Atmospheric Environment 44 (2010) 3024–3033

Contents lists available at ScienceDirect

Atmospheric Environment

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

Smoke emissions from biomass burning in a Mediterranean shrubland

C.A. Alves [a,*], C. Gonçalves [a], C.A. Pio [a], F. Mirante [a], A. Caseiro [a], L. Tarelho [a], M.C. Freitas [b], D.X. Viegas [c]

[a] Centre for Environmental and Marine Studies, Department of Environment, University of Aveiro, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal
[b] Technological and Nuclear Institute, Reactor, E.N. 10, 2686-953 Sacavém, Portugal
[c] Association for the Development of Industrial Aerodynamics, Department of Mechanical Engineering, University of Coimbra, 3030-788 Coimbra, Portugal

ARTICLE INFO

Article history:
Received 27 February 2010
Received in revised form
30 April 2010
Accepted 5 May 2010

Keywords:
Forest fires
Greenhouse gas emissions
Particulate emissions
Organic and elemental carbon
Chemical elements
Water-soluble ions

ABSTRACT

Gaseous and particulate samples from the smoke from prescribed burnings of a shrub-dominated forest with some pine trees in Lousã Mountain, Portugal, in May 2008, have been collected. From the gas phase Fourier transform infrared (FTIR) measurements, an average modified combustion efficiency of 0.99 was obtained, suggesting a very strong predominance of flaming combustion. Gaseous compounds whose emissions are promoted in fresh plumes and during the flaming burning phase, such as CO_2, acetylene and propene, produced emission factors higher than those proposed for savannah and tropical forest fires. Emission factors of species that are favoured by the smouldering phase (e.g. CO and CH_4) were below the values reported in the literature for biomass burning in other ecosystems. The chemical composition of fine ($PM_{2.5}$) and coarse ($PM_{2.5-10}$) particles was achieved using ion chromatography (water-soluble ions), instrumental neutron activation analysis (trace elements) and a thermal–optical transmission technique (organic carbon and elemental carbon). Approximately 50% of the particulate mass was carbonaceous in nature with a clear dominance of organic carbon. The organic carbon-to-elemental carbon ratios up to 300, or even higher, measured in the present study largely exceeded those reported for fires in savannah and tropical forests. More than 30 trace elements and ions have been determined in smoke aerosols, representing in total an average contribution of about 7% to the PM_{10} mass.

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1. Introduction

Researchers estimate that from 1850 to 1980 between 90×10^{15} and 120×10^{15} Pg of carbon dioxide (CO_2) were emitted to the atmosphere from forest fires in the tropics (NASA, 2009). In comparison, during the same time interval, the burning of coal, oil, and gas in industrialised countries contributed to the release of 165×10^{15} Pg of this greenhouse gas (NASA, 2009). Nowadays, an estimated 5.6 Pg of carbon are annually released into the atmosphere due to fossil fuel burning, whereas fires in tropical forests contribute another 2.4 Pg of carbon, i.e. about 40% of the total (NASA, 2009). Over the last decades, the amount of biomass burning has expanded worldwide. In particular, summer heatwaves in southern Europe are forecast to increase even more in frequency in association with projected climate change as a result of global warming, and hence the number and severity of wildfires is expected to increase in the future. In the past 25 years, the total number of fires reported has risen sharply from around 20,000 yr^{-1} to 60,000 yr^{-1} in the five Mediterranean Member States of EU15 – France, Greece, Italy, Portugal and Spain (EEA, 2006).

Besides CO_2, biomass burning results in the release into the atmosphere of significant quantities of other chemically active products. Emissions of carbon monoxide (CO) and methane (CH_4) perturb the atmospheric oxidation efficiency by reacting with hydroxyl radicals (Crutzen and Andreae, 1990). Just as in urban areas, emissions of nitric oxides (NO_x) and hydrocarbons react to form ozone, leading to higher concentrations in the tropics than in other regions due to the stronger impact of biomass burning (Thompson et al., 2001). On the other hand, smoke particles degrade visibility, could affect health and have highly uncertain impacts on climate forcing (Spracklen et al., 2007).

Current global estimates of gas and particulate emissions from biomass burning are largely varying (Ito and Penner, 2004; Jain et al., 2006; NASA, 2009; Randerson et al., 2006; Schultz et al., 2008; van der Werf et al., 2004): 220–13,500 Tg CO_2 yr^{-1}, 120–680 Tg CO yr^{-1}, 11–53 Tg CH_4 yr^{-1}, and 2–21 Tg NO_x yr^{-1}. Annual estimates of particulate matter smaller than 2.5 μm in diameter ($PM_{2.5}$) produced by biomass burning are around 38 Tg (NASA, 2009; Randerson et al., 2006).

The scientific community is placing greater emphasis on assessing more accurately the emissions from biomass burning and

* Corresponding author.
E-mail address: celia.alves@ua.pt (C.A. Alves).

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doi:10.1016/j.atmosenv.2010.05.010

on estimating its environmental impacts. Some studies focused on the characterisation of distinct types of biomass fires in savannahs and tropical forests have been recently performed (Andreae and Merlet, 2001; Koppmann et al., 2005; Neto et al., 2009; Reid et al., 2005; and references therein). However, most of these studies are exclusively based on gaseous measurements and, as far as we know, none of them concern the Mediterranean area. It is known that emissions depend wholly on the forest fuel types, combustion process, and weather conditions (Pio et al., 2008), and that emission factors are required for modelling atmospheric processes, inventories, and source apportionment studies. Thus, it is desirable to ascertain more precise emission factors reflecting country and regional conditions. The aim of this research is to obtain a detailed characterisation of smoke emissions from a Mediterranean shrubland.

2. Experimental

2.1. Sampling details

A series of experimental fires have been conducted at a shrub-dominated forest in Lousã Mountain (40°04′38″N and 08°09′35″W), central Portugal, in May 2008. Since these fires have been applied in a knowledgeable manner under selected weather conditions to accomplished predetermined research objectives, the chemical composition of their emissions may differ appreciably from wildfires. During the prescribed burns, the temperature and relative humidity were in the ranges 18–21 °C and 16–59%, respectively. These conditions were far less severe than those registered during heat wave triggered wildfires in summer. Summer wilfires occur, in particular, when the atmospheric circulation forms an important ridge associated with south-easterly flow, and a strong advection of very hot ($T > 30$ °C) and dry air from northern Africa that is additionally heated when passing over central Iberia (Pio et al., 2008).

The fuel characterisation was based on a combination of destructive and non destructive methods. To determine the fuel load and fuel bulk density, destructive sampling was used. From this basic information, specific allometric relationships between height and fuel load/bulk density could be obtained. Micro plots of 0.25 m^2 and 1.0 m^2 were established for destructive sampling of the dominant shrubs. The linear intersect method was used for determining the percent cover, height and bio-volume. In order to look over probable vegetation distribution gradients along each plot length, transects were established. Linear measurements were made on the interception of the vegetation through which the vertical plane of the line passed. These gave information on cover of shrub species and composition of the fuel complex. The height/length measurements were used to estimate the shrub loads. The fuel moisture content was obtained by drying fuel samples in an oven at 105 °C for 24 h. The vegetation cover was composed by some isolated pine trees (*Pinus pinaster*) and a continuous mass of dwarf Spanish heath (*Erica umbellata*), Spanish heather (*Erica australis*) and prickled broom (*Chamaespartium tridentatum*). On average, the moisture content of these shrubs was 40.7%, 48.7% and 45.6%, respectively. The three dominant vegetation species represented 16%, 43% and 32% of the fuel cover, correspondingly, presenting heights between 54 and 104 cm. The remainder percentage of fuel cover corresponded to parched vegetation composed of *Erica* species and *C. tridentatum* with moisture contents of about 7.9% and 5.7%, respectively. Taking into account the vegetation abundance and the individual moisture content of the plant species, a 43.7% moisture content average was obtained for the shrubland. From the allometric measurements, a fuel bulk density of 2.7 kg m^{-3} was achieved. The fuel load was estimated to be 27.7 ton ha^{-1} in a wet-weight basis, which corresponds to 15.6 ton ha^{-1} in a dry-weight basis.

A total of seven plots were burned. Each compartment was ignited by hand from its surrounding firebreak roads using a drip torch. During these prescribed fires, a tripod high-volume sampler (Tisch Environmental Inc.) with impaction plates operating at a flow of 1.13 m^3 min^{-1} was used to collect sequentially, on pre-baked quartz fibre filters, coarse ($PM_{2.5-10}$) and fine ($PM_{2.5}$) smoke particles. The impaction system for capturing PM_{10} was designed in accordance with the Marple and Rubow's (1986) theory and constructed in a local metal-mechanic industry. In parallel, Tedlar bags previously flushed with N_2 have been used for the collection of gas samples. Pre-removal of water vapour from the air stream was carried out in a U glass tube filled with glass spheres, immersed in an ice bath. In addition, and previously to the water vapour removal, the air stream was filtered through a 4.7 mm quartz filter to remove particles before passing to the collection system, which also contained a Teflon-lined diaphragm pump connected to a needle valve and a calibrated rotametre operating at a flow rate of 1 L min^{-1}. One of the Tedlar bags has been sampled in the same location prior to the fires aiming to obtain background levels. After sampling, the bags were stored in opaque containers in order to minimise U.V. radiation of the samples. The time period between sampling and analysis was reduced to a few hours to avoid secondary reactions.

2.2. Chemical analysis

All gas phase samples were examined for 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) using a Gasmet™ Dx − 4000 multicomponent analyser. This equipment includes a high-resolution Fourier transform infrared (FTIR) spectrometer, a 0.4 L rhodium coated aluminium sample cell with a fixed absorption path length of 5.0 m, and a Peltier cooled mercury–cadmium–telluride (MCT) detector with a scan frequency of 10 s^{-1} and a wavenumber range of 900–4200 cm^{-1}. The Gasmet™ Dx 4000 has an accuracy of ±2%. The instrument allows simple calibration using only single component calibration gases. It operates with the CALCMET analysis software, which gives access to a reference library.

It should be noted that there is a possibility that compounds such as methanol, SO_2 and NH_3 might have been trapped, at least partially, in the water condenser chiller of the air sampling system. In addition, compound losses due to a combination of adsorption to and diffusion through the bag walls might also have occurred. In fact, decline in concentration levels of several classes of volatile compounds with bag storage time have been observed in some researches (Beauchamp et al., 2008; Trabue et al., 2006; Wang et al., 1996). Measured concentrations for gaseous species represent, therefore, a lower limit of the true atmospheric values.

The carbonaceous content of particulate matter was analysed by a thermal–optical transmission technique (Carvalho et al., 2006). To avoid the potential interference of carbonates from soil with the signal of EC and OC, the filter samples were subjected to a pretreatment in HCl vapour. For the determination of soluble inorganic ions, small parts of the filters were extracted with ultra pure Milli-Q water. Dionex AS14 and CS12 chromatographic columns with Dionex AG14 and CG12 guard columns coupled to Dionex AMMS II and Dionex CMMS III suppressors, respectively for anions and cations, have been used. The trace metal speciation has been performed by Inducted Neutron Activation Analysis (INAA). Filter punches were rolled up and put into a thin foil of aluminium and irradiated for 7 h at a thermal neutron flux of 1.2×10^{13} cm^{-2} s^{-1} in the Portuguese Research Reactor. After irradiation, the samples were removed from the aluminium foil

and transferred to a polyethylene container. For each irradiated sample, two gamma spectra were measured with hyperpure germanium detectors, one spectrum 2–3 days after irradiation and the other one after 4 weeks. The k_0 method was used and 1 mm diameter wires of 0.1% Au–Al were co-irradiated as comparators.

2.3. Calculations

The emission factor (EF) is a parameter that relates the emission of a particular species of interest to the amount of fuel burned. It is defined as the amount of a compound released per amount of dry fuel consumed, expressed in units of g kg^{-1}. The carbon combusted in a fire is emitted into the measurable portions of a smoke plume in five forms of carbon: CO_2, CO, CH_4, non-methane hydrocarbons (NMHC), and particulate carbon (PC). The emission factor of a species, *n*, is then obtained from the ratio of the mass concentration of that species to the total carbon concentration emitted in the plume. Thus, the emission factor is expressed in units of mass of species *n* emitted per unit mass of carbon burned. To convert this emission factor to the more frequently used grams of *n* produced per kg of dry matter burned, the previous ratio is multiplied by the mass fraction of carbon in the fuel (Reid et al., 2005):

$$EF_n = \frac{[n]}{[CO_2] + [CO] + [CH_4] + [NMHC] + [PC]} \times \%C_{fuel}. \quad (1)$$

It has been estimated that the dominant shrub species in the Portuguese forest have a mean carbon content of 48% (Silva et al., 2008). It should be also noted that background levels have been subtracted from measurements in the smoke plumes. The term [NMHC] in the equation was considered to be the sum of ethane, propene, acetylene and methanol. These species are among the dominant volatile hydrocarbons emitted by fires. On the other hand, total emissions of NMHC accounted for 1–2%, or less, of fuel C burned, while CO_2 and CO comprise 87–92% (Urbanski et al., 2009). Thus, the error committed in the calculation of individual emission factors by taking just a few NMHC species appears to be negligible.

To evaluate the completeness of combustion, it can be considered that >90% of the carbon combusted in a fire is emitted in the form of CO_2 and CO, and <10% of carbon is in species such as hydrocarbons and particulate carbon. Keeping this in mind, the modified combustion efficiency (MCE) is calculated as follows:

$$MCE = \frac{[CO_2]}{[CO_2] + [CO]}. \quad (2)$$

A MCE > 90% suggests that more than 50% of the emissions were produced by flaming combustion, whereas when MCE < 90%, more than 50% of the emissions were originated by smouldering combustion (Ward and Hardy, 1991).

3. Results and discussion

3.1. Gaseous species

The MCE, i.e. the ratio of the carbon released as CO_2 to the sum of the carbon released in the form of CO_2 and CO, was 0.99 ± 0.01, indicating fires typically in the flaming phase. Among other factors, the low degree of fuel packing may have contributed to such high MCE values (Neto et al., 2009). The EFs resulting from the samples collected during the prescribed burns are presented in Fig. 1. In general, EFs are strongly dependent on MCE. Fig. 2 depicts the correlation between EFs and MCE for some gaseous compounds. The slope of the regressions indicates the importance of the burning phase (flaming versus smouldering) in estimating the emission factors, i.e. the steeper the slope, the larger the dependence on the type of combustion (Sinha et al., 2003). Positive slopes point out that emissions are promoted by flaming combustion, whereas negative values suggest that emission of the species is favoured by the smouldering phase.

The EF_{CO_2} obtained for Lousã Mountain are higher than those proposed by Andreae and Merlet (2001) for savannah and tropical forest fires. However, measurements of smoke emissions with high combustion efficiency in grassland and woodland savannah ecosystems in South Africa and Zambia provided average EF_{CO_2} of 1701 g kg^{-1} (Ward et al., 1996). Neto et al. (2009) reported EF_{CO_2} of 1631–1625 g kg^{-1} (ignition), 1690–1741 g kg^{-1} (flaming) and 1540–1548 g kg^{-1} (smouldering) for an Amazonian forest clearing fire. McMeeking et al. (2009) obtained average EF_{CO_2} of 1552 ± 150 g kg^{-1} (MCE = 0.915 ± 0.033), 1489 ± 176 g kg^{-1} (MCE = 0.905 ± 0.043), 1538 ± 125 g kg^{-1} (MCE = 0.909 ± 0.029), 1632 ± 150 g kg^{-1} (MCE = 0.930 ± 0.029) and 1311 ± 325 g kg^{-1} (MCE = 0.917 ± 0.068), from a series of laboratory burns of fuels from montane, rangeland, chaparral, coastal plain and boreal forest, respectively, reflecting the different contributions from flaming and smouldering combustion. The combination of lower particulate matter EFs and higher CO_2 EFs indicates that the prescribed fires exhibited more efficient combustion than wildfires or slash reduction burns. This is likely due to more efficient burning of fine fuels under prescription conditions, which minimises consumption of soil organic layers and smouldering of heavy fuels. Combustion of these fuel components often results in higher emission of products of incomplete combustion (Mickler et al., 2007). Taking into account a fuel load of 15.6 ton ha^{-1}, the experiment of this study provided an average emission rate of CO_2 of 26 ton ha^{-1}, which means that 89% of the carbon content of biofuels was emitted to the atmosphere in the form of carbon dioxide.

As expected, contrarily to the results obtained for CO_2, EF_{CO} in this study fall below reported values for fires in other ecosystems. Hegg et al. (1990) and Laursen et al. (1992) obtained EF_{CO} values between 34 and 175 g kg^{-1} (average of 95 ± 16 g kg^{-1}). For diverse fires in North America. Yokelson et al. (2009) reported values of 75 ± 26 g kg^{-1} and 83 ± 14 g kg^{-1} for crop residues and deforestation fires, respectively. Bertschi et al. (2003) measured EF_{CO} from 128 to 165 g kg^{-1} in residual smouldering combustion (RSC) in a series of laboratory fires and in a wooded savannah (miombo). The authors concluded that EFs for RSC-prone fuels, including downed logs, duff, and organic soils, from the boreal forest and wooded savannah are very different from the EFs for the same compounds measured in fire convection columns above these ecosystems. The EF_{RSC} for CO raised by a factor of 2.1 when comparing lofted emissions with RSC. Very high-intensity flaming combustion, such as that observed in Lousã Mountain, leads to more complete combustion and correspondingly lower proportions of incompletely oxidised combustion products like carbon monoxide.

Methane emission factors reported from the few existing studies differ by a factor of 20, varying from 1 to 23 g kg^{-1}, with higher values for smouldering combustion (Bertschi et al., 2003; Ferek et al., 1998; Radojevic, 2003). In fact, methane emissions are much higher for fires with low combustion efficiency (Koppmann et al., 2005). Ward et al. (1996) reported EF_{CH_4} of 1.0–1.6 g kg^{-1} for flaming-phase cerrado fires, whereas values up to 10.8 g kg^{-1} have been obtained for smouldering combustion in primary forest slash in Brazil. Neto et al. (2009) obtained EF_{CH_4} of 3.4 and 13.1 g kg^{-1} in an Amazonian forest clearing fire during the flaming and smouldering phases, respectively. The EF_{CH_4} obtained in this study is in the range of 0.9–5.6 g kg^{-1} measured over real biomass fires in the United States (Hegg et al., 1990). The contribution of CH_4 as a greenhouse gas is 21 times that of CO_2 (Barker

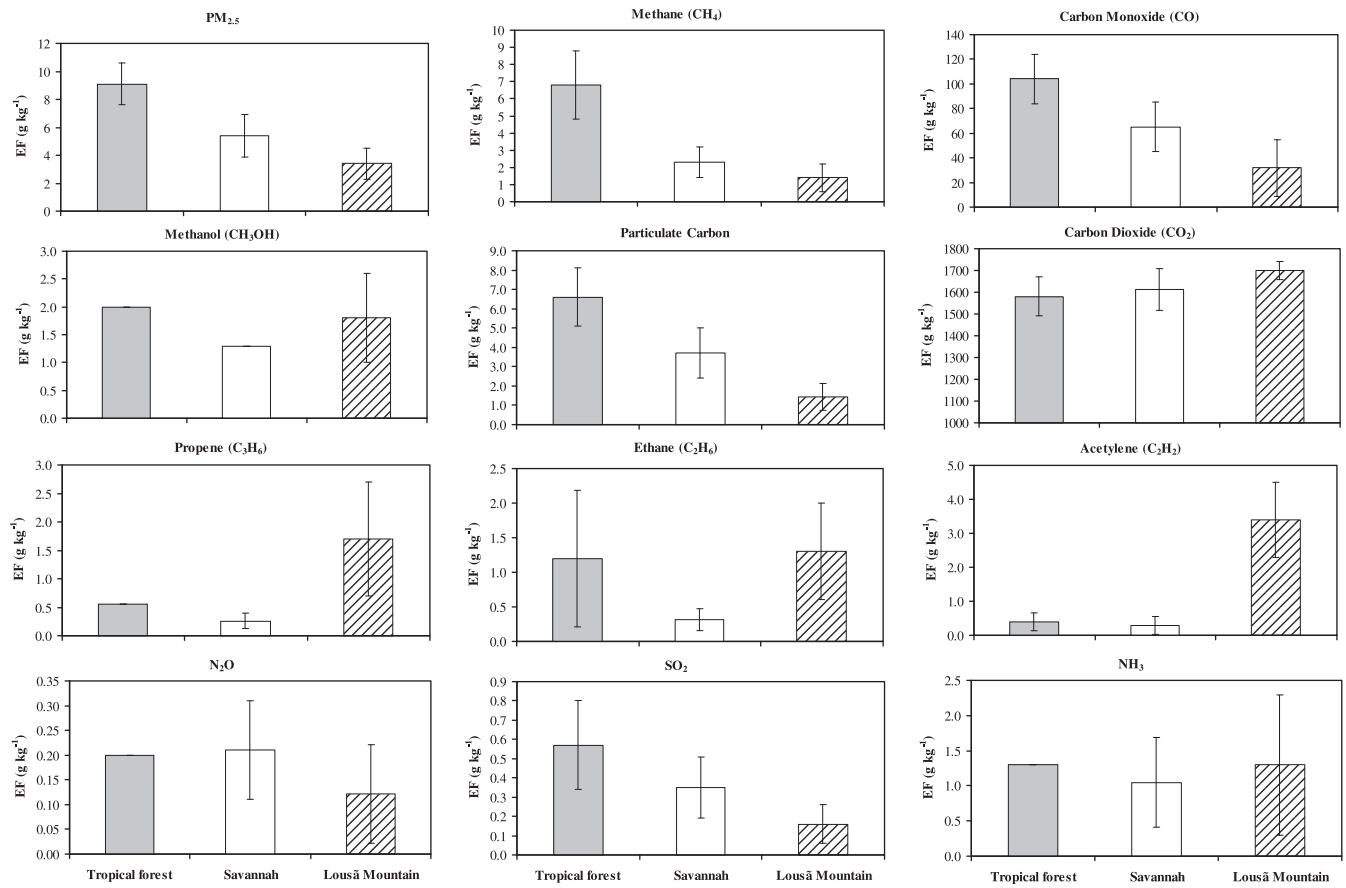

Fig. 1. Comparison of emission factors (given in gram species per kilogram dry matter burned, mean ± standard deviation) for pyrogenic species. Data source for savannah and tropical forest is Andreae and Merlet (2001).

et al., 2007). Multiplying the average EF_{CH4} of 1.4 g kg^{-1} by this number, the emission factor for CO_2 equivalent to the emitted CH_4 is 29.4 g kg^{-1}, which represents only 2% of the 1700 g kg^{-1} released originally as CO_2.

Emission factors of both NO and NO_2 in this study were always less than 0.3 g kg^{-1}, which are far below the average EF_{NOx} (as NO) of 3.9 and 1.6 g kg^{-1} published by Andreae and Merlet (2001) for savannah/grassland and tropical forest burning, respectively. Since

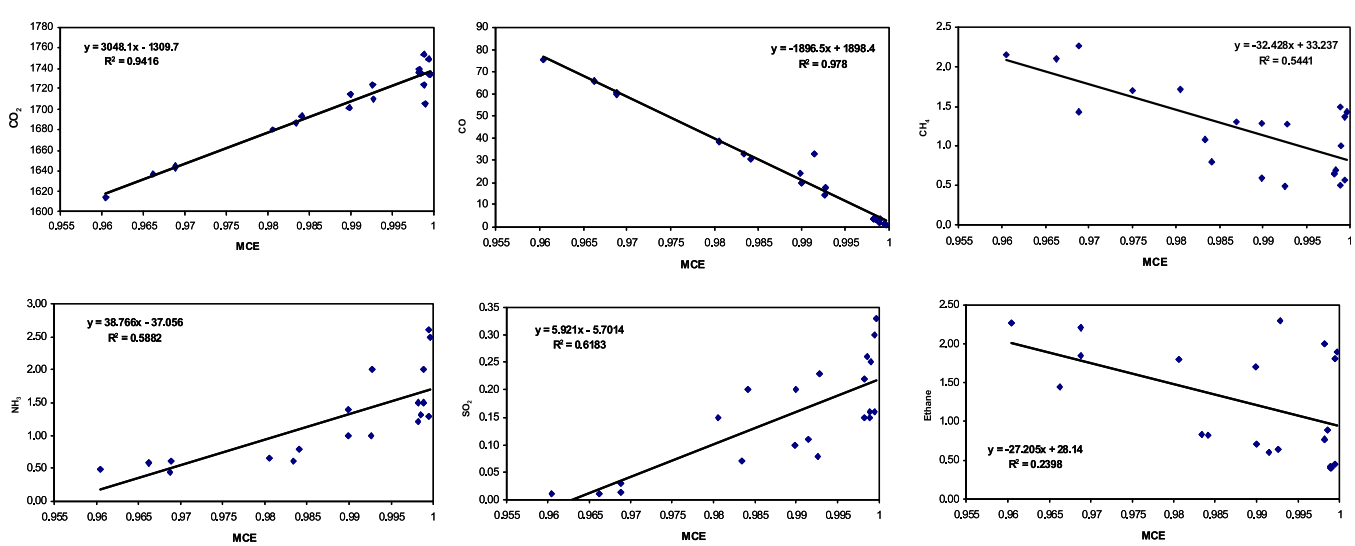

Fig. 2. Correlation between EF (g kg^{-1}, dry basis) of some gaseous species and MCE.

most of the NO_x in smoke comes from nitrogen compounds in the biomass itself (Radojevic, 2003), the differences in EFs may be due to variations in the N content of biofuels burned. In fact, while the nitrogen content in trees of Amazonia was estimated to be in the range 1.3–3.2% (Parolin et al., 2002), the dominant shrub species of the Portuguese forest have a content lower than 0.8% (Silva et al., 2008). A reduction of 25% has been observed in the nitrogen content after rainfall events (Silva et al., 2008). Given that some precipitation had been registered a few days before the biomass burning experiments, it is likely that some nitrogen leaching has occurred. However, the drawbacks associated with a possible loss of compounds during sampling must also be pointed out to explain the low EF_{NO_x} values. For NH_3, the shrub-dominated ecosystem emission factors are close to what has been measured for other temperate woods, savannah and tropical forest (Andreae and Merlet, 2001; Yokelson et al., 2007).

The EFs calculated in this study for acetylene, ethane and propene are weakly correlated with MCE, suggesting that these emissions do not present a strong dependence on the combustion process. The EF estimates show significant departure from the values quoted by Andreae and Merlet (2001) for tropical forest and savannah fires. According to Yokelson et al. (2003), many reactive initial emissions may be depleted in aged smoke, lowering the corresponding emission factors. Thus, the high values obtained for VOC species in Lousã Mountain may be associated with the very fresh nature of the smoke plumes. It must be also pointed out that VOC emission factors presented higher values for boreal forest fires than those obtained for tropical savannahs and tropical forest (Urbanski et al., 2009).

The average EF_{CH_3OH} of 1.8 g kg^{-1} inferred from these measurements is lower than the 2.73 g kg^{-1} emission factor measured in western Canada and Alaska plumes (Rinsland et al., 2007), the 2.0 g kg^{-1} extratropical forest emission factor (Andreae and Merlet, 2001) and the 2.03 g kg^{-1} measured in a large, isolated North Carolina, USA plume (Yokelson et al., 1999). An EF_{CH_3OH} of 1.07 g kg^{-1} has been derived for residual smouldering combustion of boreal fuels from laboratory fire measurements (Bertschi et al., 2003). Goode et al. (2000) reported an emission factor of 1.35 g kg^{-1} from analysis of Alaska biomass burning plumes, which approaches the 1.3 g kg^{-1} proposed for savannah burning (Andrea and Merlet, 2001). However, our EF_{CH_3OH} of 1.8 g kg^{-1} is close to the 1.71 g kg^{-1} reported by Yokelson et al. (1999) by averaging 13 measurements obtained with a wide range of techniques.

Our results for SO_2 show a positive slope for EF versus MCE, in accordance with past studies that have indicated that SO_2 is preferentially released in flaming combustion (e.g. Ferek et al., 1998; Sinha et al., 2003). The scarce EF_{SO_2} found in the literature present a large variability, since, in addition to the dependence of smoke properties on combustion phase, the fuel sulphur content varies greatly (Sinha et al., 2003). Also, the S-containing emissions depend on the partitioning of sulphur among ash, SO_2 in the gas phase and particulate matter.

3.2. Particulate matter

The $PM_{2.5}$ and $PM_{2.5\text{-}10}$ reached, respectively, concentrations up to 12.5 and 1.14 mg m^{-3} in the smoke plume. In line with other studies (Andreae and Merlet, 2001), $PM_{2.5}$ represented around 80% of the PM_{10} mass. The particulate matter emission factors estimated in this work are generally below those obtained for other smoke plumes with lower combustion efficiencies. For example, $EF_{PM_{2.5}}$ in the range 3.5–16 g kg^{-1} have been obtained in various types of measurements in the Amazonian region (Neto et al., 2009; and references therein). Ward et al. (1996) measured $EF_{PM_{2.5}}$ ranging from 1.5 to 8.0 g kg^{-1} for African savannah ecosystems. It should be noted that particle emission factors depend on the plume dilution. At low levels of dilution, semivolatile species largely occur in the particle phase, but increasing dilution reduces the concentration of semivolatile species, shifting this material to the gas phase in order to maintain phase equilibrium. Under the highly dilute conditions found in the atmosphere, partitioning of the emissions is strongly influenced by the ambient temperature and the background organic aerosol concentration (Donahue et al., 2006; Shrivastava et al., 2006).

Since emission factors of particulate matter are highly variable depending on plume dilution, fuel type and combustion efficiency (Reid et al., 2005), and taking into account differences in sampling and analytical techniques, the mass fractions of OC in biomass burning aerosols published in the few studies available are also very discrepant. The OC particulate content reported for flaming fires range between approximately 37 and 65% (Table 1). For smouldering fires, the OC content published in the literature represents 62 ± 6% of the PM mass (Reid et al., 2005). The mass fraction of EC in smoke particles is even more variable, differing by over a factor of 5 during flaming-phase combustion. The carbonaceous fraction of smoke samples from any of the fires in this study was dominated by organic carbon (OC/PC ≈ 97%) and OC/EC ratios much higher than those reported for other biomass burning events. Field and laboratory studies have attributed the high OC production in fire plumes to condensation of large hydrocarbons, enhanced isoprenoid emissions, acid-catalysed reactions and very rapid oxidation of low-volatility organic vapours (Grieshop et al., 2009; and references therein). The combination of all these factors may have contributed to the very high OC/EC ratios observed in the present study. It should be noted that high OC/EC ratios have also been found for atmospheric aerosols collected in a rural location in Portugal during the 2003 summer intense wildfire period (Pio et al., 2008). Differences between values generated by the current investigation and those reported in the literature may also derive from the methodologies used for the analysis of carbon, since an inter-laboratory comparison have shown that the OC/EC absolute split is not yet solved (Schmid et al., 2001). However, results of this international round robin test on the analysis of carbonaceous aerosols positioned the University of Aveiro within the group with "best estimates". In addition, the comparison between the methodology of the University of Aveiro and the "European Supersites for Atmospheric Aerosol Research" (EUSAAR-2) protocol (Cavalli et al., 2009) for the quantification of the different carbon fractions in atmospheric aerosol samples gave similar results for OC and EC, without significant differences at a 95% confidence level (Nunes et al., 2010).

Taking into account the gravimetric data and all identified aerosol species, it is possible to reconstruct the $PM_{2.5}$ and PM_{10} mass emissions and to infer the organic matter-to-organic carbon

Table 1
Comparison of carbon measurements of fresh biomass burning smoke (flaming phase). Values for this study are expressed as mean ± standard deviation.

	PM Size	OC/EC ratio	OC mass fraction of PM (%)
Savannah (Andreae et al., 1998)	PM_2	4.3	44
Savannah (Cachier et al., 1995)	TSP	8.3	40–66
Cerrado (Ferek et al., 1998)	PM_4	8.3	61 ± 20
Cerrado (Ward et al., 1992)	$PM_{2.5}$	16.7	57
Pasture (Ferek et al., 1998)	PM_4	9.1	66 ± 11
Temperate forest (Ward et al., 1992)	$PM_{2.5}$	10	50
Tropical forest (Ferek et al., 1998)	PM_4	6.7	53 ± 20
This study	$PM_{2.5}$	88 ± 46	50 ± 8
	$PM_{2.5\text{-}10}$	128 ± 73	44 ± 11
	PM_{10}	93 ± 23	44 ± 5

Table 2
Water-soluble ions (expressed as wt % of particle mass, mean ± standard deviation) obtained in samples from Lousã Mountain and values from the literature.

Water–soluble ions	$PM_{2.5}$Lousã	$PM_{2.5\text{-}10}$Lousã	PM_2, $PM_{2.5}$ or PM_4(literature)	Biome type (literature)
Cl^-	0.28 ± 0.20	0.33 ± 0.43	2.3–11	Savannah
			1.7	Grassland
			1.0–6.0	Cerrado
			0.2–1.7	Tropical broadleaf
NO_3^-	0.11 ± 0.10	0.09 ± 0.07	0.33–0.62	Cerrado
			0.12	Tropical broadleaf
SO_4^{2-}	0.32 ± 0.19	0.44 ± 0.14	0.35–0.72	Cerrado
			0.39–0.90	Tropical broadleaf
Na^+	0.18 ± 0.18	0.74 ± 1.15	0.13–0.8	Savannah
			0.1	Grassland
			0.01–1.0	Cerrado
			0.01–0.2	Tropical broadleaf
NH_4^+	0.05 ± 0.05	0.02 ± 0.02	0.05–0.1	Cerrado
			0.06–0.09	Tropical broadleaf
K^+	0.21 ± 0.28	0.16 ± 0.18	1.8–6.2	Savannah
			2.9	Grassland
			1.3–18	Cerrado
			0.4–5.5	Tropical broadleaf
Mg^{2+}	0.06 ± 0.04	0.16 ± 0.10	<0.06–0.6	Savannah
			0.3	Grassland
			0.03–0.5	Cerrado
			0.01–0.6	Tropical broadleaf
Ca^{2+}	0.26 ± 0.06	0.65 ± 0.42	0.0029–2.46	Savannah
			0.7	Grassland
			0.1–12	Cerrado
			0.06–5	Tropical broadleaf
Sum	1.5±0.10%	2.6±0.31%		

Data sources for savannah are Andreae et al. (1998), Cachier et al. (1995) and Maenhaut et al. (1996).
Data source for grassland is Ferek et al. (1998).
Data sources for cerrado and tropical broadleaf are Ferek et al. (1998), Ward et al. (1992) and Yamasoe et al. (2000).

(OM/OC) factor. This factor is used to compute the total organic mass concentration, accounting for associated O, H, N, and other elements, from the measured C mass concentrations attributed to OC (McMeeking et al., 2009). The equation used was as follows:

$$PM_{2.5} \text{ or } PM_{10} = \sum \text{ionic species} + \sum \text{metals} + EC + OC \times f \quad (3)$$

where f represents the OM/OC ratio. Based on these calculations, average values of 1.9 and 2 have been estimated for the OM/OC ratios in $PM_{2.5}$ and PM_{10}, respectively. In a review of biomass burning emissions, Reid et al. (2005) reported OM/OC factors of 1.4–1.8. Results from a laboratory investigation of organic aerosols from wood fires suggested an OM/OC ratio of about 2 (Grieshop et al., 2009).

The water-soluble species, ranked in order of concentrations, were Na^+, Ca^{2+}, SO_4^{2-}, Cl^-, K^+, NO_3^-, Mg^{2+} and NH_4^+, which globally represent about 4% of the PM_{10} mass (Table 2). Excepting for NO_3^-, NH_4^+ and K^+, ionic species in the coarse mode were more enriched than those in the fine mode. It has been reported that the major ionic species were Cl^-, SO_4^{2-}, K^+ and NH_4^+ for savannah fires (Andreae et al., 1998) and SO_4^{2-}, NH_4^+, K^+, NO_3^- and Cl^-, for fires in the Amazon basin (Falkovich et al., 2005). Besides the dependence on burning phase, the observed differences may be explained by the variability in biomass density, elemental composition and moisture content. Contrarily to what was observed by Andreae et al. (1998), in this study, nitrate was predominantly present in the fine aerosol fraction. The difference between results may be due to the somewhat higher age of the savannah fire plumes, which would make additional formation of HNO_3 and its subsequent absorption on mineral aerosol particles. The mass fraction of water-soluble potassium determined in this study is surprisingly lower than values reported for fires in savannah, grassland, cerrado and tropical broadleaf. However, Chen et al. (2007) found highly variable emission factors in laboratory-controlled fires by burning eight wildland fuels. Depending on the biofuel, the mass percentages of potassium were as high as 23.7%, but they were particularly low (<1%) in the smoke of certain grasses and shrubs.

The observed excess of positive ions correlates well with the concentrations of calcium ions (Fig. 3), suggesting an origin, at least in part, on calcium carbonate from soil. Large amounts of Mg^{2+} in the coarse fraction could also be due to entrainment of soil dust. The equivalents ratio between the excess of positive ions and calcium is about 1 and 1.9 for $PM_{2.5}$ and $PM_{2.5-10}$, respectively. This indicates that coarse particles are influenced by an additional source of Ca^{2+}, besides soil calcium carbonate. On the other hand, the excess of positive ions could imply that not all the major anionic components were measured. Many researchers have reported that biomass burning contains a significant fraction of water-soluble formate, acetate, oxalate and other organic anions, such as

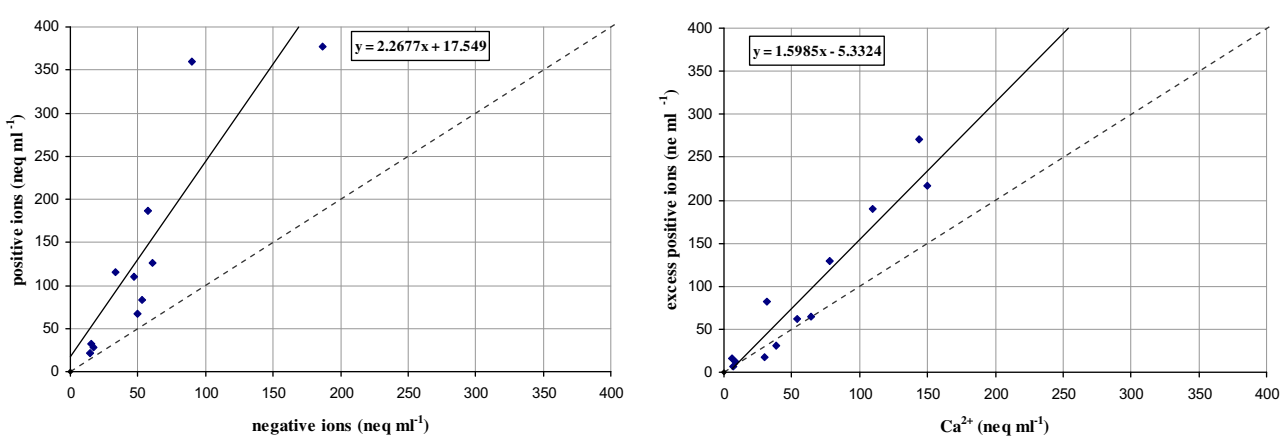

Fig. 3. Ion balance and correlation between the excess of positive ions and calcium.

Table 3
Potassium and chlorine to elemental carbon mass ratios obtained in different studies.

	This study	Yamasoe et al. (2000)		Ferek et al. (1998)	Maenhaut et al. (1996)		Andreae et al. (1998)
	Mediterranean shrubland	Tropical forest and cerrado in Amazonia		Forest, cerrado and pasture fires in Brazil	Prescribed fires in South Africa		Savannah fires
	Flaming	Flaming	Smouldering		Flaming	Smouldering	
Cl/EC	0.24	0.17	0.15	0.44	0.31	0.22	2.39
K/EC	0.48	0.24	0.20	0.60	0.20	0.17	0.62

malonate, succinate and glutarate (Song et al., 2005; and references therein).

It was observed that the major inorganic fine particles that were emitted during these flaming fires consist of KCl and NH_4Cl. These compounds are very soluble in water and, consequently, the particles are expected to be active as cloud condensation nuclei (CCN). Emissions from fires in Mediterranean shrublands may therefore notably contribute to the indirect radiative forcing on a regional scale in this region. Petters et al. (2009) examined the hygroscopic properties of aerosols freshly emitted from laboratory biomass burning experiments, concluding that most particles are CCN active at the point of emission and do not require conversion in the atmosphere to more hygroscopic compositions before they can participate in cloud formation and undergo wet deposition. The constituents of the K- and Cl-rich particles are organically bound and/or present in the fluids of the vegetation, volatilised during the combustion process and afterwards converted into the particulate phase by nucleation or condensation. Elemental mass ratios of K and Cl to elemental carbon (Table 3) compare to the signatures of cerrado and savannah fire emissions. Echalar et al. (1995) presented K/EC ratios in the range 0.007–1.14, showing lowest values for wood smoke and forest fires, and maximum values for cerrado and savannah biomass burning.

Table 4 presents the mass percentage of trace elements in smoke particulate matter. Some trace element measurements have been also presented for sugar cane (Lara et al., 2005), rice straw (Viana et al., 2008), wheat straw (Sahai et al., 2007), agricultural burning (Jimenez et al., 2006), wind tunnel derived profiles for herbaceous and wood fuels (Turn et al., 1997) and prescribed burnings in pine-dominated forests in Georgia, USA (Lee et al., 2005). More than 30 metal elements have been detected in the smoke samples from Lousã Mountain, representing about 2.5% of the PM_{10} mass. The coarse fraction was the richest in these trace components. The dominant elements were iron, barium, thulium and zinc. Gaudichet et al. (1995) also found high concentrations of Fe in savannah biomass burning aerosols, attributing its origin to soil remobilisation processes during the fires and to terrigeneous particles deposed on vegetation. As it occurred in aerosols from Lousã Mountain, Fe was predominantly found in the coarse particles, suggesting a crustal origin. However, it should be taken into account that iron is also a component of vegetation and takes part in physiological processes (Gonçalves et al., 2002; Zocchi and Cocucci, 1990). Estimates of zinc emissions by tropical savannah fires by Echalar et al. (1995) indicate that the contribution of this source should be taken into account to understand the biogeochemical cycles of this element. Zinc is present in the cytoplasms of plants and may be associated with the combustion of vegetation (Andreae et al., 1998). Many rare earth elements (REE), such as La, Ce, Nd, Pr, Sm, Tb, Tm and Yb, take place in physiological processes of plants, playing also an important role in soil microorganisms with their biosorption ability and produce organic acids that can serve as phosphate solubilisers. It has been demonstrated that many plants are accumulators of trace metals (Babula et al., 2008; Pratas et al., 2005), including REE and elements yielding medium- and long-lived radionuclides (e.g. Sc, Cr, Rb, Cs, Ba, U, etc.). Many of these elements have been detected in plants such as those growing in Lousã Mountain (Pratas et al., 2005). Thus, biofuel burning may result in the volatilisation of these trace metals which then undergo condensation or gas-to-particle type reactions, adsorbing on the surface of pre-existing aerosols. In addition, plant debris or partially

Table 4
Trace elements (expressed as wt % of particle mass) obtained in samples from Lousã Mountain and values from the literature.

Element	$PM_{2.5}$ Lousã	$PM_{2.5-10}$ Lousã	PM_2, $PM_{2.5}$ or PM_4 (literature)	Biome type (literature)
Sc	0.0003 ± 0.0002	0.0038 ± 0.0007		
Cr	0.0146 ± 0.0249	0.0170 ± 0.0374	0.013–0.023 bld-0.014	Cerrado Tropical broadleaf
Fe	0.3005 ± 0.3806	1.6786 ± 1.2263	0.05–1.3 0.03–0.9	Cerrado Tropical broadleaf
Co	0.0004 ± 0.0003	0.0047 ± 0.0087		
Zn	0.0488 ± 0.0573	0.1793 ± 0.1344		
As	0.0052 ± 0.0011	0.0052 ± 0.0008		
Se	0.0003 ± 0.0003	0.0013 ± 0.0028	0.0012–0.0034 0.0020–0.0028	Cerrado Tropical broadleaf
Br	0.0101 ± 0.0058	0.0252 ± 0.0009	0.042–0.057 0.029–0.051	Cerrado Tropical broadleaf
Rb	bdl	0.0060 ± 0.0009	0.013–0.015 0.008–0.012	Cerrado Tropical broadleaf
Sr	bdl	bdl	0.004–0.006 bdl-0.003	Cerrado Tropical broadleaf
Zr	0.0023 ± 0.0040	0.0330 ± 0.0037	bdl-0.018 bld	Cerrado Tropical broadleaf
Mo	0.0247 ± 0.0407	0.0023 ± 0.0025		
Cd	0.0010 ± 0.0002	bdl		
Sb	0.0008 ± 0.0002	0.0006 ± 0.0013		
Cs	0.0001 ± 0.0001	0.0013 ± 0.0003		
Ba	0.0270 ± 0.0206	0.2451 ± 0.1896		
La	0.0005 ± 0.0004	0.0108 ± 0.0012		
Ce	0.0035 ± 0.0047	0.0206 ± 0.0026		
Pr	0.0003 ± 0.0004	0.0019		
Nd	bdl	0.0019 ± 0.0018		
Sm	0.0003 ± 0.0003	0.0017 ± 0.0004		
Eu	0.0001 ± 0.0000	0.0001 ± 0.0002		
Tb	bdl	0.0001 ± 0.0002		
Tm	0.2451 ± 0.5480	bdl		
Yb	0.0002 ± 0.0002	0.0004 ± 0.0009		
Hf	0.0011 ± 0.0000	0.0011 ± 0.0025		
W	bdl	0.0001 ± 0.0002		
Th	0.0002 ± 0.0004	0.0018 ± 0.0004		
U	0.0003 ± 0.0002	0.0002 ± 0.0003		
Sum	0.69 ± 0.06%	2.24 ± 0.28%		

bdl – below detection limit.
Data sources for savannah are Andreae et al. (1998), Cachier et al. (1995) and Maenhaut et al. (1996).
Data source for grassland is Ferek et al. (1998).
Data sources for cerrado and tropical broadleaf are Ferek et al. (1998), Ward et al. (1992), and Yamasoe et al. (2000).

combusted foliage ash may contribute to the detection of trace metals, principally in coarse aerosol particles.

Based on the classification (cambisoils) and the average composition of soil from Lousã Mountain, enrichment factors were calculated (McKenzie et al., 2008) with Th as reference element, since it was found to be a major crustal metal in this region (Ferreira, 2004). Assuming that Th is only associated with soil-derived particles, and that the ratio of the element X versus Th is known in the parent soil, the percentages of X from noncrustal origin were derived:

$$X_{noncrustal}(\%) = (E_X - 1)/E_X \times 100 \quad (4)$$

where E_x represents the enrichment factor of element X in the particulate matter relative to the crust. In this case, the equation used for the E_x calculation was

$$E_X = (X/Th)_{\mathrm{PM}}/(Th/X)_{soil} \quad (5)$$

These calculations showed that, in $PM_{2.5-10}$, up to 80% for As and 50% for La were of crustal origin. The soil-derived dust represented about 4, 28, 21 and 6% of Ba, Co, Cr and Zn concentrations in coarse particles, respectively. It was also estimated that Fe had a significant part of its concentration (up to 28%) imposed by the soil contribution. These values must be considered as an upper limit according to the hypothesis attributing all the measured Th to the crustal source.

Due to the scarcity of data, a comparison with values from other authors is only possible for a few metals (Table 4). For these, concentrations in the smoke plumes of the experimental fires in Lousã Mountain are not very far from those obtained in Amazonia and African savannah. It should be noted, however, that in addition to the biome specificities and high variability of combustion efficiencies, different sampling strategies (ground-based measurements, masts, aircrafts, PM_2, $PM_{2.5}$, PM_4, etc.) may render a comparison of data very tricky.

4. Conclusions

This study includes novel data on emissions of trace gases from fires in a Mediterranean shrubland. The low degree of fuel packing in this type of ecosystem contributed to very high-intensity flaming combustion and to the sampling of very fresh plumes, even in seasonal and humidity conditions not yet prone to natural fire development. Under these conditions, emissions of CO_2 and NMHC were higher than those reported for fires in other biome types. Contrarily, emissions of the species that are favoured by the smouldering phase, such as CO, presented EFs lower than values proposed for fires in the African savannah and Amazonia. The emission factor for CO_2 equivalent to the emitted CH_4 from the shrubland burnings was 29.4 g kg^{-1}, which is 2.0% of the original 1700 g kg^{-1} for CO_2 only. The average emission factors for other species were as follows (g kg^{-1} of dry fuel consumed): 1.8 (methanol), 1.7 (propene), 1.3 (ethane), 3.4 (acetylene), 1.3 (NH_3) 0.122 (N_2O), <0.3 (NO_x), 0.16 (SO_2) and 3.4 ($PM_{2.5}$). $PM_{2.5}$ represented around 80% of the PM_{10} mass. More than 30 trace metals and water-soluble ions have been determined in smoke aerosols, representing in total an average contribution of about 7% to the PM_{10} mass. Approximately 50% of the particulate mass is carbonaceous in nature with a clear dominance of organic carbon and much lower EC values than those reported in the literature.

The comprehensive chemical characterisation data set obtained during this experiment is potentially very useful for numerical models to evaluate the impact of forest fires on the microscale to regional-scale atmosphere in the Mediterranean region. Taking into account that, besides emission inventories, climate change, atmospheric photochemical and source apportionment models use emission profiles which should reflect the regional characteristics of biofuels, and that considerable uncertainties remain regarding the magnitude of carbon exchanges between the wildland burning and the atmosphere, it has yet to be estimated more specific emission profiles for wildfires in wood-dominated forests in Southern Europe, especially under extreme weather conditions.

Acknowledgments

This work was funded by the Portuguese Science Foundation (FCT) through the project "Contribution of biomass combustion to air pollutant emissions", PTDC/AMB/65706/2006 (BIOEMI). C. Gonçalves acknowledges the PhD grant SFRH/BD/36540/2007 from FCT. We are also grateful to the FUMEXP project team members for the sampling campaign logistics.

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