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PAPER

Emission factors from residential combustion appliances burning Portuguese biomass fuels

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Smoke from residential wood burning has been identified as a major contributor to air pollution, motivating detailed emission measurements under controlled conditions. A series of experiments were performed to compare the emission levels from two types of wood-stoves to those of fireplaces. Eight types of biomass were burned in the laboratory: wood from seven species of trees grown in the Portuguese forest (*Pinus pinaster*, *Eucalyptus globulus*, *Quercus suber*, *Acacia longifolia*, *Quercus faginea*, *Olea europaea* and *Quercus ilex rotundifolia*) and briquettes produced from forest biomass waste. Average emission factors were in the ranges 27.5–99.2 g CO kg^{-1}, 552–1660 g CO_2 kg^{-1}, 0.66–1.34 g NO kg^{-1}, and 0.82–4.94 g hydrocarbons kg^{-1} of biomass burned (dry basis). Average particle emission factors varied between 1.12 and 20.06 g kg^{-1} biomass burned (dry basis), with higher burn rates producing significantly less particle mass per kg wood burned than the low burn rates. Particle mass emission factors from wood-stoves were lower than those from the fireplace. The average emission factors for organic and elemental carbon were in the intervals 0.24–10.1 and 0.18–0.68 g kg^{-1} biomass burned (dry basis), respectively. The elemental carbon content of particles emitted from the energy-efficient "chimney type" logwood stove was substantially higher than in the conventional cast iron stove and fireplace, whereas the opposite was observed for the organic carbon fraction. *Pinus pinaster*, the only softwood species among all, was the biofuel with the lowest emissions of particles, CO, NO and hydrocarbons.

1. Introduction

In 1997, the European Union started working towards a target of a 12% share of renewable energy in gross inland consumption by 2010 representing a doubling of the contribution from this energy compared with 1997. An increased usage of biofuels will play an important role in meeting this objective. However, it has been found that biomass burning represents an important source of air pollution in many rural and urban areas of the developed and developing world.[1–7] Epidemiological studies showed that pollutants resulting from biomass combustion have effects similar to well-known problems caused by emissions from fossil fuel combustion, such as breathing difficulties and lung cancer.[8] In addition, emissions from biomass combustion include a wide range of gaseous compounds and particles that contribute significantly to the tropospheric budgets on local, regional, and even global scales, playing an important role in the biogeochemical cycles, atmospheric chemistry and climate forcing.[9,10] Besides greenhouse gases, the emission of carbonaceous particles from biomass combustion deserves special attention. These particles are formed by a complex mixture of organic compounds, normally referred to as organic carbon (OC), and

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Environmental impact

In Portugal, it was estimated that up to 80% of the atmospheric aerosol loads may be attributed to wood combustion in fireplaces and stoves, which are extensively used for heating purposes. However, nothing is known about the emission factors of both gases and particles. Since the magnitude of emissions may change with wood type and burning appliance, it is desirable to obtain specific emission factors for each region in order to attain more correct source apportionment estimates. In addition, specific emission factors are also needed to improve emission inventories and climate change models. This work may represent a significant advance in the field of atmospheric science, especially in Southern Europe.

a mass of carbon atoms (black in colour) with a graphitic-like structure that is normally called elemental carbon (EC). EC has optical and chemically catalytic properties, causing visibility reduction, positive radiative forcing and an impact on atmospheric photochemistry.[11,12] On the other hand, OC presents light scattering properties and, since a significant fraction is water soluble, participates in various aerosol–cloud interactions.[13]

In Portugal, it was estimated that around 390 000 tonnes of wood are annually used in domestic combustion appliances,[14] though the chemical characterisation of the emissions from this equipment has not yet been performed. Emission inventories and source apportionment, photochemistry and climate change models use values obtained for American,[15,16] Alpine[17] or Scandinavian[18–20] wood-fuels and combustion appliances, which are not characteristic of Southern Europe. Previous work suggested that the species of wood and the type of combustion appliance used can have a huge influence on both gaseous and particle emissions.[16,19,21,22] Therefore, any significant differences in emissions from distinct fuel types and combustion equipment (stoves and fireplaces) should be accounted for in regional control strategies aimed at residential wood burning. On the other hand, specific emissions and flue gas characteristics from residential wood combustion in each region are helpful for source apportionment purposes to yield an estimate of the contribution of solid biomass combustion to atmospheric pollution loads measured during monitoring campaigns.

The purpose of this work was to compare the emissions from combustion of wood species typical of Portugal in different residential appliances.

2. Experimental

In accordance with the Portuguese Forest Inventory (2005),[23] the wood from the seven most prevalent tree species was chosen for the combustion experiments in residential appliances (Table 1). Besides wood biomass, briquettes from forest waste were also used as fuel. The chemical composition of the biomass used is presented in Table 2.

Two set of experiments were performed (Table 3) with distinct residential combustion appliances used for heating purposes, one set at the Vienna University of Technology (Austria), and another set at the University of Aveiro (Portugal). At both institutions, the experimental infra-structure was composed of the combustion system (stove or fireplace), the exit flue gas duct (stove or fireplace chimney), the flue gas sampling and characterisation system for gaseous compounds, and the dilution tunnel (downstream the stove chimney) and respective particulate matter sampling system. The dilution tunnel is used to characterise particle emissions from combustion and other high-temperature sources because it simulates the rapid cooling and dilution that occurs as exhaust mixes with the atmosphere.[24]

Table 1 Portuguese biomass fuels selected for the combustion experiments

Scientific name	Common name	% forest cover in Portugal
Pinus pinaster	Maritime pine	29.1
Quercus suber	Cork oak	21.3
Eucalyptus globulus	Eucalyptus	20.1
Quercus ilex	Holm oak	13.8
Olea europaea	Olive	9.7
Quercus faginea	Portuguese oak	3.9
Acacia longifolia	Golden wattle	0.6
—	Briquettes	—

At the Vienna University of Technology, a “chimney type” logwood stove with a nominal power output of 6 kW, found commonly in Austria, Hungary, Germany, Switzerland, Bohemia, Northern Italy and Scandinavia, was used. This device can also be found in luxury houses and eco-friendly constructions in Portugal. The stove was operated manually in batch mode and with manual control of combustion air (primary air underbed feed). Combustion air enters the burning chamber (28 × 25 × 25 cm) through a grate in the bottom (primary air) and a slit in the black wall (secondary air). The wood selected for the combustion experiments in this device was pine, eucalyptus, cork oak and golden wattle (Table 3). The wood was burned as split logs of 30–50 cm in length and around 10 cm in diameter. During each combustion experiment, which lasted between 95 and 139 minutes, about 6 kg of wood was burned, using three consecutive batches of around 2 kg each. The stove temperature (at the centre of the combustion chamber) and its exit flue gas characteristics, such as temperature, O_2, CO_2, CO, NO, and total hydrocarbons, were monitored continuously at the exit of the stove chimney at 2.0 m above the exit of the stove combustion chamber. The temperature was monitored using K-type thermocouples. The measurement principles of the gas analysers were non-dispersive infrared (CO and CO_2), paramagnetic (O_2), chemiluminescence (NO) and flame ionisation (total hydrocarbons expressed as methane equivalents). Each gas analyser was calibrated with appropriate gas on zero and span points. The detection limits of the gas analysers were about 0.5% of the full scale range.

Dilution factors used in the dilution tunnel ranged from 1 : 10 to 1 : 15. Particulate matter with aerodynamic diameter below 10 μm (PM_{10}) was sampled from the dilution tunnel with a low volume sampling head (Digitel AG, Switzerland) working on a one-stage impactor principle at a flow of 2.3 $m^3\ h^{-1}$, which was further distributed by 2 cellulose and 6 quartz fibre filter holders (47 mm diameter). The sampling flow through quartz fibre filters was set to 0.33 $m^3\ h^{-1}$ per filter. Detailed descriptions of the experimental facility can be found elsewhere.[17,25]

At the University of Aveiro, two types of residential biomass combustion appliances were tested: (i) a cast iron wood stove (Solzaima, model Sahara), operated manually in batch mode and with manual control of combustion air (primary air underbed feed) and (ii) a traditional Portuguese brick open fireplace operated manually in batch mode and with no control of combustion air. According to a recent survey questionnaire carried out to assess residential wood combustion practices in the 18 districts of mainland Portugal,[26] fireplaces are used by 43% of the population, while traditional stoves, such as the one tested in this study, represent about 44% of the total number of appliances. The percentage of use of pellet stoves and other innovative appliances is about 7%. This reality is quite different from that in Scandinavian countries, where high efficiency biomass-fired district heating systems are common. Thus, the burning devices of the present study are very widespread in Portugal and also represent relatively well the Southern European market.

Table 2 Biomass characteristics

	Proximate analysis (wt%, as received)		Ultimate analysis (wt%, dry basis)					
Biomass fuel	Moisture	Ash	C	H	N	S	O[a]	Ash
Maritime pine	9.10	0.32	51.40	6.20	0.16	<0.01	41.88	0.36
Eucalyptus	11.30	0.34	48.60	6.20	0.16	<0.01	44.28	0.75
Cork oak	12.20	2.04	51.61	6.03	0.18	<0.01	40.76	1.41
Golden wattle	8.40	0.69	50.83	6.43	0.18	<0.02	41.80	0.75
Olive	15.50	1.64	53.56	7.68	0.18	n/d	36.64	1.94
Portuguese oak	14.10	0.61	50.26	7.32	0.19	n/d	41.85	0.38
Holm oak	8.70	1.87	50.61	7.14	0.18	n/d	39.75	2.32
Briquettes	8.40	0.83	50.76	7.01	0.16	n/d	41.16	0.91

[a] By difference.
n/d—not determined.

The wood used in the combustion experiments was pine, eucalyptus, cork oak, olive, Portuguese oak, holm oak, golden wattle and commercial briquettes (Table 3). During each combustion experiment, which lasted between 45 and 90 minutes, about 6 kg of wood was burned, using three consecutive batches of around 2 kg each, and logs with similar dimensions as the ones used at Vienna University of Technology. The stove and fireplace temperatures (at the centre of the combustion chamber) and the combustion flue gas characteristics (temperature, O_2, CO_2, and CO) were monitored continuously at the chimneys of the burning appliances at 1.98 m above the exit of the combustion chamber. The detection limits of the gas analysers were similar to those reported for the experiments in Vienna. The temperature was monitored using K-type thermocouples, and the measurement principles of the gas analysers were the same as described for the Austrian experiments. Each gas analyser was calibrated with appropriate gas on zero and span points.

Collection of particulate matter with aerodynamic diameters below 2.5 µm was made in the dilution tunnel, which is similar to other systems reported in previous studies.[16,18,20,27,28] Dilution factors used in the dilution tunnel were around 1 : 23. Temperature and gas flow monitoring in the dilution tunnel were made using a K-type thermocouple and a Pitot tube (Testo AG 808). The particulate matter ($PM_{2.5}$) was sampled using an Echo PM sampling head (TECORA, model 2.004.01, Italy) operating at a flow of 2.3 m^3 h^{-1}, onto single quartz fibre filters (47 mm diameter). During each combustion experiment the quartz filter was replaced 3 times, that is, 4 filters were used. Since each replacement took less than 1 minute, the overall particle emission factor for each combustion cycle was considered to not be significantly affected. Fernandes (2009)[29] described the Portuguese experimental facility and its operating conditions in detail.

The quartz fibre filters used for particulate matter collection in the dilution tunnel of both experimental facilities were previously

Table 3 Combustion experiments[a]

	Biomass fuel			
Combustion appliance		Moisture content (wt%, as received)	Number of experiments	Combustion gas monitoring
"Chimney type" logwood stove (Austrian stove)	Maritime pine	13.92	4	PM_{10}, O_2, CO_2, CO, NO, and C_xH_y
	Eucalyptus	12.46	4	
	Cork oak	14.79	3	
	Golden wattle	6.99	3	
Traditional brick fireplace and cast iron wood stove (Portuguese stove)	Maritime pine	9.10	3 (stove) 3 (fireplace)	$PM_{2.5}$, O_2, CO, and CO_2
	Eucalyptus	11.30	3 (stove) 3 (fireplace)	
	Cork oak	12.20	3 (stove) 3 (fireplace)	
	Olive	15.50	3 (stove) 3 (fireplace)	
	Portuguese oak	14.10	3 (stove) 3 (fireplace)	
	Holm oak	8.70	3 (stove) 3 (fireplace)	
	Golden wattle	8.40	3 (stove) 3 (fireplace)	
	Briquettes	8.40	3 (stove) 3 (fireplace)	

[a] PM_{10}—particulate matter ≤10 µm in diameter; $PM_{2.5}$—particulate matter ≤2.5µm in diameter; C_xH_y—total hydrocarbons (expressed as methane equivalents).

Table 4 Emission factors of particulate matter (PM) and carbonaceous constituents (TC = OC + EC), mass percentages of carbonaceous constituents in particulate matter (OC/PM, EC/PM and TC/PM), and organic-to-elemental carbon ratios (OC/EC). Emission factors are referred to dry biomass fuel basis

Biomass fuel	Combustion appliance and particulate matter (PM) type	$gPM\ kg^{-1}_{biomass}$	$gOC\ kg^{-1}_{biomass}$	$gEC\ kg^{-1}_{biomass}$	$gTC\ kg^{-1}_{biomass}$	OC/PM (wt%)	EC/PM (wt%)	TC/PM (wt%)	OC/EC
Maritime pine	Cast iron stove, $PM_{2.5}$	5.17 ± 4.27	2.54 ± 2.51	0.61 ± 0.43	2.37 ± 1.62	39.13 ± 5.45	12.38 ± 6.91	51.50 ± 6.01	4.52 ± 3.57
	Logwood stove, PM_{10}	1.12 ± 0.25	0.29 ± 0.12	0.44 ± 0.24	0.72 ± 0.26	26.05 ± 10.28	37.10 ± 12.24	63.15 ± 5.92	0.85 ± 0.66
	Fireplace, $PM_{2.5}$	6.89 ± 3.61	2.91 ± 1.30	0.62 ± 0.49	3.53 ± 1.58	41.01 ± 5.11	11.75 ± 5.10	52.76 ± 7.44	4.84 ± 3.98
Golden wattle	Cast iron stove, $PM_{2.5}$	7.93 ± 4.27	4.07 ± 2.65	0.29 ± 0.18	4.36 ± 2.79	45.06 ± 8.14	3.41 ± 1.57	48.47 ± 8.23	15.59 ± 6.49
	Logwood stove, PM_{10}	1.22 ± 0.19	0.24 ± 0.10	0.29 ± 0.10	0.52 ± 0.01	19.68 ± 7.01	24.26 ± 9.70	43.94 ± 3.58	1.02 ± 0.78
	Fireplace, $PM_{2.5}$	7.82 ± 6.16	3.53 ± 3.13	0.34 ± 0.26	3.86 ± 3.28	39.87 ± 6.41	5.56 ± 3.47	45.42 ± 5.50	10.65 ± 8.95
Eucalyptus	Cast iron stove, $PM_{2.5}$	10.18 ± 6.72	5.16 ± 4.03	0.37 ± 0.30	5.53 ± 4.26	50.56 ± 8.28	4.08 ± 1.52	54.64 ± 8.59	14.42 ± 7.05
	Logwood stove, PM_{10}	2.07 ± 0.85	0.66 ± 0.31	0.27 ± 0.19	0.93 ± 0.35	31.83 ± 4.55	13.37 ± 8.26	45.20 ± 4.23	3.14 ± 1.72
	Fireplace, $PM_{2.5}$	11.83 ± 7.55	5.11 ± 3.90	0.36 ± 0.36	5.47 ± 4.24	40.75 ± 9.19	2.61 ± 1.42	43.36 ± 9.95	20.26 ± 12.91
Cork oak	Cast iron stove, $PM_{2.5}$	8.25 ± 6.10	4.80 ± 3.38	0.42 ± 0.33	5.22 ± 3.58	52.68 ± 7.95	5.42 ± 3.82	58.10 ± 8.28	14.39 ± 8.43
	Logwood stove, PM_{10}	2.89 ± 0.90	1.24 ± 0.25	0.33 ± 0.18	1.57 ± 0.38	42.83 ± 2.02	11.28 ± 4.50	54.11 ± 3.21	4.39 ± 2.29
	Fireplace, $PM_{2.5}$	17.85 ± 9.96	10.06 ± 5.24	0.68 ± 0.40	10.74 ± 5.60	51.52 ± 4.09	3.63 ± 1.14	55.15 ± 3.83	15.53 ± 4.98
Olive	Cast iron stove, $PM_{2.5}$	8.71 ± 4.46	4.55 ± 2.22	0.46 ± 0.24	5.01 ± 2.22	49.87 ± 5.53	6.46 ± 5.26	56.32 ± 4.07	12.90 ± 9.07
	Fireplace, $PM_{2.5}$	20.06 ± 11.41	9.10 ± 5.74	0.39 ± 0.16	9.48 ± 5.82	49.05 ± 2.12	2.59 ± 1.05	51.64 ± 1.82	23.31 ± 13.01
Holm oak	Cast iron stove, $PM_{2.5}$	5.80 ± 3.92	3.03 ± 2.05	0.23 ± 0.09	3.26 ± 2.06	55.15 ± 11.64	5.99 ± 3.82	61.14 ± 11.60	14.78 ± 11.33
	Fireplace, $PM_{2.5}$	13.06 ± 8.06	7.22 ± 4.03	0.30 ± 0.11	7.52 ± 4.10	49.96 ± 2.97	2.42 ± 0.92	52.38 ± 3.38	23.72 ± 9.81
Portuguese oak	Cast iron stove, $PM_{2.5}$	12.79 ± 8.28	6.17 ± 4.62	0.32 ± 0.15	6.49 ± 4.71	46.66 ± 2.87	2.91 ± 1.05	49.57 ± 3.37	18.68 ± 9.04
	Fireplace, $PM_{2.5}$	14.20 ± 9.72	6.06 ± 3.40	0.32 ± 0.20	6.37 ± 3.57	48.01 ± 4.51	2.46 ± 0.54	50.47 ± 4.39	20.47 ± 5.54
Briquettes	Cast iron stove, $PM_{2.5}$	7.13 ± 4.82	3.73 ± 3.09	0.18 ± 0.12	3.90 ± 3.07	40.27 ± 12.37	3.62 ± 3.10	43.89 ± 12.35	20.51 ± 16.68
	Fireplace, $PM_{2.5}$	12.46 ± 7.72	5.93 ± 4.23	0.29 ± 0.25	6.22 ± 4.26	45.41 ± 5.63	2.98 ± 1.82	48.39 ± 6.20	19.93 ± 9.49

treated at 500 °C for 4 h. The particulate matter mass was obtained by gravimetric determination after 24 h equilibration of the filters in a conditioned room (20 ± 1 °C, 50 ± 2% relative humidity). A microbalance (Sartorius M5P with range up to 1 g, reading to ±0.5 μg) was used for that purpose. The detection limit (three times the standard deviation of the mass of blank filters) was estimated to be 100 μg per filter, which corresponds to a minimum detectable emission factor of 200 μg PM kg^{-1} biofuel burned.

The carbonaceous content (OC and EC) of particulate matter collected on the quartz fibre filters was analysed using a thermal–optical technique.[30] Separation between OC and EC was achieved by initially heating the filter punches under an inert atmosphere to evaporate first the OC fraction. The remaining fraction is sequentially evaporated/burnt under a gas flow containing O_2. This last carbon fraction contains initial EC plus OC that has pyrolysed during heating under an inert atmosphere. The interference between pyrolysed carbon and EC can be controlled by continuous evaluation of the blackening of filter using a laser beam and a photodetector measuring the filter light transmittance. The detection limits for the OC and EC determinations were estimated to be 48.5 and 5 μg per filter, respectively, which correspond to minimum detectable emission factors of 97 μg OC kg^{-1} and 10 μg EC kg^{-1} biofuel burned.

Some of the filters from these residential wood combustion experiments have been subjected to a detailed chemical speciation. The relative mass fractions of PM_{10} of water-soluble ions, elements, humic-like substances, organic tracers and radionuclides emitted by the chimney type stove can be found in Gonçalves *et al.* (2010).[31] Selected filters from the wood combustion in the fireplace and in the wood stove were analysed for almost 200 organic compounds, including anhydrosugars (*e.g.* levoglucosan) and other tracers,[32] as well as for inorganic components, such as water-soluble ions and 67 trace elements.[33]

3. Results and discussion

3.1. Particle emission factors

Particulate matter emission factors from the wood combustion experiments are listed in Table 4. The combustion of pine, the only softwood among all biofuels, generated the lowest particle emissions for all types of burning appliances, while the highest levels were produced when olive wood, followed by oak species, were burned. The combustion of briquettes contributed to similar amounts of particle emissions when compared to oak species. The biomass fuel ash content was found to be a likely factor influencing the emission of particulate matter. In general, particle emission factors were observed to increase as the fuel ash content increased (Tables 2 and 4). Particle emission factors also increased with increasing fuel moisture content (Fig. 1).

Particle emission factors from residential biomass combustion reported in the literature vary widely, ranging from a few hundreds of mg kg^{-1} to values higher than 60 g kg^{-1} (dry basis).[34] Table 5 compares the average particle emission factors obtained in this study with those reported in the recent literature. In addition to the variability of biomass types and characteristics of combustion appliances, differences in emission patterns among the various studies may be due to the dilution techniques

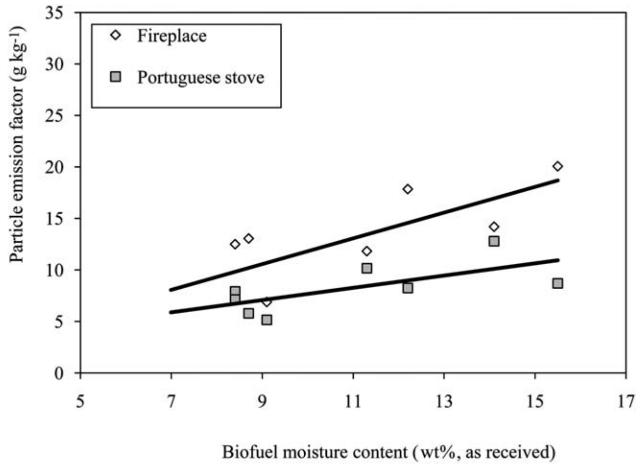

Fig. 1 Relationship between the particle emission factors and the biomass fuel moisture content for the Portuguese wood burning appliances. Emission factors are referred to dry biomass fuel basis.

employed or other differences in experimental procedures (combustion experiments or sampling techniques).[16] One general conclusion that can be drawn is that fireplaces account for the highest particle emission factors, followed by conventional stoves, while modern pellet stoves and wood log boilers with good burn out represent the smallest contribution to ambient wood smoke.

The overall means for all combustion tests were, respectively, 1.85 ± 0.91, 8.05 ± 3.05 and 12.59 ± 5.88 g PM kg^{-1} biofuel burned (dry basis) for the "chimney type" stove, conventional cast iron stove and fireplace. These means were compared to determine whether there were statistically significant differences between them. It should be noted that while the particle emissions from the "chimney type" stove refer to PM_{10}, the other two burning devices were tested to obtain $PM_{2.5}$ emissions. This fact is not of great concern, because the mass size distributions of emissions from residential wood combustion indicated that more than 80% of the mass is concentrated in fine particles.[20] After application of the *t*-test, the null hypothesis of equality of means was rejected at the 0.05 level. Results of additional *t*-tests indicated that there were also significant differences between the means of particle emissions for pine, eucalyptus and golden

Table 5 Comparison between particle emission factors and organic or elemental carbon mass fractions of this study and values from the literature

Biofuel type	Burning appliance	Particle emission factors	Ref.
Australian trees: Potted Gum (*Corymbia citriodora*), Blue Gum (*Eucalyptus tereticornis*), Bloodwood (*Eucalyptus intermedia*), Iron Bark (*Eucalyptus crebra*), and Stringybark (*Eucalyptus umbra*)	Modified commercial stove	• *fast burning conditions*: 0.14–0.21 g $PM_{2.5}$ kg^{-1} for wood (wet basis) 0.45–4.7 g $PM_{2.5}$ kg^{-1} for leaves and branches (wet basis) • *slow burning conditions*: 0.12–0.48 g $PM_{2.5}$ kg^{-1} for wood (wet basis) 3.3–4.9 g $PM_{2.5}$ kg^{-1} for leaves and branches (wet basis)	47
Prevalent USA tree species	Non-catalytic stove	0.88–3.4 g $PM_{2.5}$ kg^{-1} biomass (wet basis)	16
	Catalytic stove	1.2–2.2 g $PM_{2.5}$ kg^{-1} biomass (wet basis)	
	Fireplace	3.3–6.8 g $PM_{2.5}$ kg^{-1} biomass (wet basis)	
Oak and Douglas fir	Factory-built fireplaces	3.3–14.9 g total particles kg^{-1} biomass (dry basis)	44
Acacia nilotica and briquettes	Indian traditional stoves	0.8–1.8 g PM_{10} kg^{-1} biomass (dry basis)	42
	Improved stoves	2.1–2.2 g PM_{10} kg^{-1} biomass (dry basis)	
Portuguese woods and briquettes	"Chimney type" logwood stove	1.12–2.89 g PM_{10} kg^{-1} biomass (dry basis)	This study
	Cast iron traditional stove	5.17–12.8 g $PM_{2.5}$ kg^{-1} biomass (dry basis)	
	Fireplace	6.89–20.1 g $PM_{2.5}$ kg^{-1} biomass (dry basis)	
Biofuel type	**Burning appliance**	**OC/PM and EC/PM mass percentages**	**Ref.**
Chinese woody fuels	Chinese stoves	19–59% (avg. 37%) and 36–71% (avg. 47%)	41
Wood	Cook stoves in Honduras	28–65% (avg. 43%) and 4–55% (avg. 21%)	48
Alpine woods	Tiled stove (*Kachelofen*)	41–56% and 9.8–31%	17
Portuguese woods and briquettes	"Chimney type" logwood stove	20–43% and 11–37%	This study
	Cast iron traditional stove	39–55% and 3–12%	
	Fireplace	40–52% and 2–12%	

wattle when the "chimney type" stove and the other devices were compared. In fact, the mean values obtained for the Portuguese appliances were not included in the 95% confidence intervals of the differences between means. The comparison of mean values obtained for the conventional Portuguese stove against those of the fireplace indicated that there were statistically significant differences, at the 0.05 level, between the set of values for olive, Holm oak and briquettes.

Based on the measured time needed for consumption of a batch of wood, biomass combustion rates in both Portuguese devices were calculated for the fireplace and the cast iron stove. The influence of this parameter on the particle emission factor is presented in Fig. 2. Higher biomass combustion rates were observed for the fireplace than for the stove. This can be related to the fact that fireplaces operate at high excess air levels due to the uncontrolled amount of air admitted to the combustion chamber. For both appliances, an inverse correlation between particle emission factors and biomass combustion rates was observed (Fig. 2). The $PM_{2.5}$ emission factor reached a maximum at around 26 g kg^{-1} biomass (dry basis) fuel burned for the fireplace when the biomass combustion rate is less than 0.4 g s^{-1} (dry fuel basis). The cast iron stove showed a maximum particle emission factor at a biomass combustion rate of about 0.31 g s^{-1}. Jordan and Seen (2005)[21] performed combustion experiments with white gum (*Eucalyptus viminalis*) in 3 different models of wood-heaters, and observed particle emission factors between 3 and 36 g kg^{-1} dry wood, with higher burn rates producing significantly less particle mass per kg wood burned than the low burn rates. These researchers found that the particle emission factors peaked at values around 35–40 g kg^{-1} dry wood fuel burned for most experiments where the combustion rate was less than 0.42 or 0.28 g s^{-1} (dry basis), depending on the heater model, which is in accordance with the present study.

It should be noted that polycyclic aromatic hydrocarbon (PAH) extracts of the smoke particles obtained in the combustion experiments of this study were tested for mutagenic activities using the Ames test with *Salmonella typhimurium* TA98 and TA100.[35] A mutagenic/weak mutagenic response was recorded for all wood species, except golden wattle. The extracts with indirect acting mutagenicity were mainly obtained from fireplace and cold start conditions. Several samples were weak mutagens at low concentration of PAHs. Bølling *et al.* (2009)[36] reviewed recently the literature regarding the physicochemical properties of wood smoke particles. The authors found evidence that suggest an association between wood smoke exposure and various health outcomes, such as decreased lung function, reduced resistance to infections and increased severity/incidences of acute asthma. Moreover, inhalation studies have demonstrated that wood smoke exposure may induce systemic effects, providing a possible link to cardiovascular effects. The influence of the physicochemical properties of wood smoke particles, and of the combustion conditions, on various biological endpoints is largely unknown, though *in vitro* studies indicate that particles from incomplete combustion conditions are more toxic than particles produced under more complete combustion conditions.

3.2. Carbonaceous content of particle emissions

The particle mass emitted was composed primarily of organic carbon (OC) with the second largest component being elemental carbon (EC). The majority of the combustion experiments generated particles with a total carbon content of 20–55% (wt) (Table 4).

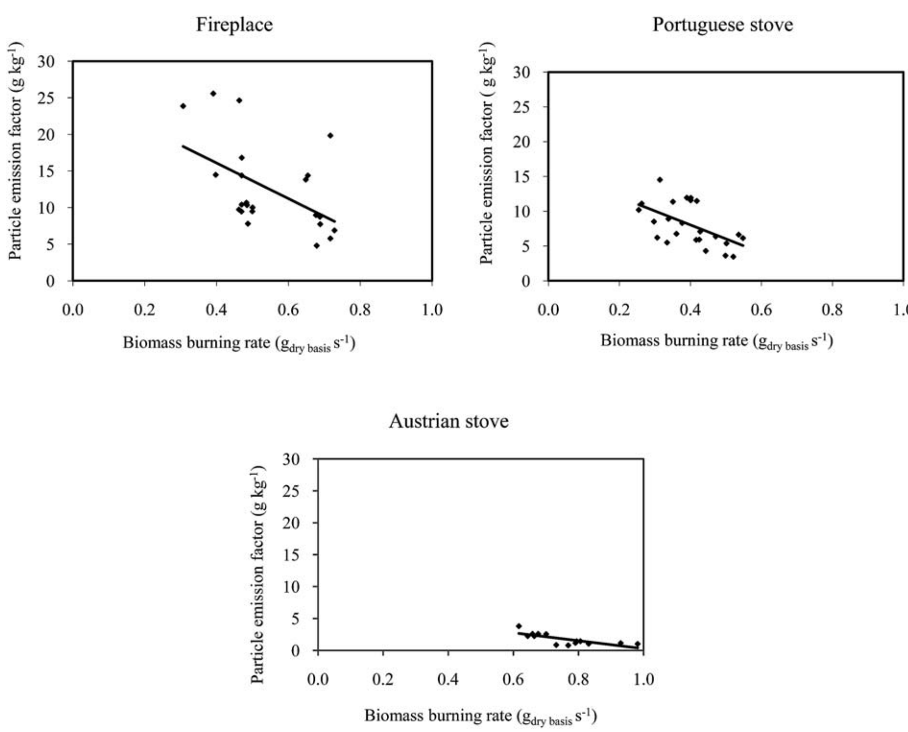

Fig. 2 Particle emission factors from wood combustion appliances operated with different biomass fuel consumption rates. Emission factors are referred to dry biomass fuel basis.

Biomass combustion in the "chimney type" logwood stove produced particles with the lowest OC and the highest EC contents. The mass percentages of OC and EC in particles emitted by the Austrian stove, regardless of the biofuel type, were found, through a *t*-test ($\alpha = 0.05$), to be statistically different from those of the two Portuguese appliances. The high EC mass fraction in particulate matter emitted from woody fuel combustion in the "chimney type" logwood stove can be explained by its improved combustion efficiency. Higher combustion temperatures and more vigorous flaming conditions in the Austrian stove, consistent with the flame-dependent formation mechanism of soot particles, likely contribute to higher EC emissions[37] than those resulting from the other two burning appliances. The lower OC content in PM_{10} from the "chimney type" logwood stove can be due, at least in part, to the fact that less volatile organic compounds from biomass had condensed at the higher dilution tunnel temperature.[25] The lower OC content in particles emitted by the Austrian appliance may also be related to less unburned gaseous compounds in the combustion flue gas due to higher operating temperatures.

An earlier study in the USA found that an average of 9 wt% of the $PM_{2.5}$ mass emitted from hardwood combustion in wood stoves consisted of EC.[22] The study of fine particles emitted during the combustion in a stove of common USA woods[16] revealed that their EC was, with the exception of burning loblolly pine, generally higher than that observed in a fireplace. Moreover, Fine *et al.* (2004)[16] observed that the use of a catalytic stove tended to increase the EC content of emitted particles. It was argued that the further pyrolysis of organic compounds during catalytic secondary combustion may contribute to higher EC mass fraction in $PM_{2.5}$. The OC and EC mass fractions in smoke particles obtained in other studies are summarised in Table 5.

According to the above analysis, it can be concluded that there is a large variability in particle, OC and EC emission factors among literature values. Some of the reasons that can contribute to this variability are: (i) the chemical and physical properties of solid biofuels, (ii) the characteristics of the combustion equipment and its operating conditions, (iii) the biomass combustion rate, and (iv) the methodologies used for the analysis of carbon,

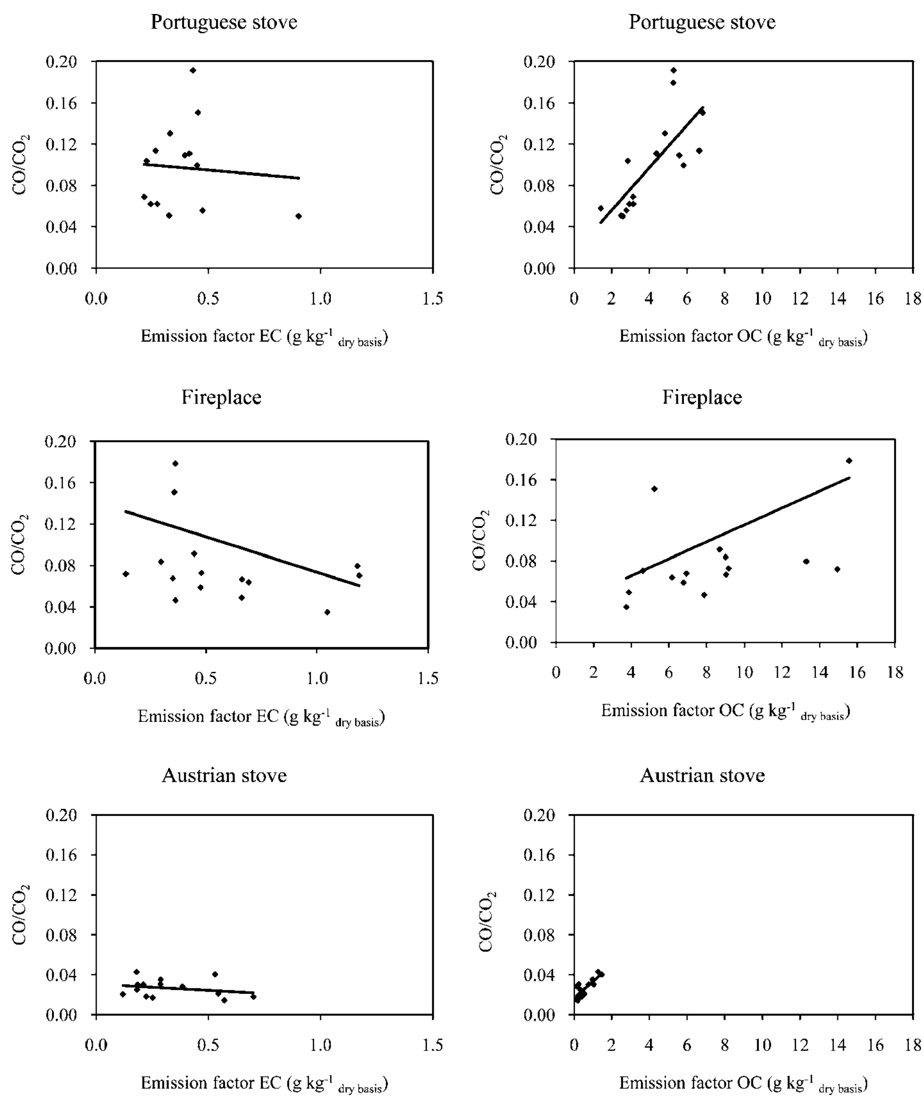

Fig. 3 Relationships between the CO/CO_2 ratio in combustion flue gases and the OC or EC emission factors.

since various inter-laboratory comparisons have shown that the OC/EC absolute split is not yet solved.[38]

The OC/EC ratio can be helpful in distinguishing sources of carbonaceous particulate matter. Lower ratios are characteristic of emissions from fossil fuel combustion, while higher ratios are generally typical of biomass burning.[39] Values ranging from 1.3 to 5.7 were reported for residential wood burning of Austrian solid biofuels.[17] McDonald *et al.* (2000)[22] obtained an average OC/EC ratio of 3.9 for softwood, as compared to 9.0 for hardwood combustion in a fireplace and 7.9 in a stove. In our study, the highest average OC/EC ratios were found for briquette combustion. These values are between those obtained for wood

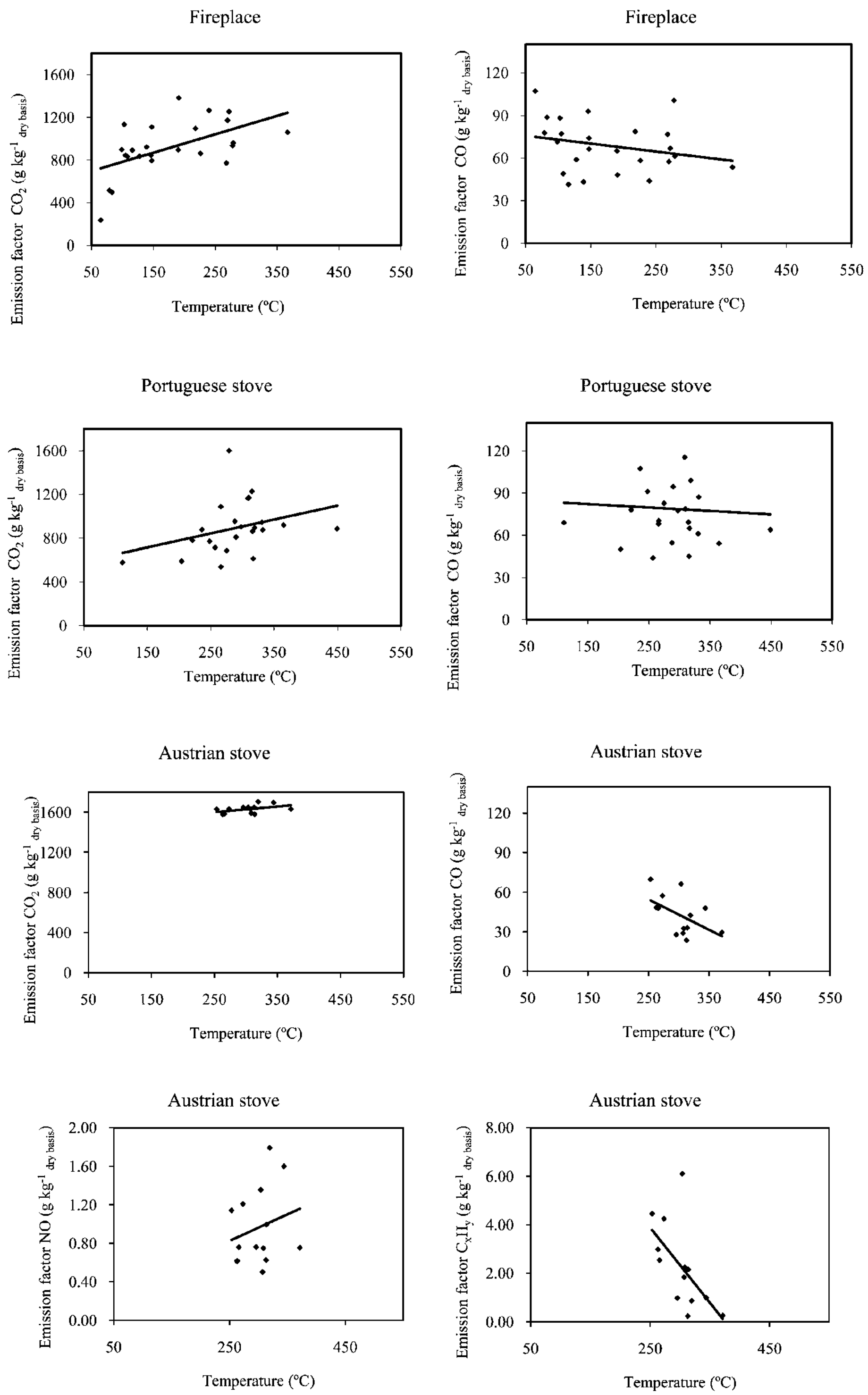

Fig. 4 Relationships between the CO_2, CO, NO, and C_xH_y emission factors and the combustion temperature (temperature at the centre of the combustion chamber). Emission factors are referred to dry biomass fuel basis.

combustion and the higher OC/EC ratios observed in particulate matter emitted by forest fires.[40] Schmidl *et al.* (2008)[17] reported an average OC/EC of 1.32 for spruce briquette combustion in an Austrian stove, which is much lower than the values observed in our study (Table 4). The reason for such differences can be in part due to the use of distinct biomass raw material as fuel and methods of briquetting, namely screw press briquettes in Vienna and piston press briquettes in Portugal. While the briquettes produced by a piston press are a solid cylinder, on the other hand, screw press briquettes have a concentric hole which improves the combustion characteristics of the fuel due to a larger superficial specific area available for reaction. Moreover, the screw-pressed briquettes break up under combustion conditions, and this improves the contact of oxygen with the fuel, since a higher reactive surface is made available, when compared to what is observed in the case of wood logs or piston press briquettes. Consequently, this leads to a more efficient combustion process and to a higher degree of oxidation of the combustible compounds.[17]

3.3. Gaseous emissions

The CO/CO_2 ratio is a relative measure of combustion efficiency, in terms of biomass fuel conversion. A higher ratio means lower combustion efficiency. Typical CO/CO_2 ratios during the flaming phase are lower than 0.1.[41] For the majority of combustion experiments, the average CO/CO_2 ratios were lower than 0.10 (Fig. 3), indicating that the flaming phase was dominant. The lowest CO/CO_2 ratios were observed for the combustion in the "chimney type" logwood stove, indicating higher combustion efficiency. The EC emission factor increased with decreasing CO/CO_2 ratios, whilst the opposite was observed for OC.

The CO emission factors increased with decreasing combustion temperature in stoves, indicating more incomplete combustion at lower powers of operation. A clear relationship between the combustion temperature in the fireplace and the CO emission factors was observed (Fig. 4). The CO emission factors are comparable to those reported in studies with stoves and masonry heaters.[42,43] Purvis *et al.* (2000)[44] presented CO and CO_2 emission factors from 46 to 123 g kg^{-1} biomass (dry basis) fuel and from 1789 to 2608 g kg^{-1} biomass (dry basis) fuel, respectively, for oak and Douglas fir combustion in fireplaces. Emission factors in the range of 8–9 and 14–29 g CO kg^{-1} biomass (dry basis) fuel, respectively, were observed during the combustion of biomass briquettes and *Acacia* in Indian stoves.[20,42,43] High CO emission factors, up to 300 g kg^{-1} biomass (dry basis fuel), have been observed in old-type wood log boilers with large batch size.[19]

As expected, and in contrast to what was observed for CO, the CO_2 emission factors increased with increasing combustion temperature (Fig. 4), as a result of a more efficient biomass fuel conversion at higher temperatures in the combustion chamber.

In the biomass combustion facility at Vienna, it was observed that the CO_2 and NO concentrations in the flue gases peaked at the same time as temperature. Hydrocarbon concentrations peaked somewhat later. The lowest NO and hydrocarbon (here referred to as C_xH_y) emission factors, only measured and calculated in the "chimney type" logwood stove (at Vienna), were observed for softwood (Table 6). NO_x emissions of 0.66–1.34 g kg^{-1} biomass (dry basis) fuel were obtained from birch combustion in conventional masonry heaters.[20] During US soft- and hardwood combustion in domestic appliances, average emission factors (dry basis) of 110 g CO kg^{-1} biomass fuel, 1.5 g C_xH_y kg^{-1} biomass fuel, and 0.7 g NO_x kg^{-1} biomass fuel were observed.[45] Ozil *et al.* (2009)[46] compared the emission factors of old and new generation wood heating stoves with equivalent combustion efficiencies. During the combustion of beech logs, these researchers obtained mean values of 49 g CO kg^{-1} and 5.3 g C_xH_y kg^{-1} biomass (dry basis) fuel in the old stove and in the absence of catalyst. The emission factors for the modern stove were 20.9 g CO kg^{-1} and 1.3 g C_xH_y kg^{-1} biomass (dry basis) fuel, also in the absence of catalyst. The authors observed that the presence of catalysts (composed of Pd, Pt and Ce, or supported on cordierite) induced a decrease of the CO and hydrocarbon

Table 6 Emission factors for carbon oxides, nitrogen oxide and hydrocarbons. Emission factors are referred to dry biomass fuel basis

Biomass fuel	Combustion appliance	gCO_2 kg$^{-1}_{biomass}$	gCO kg$^{-1}_{biomass}$	gNO kg$^{-1}_{biomass}$	gC_xH_y kg$^{-1}_{biomass}$
Maritime pine	Cast iron stove	1045 ± 471	57.11 ± 51.15	—	—
	Logwood stove	1640 ± 9.71	27.49 ± 2.68	0.66 ± 0.12	0.82 ± 0.76
	Fireplace	1129 ± 257	51.12 ± 6.89	—	—
Golden wattle	Cast iron stove	980 ± 794	96.49 ± 71.86	—	—
	Logwood stove	1660 ± 70.65	46.36 ± 3.23	1.34 ± 0.63	1.61 ± 1.19
	Fireplace	1112 ± 135	61.82 ± 3.79	—	—
Eucalyptus	Cast iron stove	808 ± 405	67.59 ± 42.84	—	—
	Logwood stove	1580 ± 8.52	40.48 ± 8.97	0.78 ± 0.16	2.48 ± 0.37
	Fireplace	959 ± 132	78.91 ± 7.35	—	—
Cork oak	Cast iron stove	895 ± 693	99.20 ± 92.44	—	—
	Logwood stove	1638 ± 9.71	64.56 ± 6.41	1.24 ± 0.11	4.94 ± 1.02
	Fireplace	552 ± 306	85.54 ± 21.99	—	—
Olive	Cast iron stove	790 ± 439	64.92 ± 47.21	—	—
	Fireplace	780 ± 259	81.03 ± 8.02	—	—
Holm oak	Cast iron stove	985 ± 570	63.72 ± 55.91	—	—
	Fireplace	735 ± 193	61.81 ± 24.46	—	—
Portuguese oak	Cast iron stove	786 ± 299	85.97 ± 38.73	—	—
	Fireplace	873 ± 65	78.45 ± 17.57	—	—
Briquettes	Cast iron stove	746 ± 357	62.86 ± 47.37	—	—
	Fireplace	1012 ± 97	58.24 ± 16.96	—	—

emission factors up to 70%. One explanation for the variability in emission factors is that the burning rate can significantly affect the emission profiles of gaseous species. It has been observed that higher burning rates lead to lower CO and higher NO_x emissions.[45] Other reasons for the variability in emission factors of gaseous compounds reported in the literature for biomass combustion in domestic appliances are: (i) the biomass characteristics, (ii) the type of combustion appliance, (iii) the mode of operation (batch *versus* continuous), (iv) the combustion temperature, and (v) different methodological approaches of sampling (*e.g.* grab samples *versus* continuous measurements). Due to these reasons, comparisons among existing research studies become very tricky.

4. Conclusions

Gaseous and particle emission factors from combustion of the most common Portuguese biomass fuels used in residential appliances for heating purposes were obtained for the first time. The comparison of emissions from this study with literature data showed dissimilarities, confirming the need to establish specific values for Mediterranean biomass fuel types (mostly wood) and not to import data values from other regions. Softwood showed lower particle, CO, NO and hydrocarbon emission factors than hardwood species. In general, the Portuguese fireplace was the combustion appliance with the highest particle and OC emission factors. Burning in the energy-efficient Austrian "chimney-type" logwood stove contributed to the lowest particle, OC and CO emissions whilst the CO_2 values were the highest.

As there is a general lack of understanding concerning residential combustion emissions in Portugal, this study has improved knowledge and measurement of emissions of aerosols and gases from the domestic wood burning, and has paved the way for a more accurate estimate of emissions that have air quality and climate impacts in the Mediterranean region.

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