wildfires in western US forests: a status of knowledge review, Fire Ecology, 16, 18, https://doi.org/10.1186/s42408-020-00077-x, 2020.

Jacobson, M. Z.: Strong radiative heating due to the mixing state of black carbon in atmospheric aerosols, Nature, 409, 695–697, https://doi.org/10.1038/35055518, 2001.

Li, W., Li, P., Sun, G., Zhou, S., Yuan, Q., and Wang, W.: Cloud residues and interstitial aerosols from non-precipitating clouds over an industrial and urban area in northern China, Atmos. Environ., 45, 2488–2495, https://doi.org/10.1016/j.atmosenv.2011.02.044, 2011.

Liao, K., Buch, J., Lamb, K. D., and Gentine, P.: Simulating the air quality impact of prescribed fires using graph neural network-based PM 2.5 forecasts, Environmental Data Science, 4, https://doi.org/10.1017/eds.2025.4, 2025.

Loomis, D., Grosse, Y., Lauby-Secretan, B., Ghissassi, F. El, Bouvard, V., Benbrahim-Tallaa, L., Guha, N., Baan, R., Mattock, H., and Straif, K.: The carcinogenicity of outdoor air pollution, Lancet Oncol., 14, 1262–1263, https://doi.org/10.1016/S1470-2045(13)70487-X, 2013.

Luyssaert, S., Schulze, E. D., Börner, A., Knohl, A., Hessenmöller, D., Law, B. E., Ciais, P., and Grace, J.: Old-growth forests as global carbon sinks, Nature, 455, 213–215, https://doi.org/10.1038/nature07276, 2008.

Mamane, Y., Willis, R., and Conner, T.: Evaluation of Computer-Controlled Scanning Electron Microscopy Applied to an Ambient Urban Aerosol Sample, Aerosol Science and Technology, 34, 97–107, https://doi.org/10.1080/02786820118842, 2001.

Martín, P. and Oria de Rueda, J. A.: Guía técnica de gestión de matorrales ibéricos. Prevención de incendios y producción de hongos comestibles, 2021.

McCarty, J. L.: Remote sensing-based estimates of annual and seasonal emissions from crop residue burning in the contiguous United States, J. Air Waste Manage. Assoc., 61, 22–34, https://doi.org/10.3155/1047-3289.61.1.22, 2011.

McMorrow, J.: Wildfire in the United Kingdom: Status and key issues, Proceedings of the Second Conference on the Human Dimensions of Wildland Fire, 13, 2011.

Moffet, R. C. and Prather, K. A.: In-situ measurements of the mixing state and optical properties of soot with implications for radiative forcing estimates, Proc. Natl. Acad. Sci. U. S. A., 106, 11872–11877, https://doi.org/10.1073/pnas.0900040106, 2009.

Petters, M. D., Carrico, C. M., Kreidenweis, S. M., Prenni, A. J., DeMott, P. J., Collett, J. L., and Moosmüller, H.: Cloud condensation nucleation activity of biomass burning aerosol, Journal of Geophysical Research Atmospheres, 114, 1–16, https://doi.org/10.1029/2009JD012353, 2009.

Pio, C., Cerqueira, M., Harrison, R. M., Nunes, T., Mirante, F., Alves, C., Oliveira, C., Sanchez, A., Campa, D., Artíñano, B., and Matos, M.: OC / EC ratio observations in Europe : Re-thinking the approach for apportionment between primary and secondary organic carbon, Atmos. Environ., 45, 6121–6132, https://doi.org/10.1016/j.atmosenv.2011.08.045, 2011.

Pio, C. A., Legrand, M., Alves, C. A., Oliveira, T., Afonso, J., Caseiro, A., Puxbaum, H., Sanchez-Ochoa, A., and Gelencsér, A.: Chemical composition of atmospheric aerosols during the 2003 summer intense forest fire period, Atmos. Environ., 42, 7530–7543, https://doi.org/10.1016/j.atmosenv.2008.05.032, 2008.

Pósfai, M., Gelencsér, A., Simonics, R., Arató, K., Li, J., Hobbs, P. V., and Buseck, P. R.: Atmospheric tar balls: Particles from biomass and biofuel burning, Journal of Geophysical Research: Atmospheres, 109, https://doi.org/10.1029/2003jd004169, 2004.

Reid, J. S., Eck, T. F., Christopher, S. A., Koppman, R., Dubovik, O., Eleuterio, D. P., Holben, B. N., Reid, E. A., and Zhang, J.: A review of biomass burning emissions part III: Intensive optical properties of biomass burning particles, Atmos. Chem. Phys., 5, 827–849, https://doi.org/10.5194/acp-5-827-2005, 2005.

Reinhardt, E. D., Keane, R. E., Calkin, D. E., and Cohen, J. D.: Objectives and considerations for wildland fuel treatment in forested ecosystems of the interior western United States, For. Ecol. Manage., 256, 1997–2006, https://doi.org/10.1016/j.foreco.2008.09.016, 2008.

Saleh, R., Marks, M., Heo, J., Adams, P. J., Donahue, N. M., and Robinson, A. L.: Contribution of brown carbon and lensing to the direct radiative effect of carbonaceous aerosols from biomass and biofuel burning emissions, Journal of Geophysical Research: Atmospheres, 120, https://doi.org/10.1002/2015JD023697, 2015.

Soares Neto, T. G., Carvalho, J. A., Veras, C. A. G. G., Alvarado, E. C., Gielow, R., Lincoln, E. N., Christian, T. J., Yokelson, R. J., and Santos, J. C.: Biomass consumption and CO2, CO and main hydrocarbon gas emissions in an Amazonian forest clearing fire, Atmos. Environ., 43, 438–446, https://doi.org/10.1016/j.atmosenv.2008.07.063, 2009.

Szyłak-Szydłowski, M.: Odour Samples Degradation During Detention in Tedlar® Bags, Water Air Soil Pollut., 226, 227, https://doi.org/10.1007/s11270-015-2495-2, 2015.

Töpperwien, K., Vignat, G., Feinberg, A. J., Daube, C., Alton, M. W., Fortner, E. C., Canagaratna, M. R., Kling, M. F., Johnson, M., Nadeau, K., Herndon, S., Jayne, J. T., and Ihme, M.: Burn parameters affect PAH emissions at conditions relevant for prescribed fires, Atmos. Pollut. Res., 16, https://doi.org/10.1016/j.apr.2025.102438, 2025.

Turco, M., Marcos-Matamoros, R., Castro, X., Canyameras, E., and Llasat, M. C.: Seasonal prediction of climate-driven fire risk for decision-making and operational applications in a Mediterranean region, Science of the Total Environment, 676, 577–583, https://doi.org/10.1016/j.scitotenv.2019.04.296, 2019.

UNE: UNE 32004:1984 - Solid mineral fuels. Determination of ash., 1984a.

UNE: UNE 32019:1984 - Hard coal and coke. Determination of volatile matter content., 1984b.

UNE: UNE 32006:1995 - Solid mineral fuels. Determination of gross calorific value by automatic calorimeter., 1995.

UNE: UNE-EN 14775:2010 - Solid biofuels - Determination of ash content, 2010.

Urbanski, S.: Wildland fire emissions, carbon, and climate: Emission factors, For. Ecol. Manage., 317, 51–60, https://doi.org/10.1016/j.foreco.2013.05.045, 2014.

Urbanski, S. P., Hao, W. M., and Baker, S.: Chapter 4 Chemical Composition of Wildland Fire Emissions, in: Developments in Environmental Science, vol. 8, 79–107, https://doi.org/10.1016/S1474-8177(08)00004-1, 2008.

Vandvik, V., Töpper, J. P., Cook, Z., Daws, M. I., Heegaard, E., Måren, I. E., and Velle, L. G.: Management-driven evolution in a domesticated ecosystem, Biol. Lett., 10, 1–6, https://doi.org/10.1098/rsbl.2013.1082, 2014.

Vega, J. A., Arellano-Pérez, S., Álvarez-González, J. G., Fernández, C., Jiménez, E., Fernández-Alonso, J. M., Vega-Nieva, D. J., Briones-Herrera, C., Alonso-Rego, C., Fontúrbel, T., and Ruiz-González, A. D.: Modelling aboveground biomass and fuel load components at stand level in shrub communities in NW Spain, For. Ecol. Manage., 505, https://doi.org/10.1016/j.foreco.2021.119926, 2022.

Ward, D. E. and Hardy, C. C.: Smoke emissions from wildland fires, Environ. Int., 17, 117–134, https://doi.org/10.1016/0160-4120(91)90095-8, 1991.

Wotton, B. M., Gould, J. S., McCaw, W. L., Cheney, N. P., and Taylor, S. W.: Flame temperature and residence time of fires in dry eucalypt forest, Int. J. Wildland Fire, 21, 270–281, https://doi.org/10.1071/WF10127, 2012.

Yang, X., Ma, Y., Wang, G., Alvarado, E. C., Tigabu, M., Ju, Y., and Guo, F.: Characterization of pollutants emitted during burning of eight main tree species in subtropical China, Atmos. Environ., 215, 116899, https://doi.org/10.1016/j.atmosenv.2019.116899, 2019.

Yokelson, R. J., Urbanski, S. P., Atlas, E. L., Toohey, D. W., Alvarado, E. C., Crounse, J. D., Wennberg, P. O., Fisher, M. E., Wold, C. E., Campos, T. L., Adachi, K., Buseck, P. R., and Hao, W. M.: Emissions from forest fires near Mexico City, Atmos. Chem. Phys., 7, 5569–5584, https://doi.org/10.5194/acp-7-5569-2007, 2007.

Yokelson, R. J., Crounse, J. D., DeCarlo, P. F., Karl, T., Urbanski, S., Atlas, E., Campos, T., Shinozuka, Y., Kapustin, V., Clarke, A. D., Weinheimer, A., Knapp, D. J., Montzka, D. D., Holloway, J., Weibring, P., Flocke, F., Zheng, W., Toohey, D., Wennberg, P. O., Wiedinmyer, C., Mauldin, L., Fried, A., Richter, D., Walega, J., Jimenez, J. L., Adachi, K., Buseck, P. R., Hall, S. R., and Shetter, R.: Emissions from biomass burning in the Yucatan, Atmos. Chem. Phys., 9, 5785–5812, https://doi.org/10.5194/acp-9-5785-2009, 2009.

Yokelson, R. J., Burling, I. R., Gilman, J. B., Warneke, C., Stockwell, C. E., De Gouw, J., Akagi, S. K., Urbanski, S. P., Veres, P., Roberts, J. M., Kuster, W. C., Reardon, J., Griffith, D. W. T., Johnson, T. J., Hosseini, S., Miller, J. W., Cocker, D. R., Jung, H., and Weise, D. R.: Coupling field and laboratory measurements to estimate the emission factors of identified and unidentified trace gases for prescribed fires, Atmos. Chem. Phys., 13, 89–116, https://doi.org/10.5194/acp-13-89-2013, 2013.

Yu, J., Yan, C., Liu, Y., Li, X., Zhou, T., and Zheng, M.: Potassium: A Tracer for Biomass Burning in Beijing?, Aerosol Air Qual. Res., 18, 2447–2459, https://doi.org/10.4209/aaqr.2017.11.0536, 2018.