

Forest fires in Portugal in summer 2010: contribution to atmospheric pollution

A.I. Calvo¹, A.P. Fernandes¹, T. Nunes¹, C.A. Alves¹, A.M. Vicente¹, M. Evtyugina¹,
A.C. Monteiro¹, C.V. Gonçalves¹, L.A.C. Tarelho¹, C. Pio¹

Abstract — Trace gases and aerosol particle emissions from several wildfires occurring in Portugal were sampled in summer 2010. Coarse (PM_{2.5-10}) and fine (PM_{2.5}) smoke particles were collected. Sampling was performed at 1.5 m above ground, downwind from the burning area, at distances of 10 e 200 m from the flame. Tedlar bags were used for the collection of gas samples in parallel with aerosol sampling. Total volatile hydrocarbons (THC) and carbon oxides (CO₂ and CO) concentrations were determined. PM_{2.5} constitutes an important fraction of PM₁₀, with a PM_{2.5}/PM₁₀ average ratio of 0.91±0.05. A clear predominance of carbonaceous aerosol was observed, with OC concentration always remaining much higher than EC in both size ranges (OC/TC ratios ranged between 0.99 and 0.71 for both sizes). Water-soluble inorganic ions represented less than 4% of the aerosol mass. The CO and CO₂ emission factors (EF) were around 67-383 and 1029-1655 g kg⁻¹ biomass (dry basis) burned, respectively. The EF ranged between 4 and 68 g kg⁻¹ for PM_{2.5} and between 5 and 72 g kg⁻¹ (dry basis) for PM₁₀. For THC, EF reached values up to 28 g kg⁻¹ (dry basis). Levoglucosan was always present at higher concentrations than those of galactosan and mannosan.

Keywords — Emission factors, particulate matter, trace gases, wildfires

1 INTRODUCTION

Wildfires are an important source of aerosol particles and trace gases, with an important impact on human health, visibility, biogeochemical cycles, atmospheric chemistry, global and regional climate [1], [2], [3], [4], [5], [6]. Biomass burning emissions depend strongly on the combustion conditions, which are broadly classified as flaming - in which a more complete oxidation is involved - and smouldering [7], [8]. A complete characterisation of these two phases is required when biomass burning emissions are estimated.

In the Mediterranean region, where forest fires are highly frequent during summer, Portugal and Spain register one of the largest number of fires in the European region. In Portugal, where most wildfires occur in northern and central area of the country, wildfires destroy every year thousands of hectares, with important losses in terms of environmental damage, economic disruptions and several human lives.

According to the last Portuguese National Forest Inventory (INF) -2005/2006- of the General Directorate of Forest Resources, a percentage of 38% of the total land of Portugal is occupied by forest (around 3.4 millions of ha), with the major area covered by *Pinus pinaster* (23%), *Quercus*

suber (23%) *Eucalyptus* (21%) and *Quercus ilex* (12%). During the period 1980–2000, the mean area burnt by wildland fires in Portugal was higher than 90 000 ha per year. During the period 2000–2009, this area was higher than 145 000 ha per year, with more than 25 000 forest fires/year. In 2010 (from 1 January to 15 October), 21 424 forest fires were registered with a total of 128 842 ha destroyed [9].

When fire regimen of an area is studied, climate and weather play a crucial role [10], [11]. Summer heat-waves in southern Europe have become more frequent and are forecast to increase in association with projected global warming. Thus, the number and severity of wildfires is projected to enhance in the future. In this way, it is worth noting that future area burned in Portugal is predicted to increase by more than 450% under a CO₂ duplication scenario [12].

To understand how fires influence and interact with the Earth system, quantitative information on wildfire emissions is required [13]. Thus, in order to calibrate and/or validate fire modules in different models, improvements in emissions factors (EF) for both particles and gases are necessary [14], [15]. EF have been estimated in some laboratory studies and in field campaigns [16], [17], but many uncertainties persist. Emissions from American fuels, and savannah/grassland, tropical and extratropical forest have been studied the most [18], [19]. Less is known about the emissions from the significant amounts of open biomass burning that occur in Europe [13], [20], where the Mediterranean area is particularly uncovered. Only Alves et al. [21], [22], [23] have carried out a characterization of emissions from fires in Mediterranean ecosystems.

1. Centre for Environmental and Marine Studies (CESAM), University of Aveiro, 3810-193 Aveiro, Portugal. E-mail: anacalvo@ua.pt; apsfernandes@ua.pt; tmunes@ua.pt; celia.alves@ua.pt; anavicente@ua.pt; margarita@ua.pt; anacristina@ua.pt; catiagoncalves@ua.pt; ltarelho@ua.pt; casimiro@ua.pt

This study presents a characterisation of aerosols and trace gases emitted during several wildfires occurring in Portugal during summer 2010. Flaming and smouldering emissions have been sampled and characterised.

2 METHODOLOGY

2.1 Measurement equipment

Sequential filtration was used for collecting samples. A tripod high volume sampler (TE-5200, Tisch Environmental Inc.) operating at a flow of $1.13 \text{ m}^3 \text{ min}^{-1}$ was used to collect sequentially, on pre-baked quartz fibre filters, coarse ($\text{PM}_{2.5-10}$) and fine ($\text{PM}_{2.5}$) smoke particles. The impaction system for removing PM_{10} was designed in accordance with the Marple and Rubow [24] theory at the University of Aveiro. In parallel, Tedlar bags previously flushed with N_2 were used for the collection of gas samples. Pre-removal of water vapor from the air stream was carried out in a glass U tube filled with glass spheres, immersed in an ice bath. In addition, the air stream was filtered through a 47 mm quartz filter to remove particles before passing to the collection system, which also contained a Teflon-line diaphragm pump connected to a needled valve and a calibrated rotameter operating at a flow rate of 1 L min^{-1} . In order to guarantee the collection of particles and gases at the same time and from the same air masses, the air sample inlet was positioned at a distance of about 6 cm from the filter holder.

The sampler was connected only when impacted by the smoke plume. Opaque containers were used for storing the bags after sampling, in order to minimise U.V. radiation of samples. With the aim of avoiding secondary reactions, the time period between sampling and analysis was reduced as much as possible. Filters were stored in the freezer until analysis. After the fire periods, several Tedlar bags were sampled at different places close to the sampling locations in order to obtain background levels.

2.2 Sampling points and data gathering

Fire occurrences were followed through the National Authority for Civil Protection of Portugal web-site (www.prociiv.pt). When a wildfire relatively close to Aveiro occurred (no more than 200 km far away), the study team moved close to the fire location using a four wheel drive (4x4) vehicle, to where the measurement equipment was transported. Once we arrived to the place, we contacted with the fire brigade in order to inform about our presence and to ask about a safe place for sampling. Sampling was carried out as close as possible to the fire.

Emissions of trace gases and aerosols of a total of eleven wildfires were sampled in summer 2010 (Fig 1). Different types of biomass burned - with

predominance of eucalyptus and pine - and emissions from both smouldering and flaming phases were sampled (Table 1).

2.3 Analytical methodology

The particulate matter deposited on the filters was quantified by gravimetric analysis. Filters were analysed by different techniques in order to determine the concentrations of carbonaceous content, soluble inorganic ions and organic biomass burning tracers (levoglucosan, mannosan and galactosan). Trace gases collected in Tedlar bags were also analysed in order to determine the concentration of CO , CO_2 and total volatile hydrocarbons (THC).

2.3.1. Total hydrocarbons and carbon oxides

Total hydrocarbons and carbon oxides (CO_2 and CO) in the Tedlar bags were measured using automatic analyzers with flame ionization (DynaFID, model SE-310) and non-dispersive infrared (Environnement, MIR 9000) detectors, respectively.

Each gas analyser was calibrated with appropriate gas on zero and span points. The hydrocarbon concentrations were determined in methane-equivalents.

2.3.2. Carbonaceous aerosols

The carbonaceous content (elemental carbon, EC, organic carbon, OC, and total carbon, $\text{TC}=\text{OC}+\text{EC}$) of particulate matter was analyzed by a thermal-optical transmission technique [22], [25]. This method enables the differentiation between organic and elemental carbon thanks to an optical correction of the pyrolyzed organic carbon (charring) which is essential for a less-biased measurement of carbon fractions. In each analytical run, strips representing 1/20 of the total area in the case of $\text{PM}_{2.5-10}$ and two 9 mm diameter filter punches, in the case of $\text{PM}_{2.5}$ samples were used. A set of field blank samples was analyzed to apply corrections to the values obtained.



Fig. 1. Location of wildfires during summer 2010 in Portugal for which smoke samples have been collected.

Table 1. Wildfires episodes over Portugal in summer 2010 for which smoke samples were obtained.

n°	Sampling locations	Latitude/Longitude	Altitude (a.s.l.)	Date	Major types of biomass	Number of samples (PM _{2.5} +PM ₁₀)	MCE
1	Mangualde	40°35'42"N/7°41'17"W	384	25 Jul.	<i>Cytisus striatus</i> / <i>Pteridium aquilinum</i>	2	0.65
2	Sever do Vouga	40°43'45"N/8°21'45"W	231	26 Jul.	<i>Pteridium aquilinum</i> / <i>Agrostis</i> / <i>Grasses</i> / <i>Mixed forest (Pinus pinaster and Eucalyptus globulus)</i>	4	0.78-0.79
3	Dornelas	40°46'31"N/8°23'49"W	227	26 Jul.	<i>Eucalyptus globulus</i> / <i>Furze</i> / <i>Grasses</i>	2	0.87
4	Rebordelo	40°59'47"N/8°25'14"W	244	27 Jul.	<i>Vineyards</i> / <i>Castanea sativa</i> / <i>Grasses</i> / <i>Eucalyptus globulus</i> / <i>Pterospartum tridentatum</i> / <i>Gorse</i> / <i>Ericaceae</i>	6	0.83-0.94
5	Albergaria-a-Velha	40°43'01"N/8°29'07"W	173	3 Aug.	<i>Eucalyptus globulus</i> / <i>Acacia saligna</i> / <i>Pteridium aquilinum</i>	4	0.85
6	Fontanheiras	40°34'46"N/7°52'41"W	334	3 Aug.	<i>Pinus pinaster</i>	2	0.81
7	Albergaria-a-Velha	40°42'19"N/8°30'04"W	162	6 Aug.	<i>Pinus pinaster</i> / <i>Eucalyptus globulus</i> / <i>Bush</i> / <i>Ericaceae</i> and forest litter	2	0.89
8	Chão do Coto (Oliveira de Frades)	40°45'49"N/8°11'19"W	275	6 Aug.	<i>Eucalyptus globulus</i> and bush	2	0.79
9	Sobrosa (São Pedro do Sul)	40°46'48"N/8°09'40"W	282	7 Aug.	<i>Pinus pinaster</i> / <i>Pteridium aquilinum</i> / <i>Ericaceae</i> / <i>Cistus</i>	12	0.76-0.84
10	Junqueira (Vale de Cambra)	40°48'38"N/8°20'38"W	246	11 Aug.	<i>Pinus pinaster</i> / <i>Eucalyptus globulus</i> / <i>Cytisus striatus</i>	4	0.87-0.91
11	Vila Nova de Tazem	40°30'56"N/7°41'48"W	374	13 Aug.	<i>Pinus pinaster</i> and <i>pineae</i> / <i>Cytisus striatus</i> / <i>Acacia saligna</i> / <i>Quercus suber</i> / <i>Rubus fruticosus</i> / <i>Arbustus unedo</i> / <i>Olea europaea</i> L.	12	0.64-0.84

MCE: Modified combustion efficiency

2.3.3. Soluble inorganic ions

The analysis of major soluble inorganic ions was carried out by ionic chromatography in liquid phase. The contents of small parts of the filters were extracted ultrasonically with ultra pure Milli-Q water. Cations (Na⁺, NH₄⁺, K⁺, Mg²⁺, Ca²⁺) were analysed using a CS12 (4 mm) column with a CG12 on guard. A Dionex CMMS III suppressor was used in these analyses. For anions (Cl⁻, NO₃⁻, SO₄²⁻) determination, an AS4 (4 mm) column with a AG4 guard column were used coupled to a Dionex AMMS II suppressor. For the final results blank values were taken into account.

2.3.4. Particulate organic tracers

Concentrations of levoglucosan, galactosan and mannosan, which are thermal degradation products of cellulose and hemicellulose, were determined by gas chromatography-mass spectrometry (GC-MS from Hewlett-Packard, models 6890 and 5973, respectively, quadrupole) with a TRB-5MS 60m x 0.25mm x 0.25 µm column. Extraction and analysis have been described in detail by Alves et al. [23]

2.4 Meteorological Analysis

Synoptic analysis (www.wetterzentrale.de) showed the presence of high pressure affecting the Iberian Peninsula during the period in which sampling of wildfire plumes was carried out (from 25th July to 13th August 2010). The Peninsula was under the clear influence of an Atlantic high, generating high temperatures, a great stability and no rain. This

situation hinders the dispersive capacity of the atmosphere. Because of the isobars configuration and their duration, this situation is typical of Iberian Peninsula summers.

At 850 hPa, a ridge from Africa enters warm air to the north, affecting the whole. From 8th August, at 700 hPa, there is wetter air in some areas of the Peninsula than around. This is the case of the center-southern of Portugal.

At surface level, the isobars configuration, frequently not very well defined and separated, suggests that there is calm or the winds are weak. At height level, it is neither possible to speak about strong winds, except from 9th August, when the closely spaced contours that indicate stronger wind, touch the north of Peninsula coasts and the closely packed isohypses enter in the Peninsula a few days later (Fig. 2).

2.5 Emission factor (EF) and modified combustion efficiency (MCE)

In order to characterize emissions from forest fires, the emissions factors have been calculated. This parameter is defined as the amount of a compound released per amount of dry fuel consumed, expressed in units of g kg⁻¹. The total carbon released is usually estimated by adding the measured concentrations of CO₂, CO, THC (including oxygenated volatile organic compounds) and total particulate carbon (TC=OC+EC). The emission factor can then be expressed as:

$$EF_n = \frac{n}{[CO_2] + [CO] + [THC] + [TC]} \%C_{fuel} \quad (1)$$

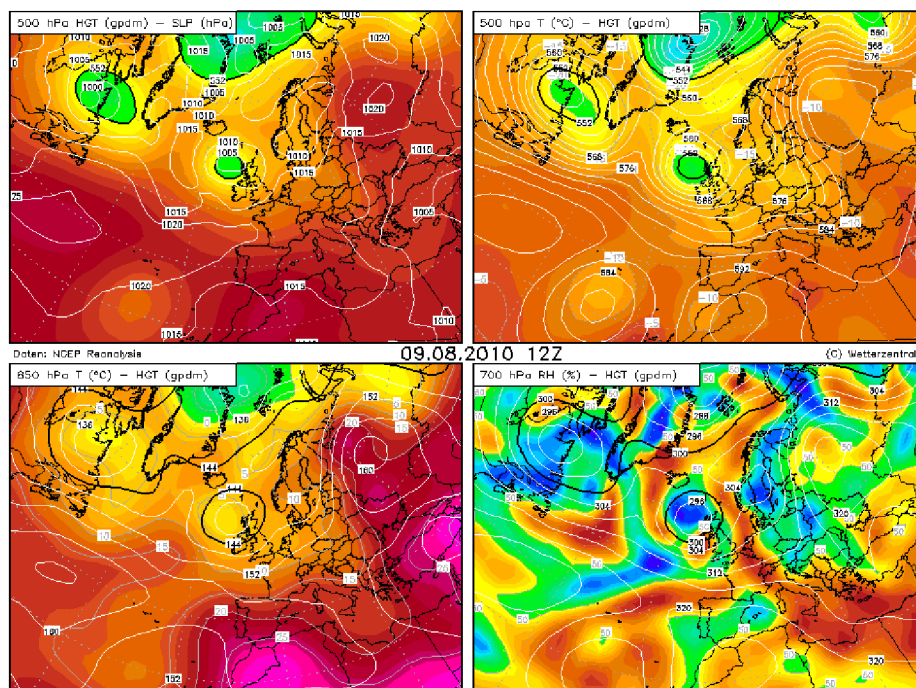


Fig. 2. Synoptic situation on 9th August 2010 at 12 at 500 hPa, 700 hPa and 850 hPa.

where n is the concentration of a given chemical species in the smoke, $[\text{CO}_2]$, $[\text{CO}]$, etc., are the concentrations of the various carbon species in the smoke and C_{fuel} is the mass fraction of carbon in the fuel. In this case, a fuel carbon content of $48 \pm 2\%$ has been estimated for dominant species in the Portuguese forest fires [26]. Background levels have been subtracted from measurements in the smoke plumes.

The chemical composition of emissions and the plume dynamics of the fire are conditioned by the presence of flaming combustion [27], [28]. The relative amount of flaming and smouldering combustion in a forest fire may be described using the modified combustion efficiency, or MCE [29]. It is calculated as follows:

$$\text{MCE} = \frac{[\text{CO}_2]}{[\text{CO}_2] + [\text{CO}]} \quad (2)$$

This expression is used given 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. The flaming combustion usually presents MCE values higher than 0.90 and smouldering combustion is characterized by MCE values lower than 0.90 [30], [1]. MCE values lower than 0.8 are found for wet fuels [31].

3 RESULTS AND DISCUSSION

3.1 Gaseous species

The modified combustion efficiency (MCE) ranged between 0.94 and 0.64, with an average ratio of 0.81 ± 0.07 . The lower MCE values were due to the discharge of water by the fire brigades. MCE and emission factors for gaseous species have been presented in Table 2.

The CO emission factor (EF) ranged between 67 and 383 g kg^{-1} biomass (dry basis) burned, representing $18.4 \pm 7.1\%$ of the carbon emitted. The EF_{CO} obtained for wildfires in summer 2010 in Portugal ($206 \pm 79 \text{ g kg}^{-1}$) are similar to those obtained in 2009, with values of $231 \pm 177 \text{ g kg}^{-1}$ [22]. Yokelson et al. [20] report lower CO emission factors for different biomass combusted, with mean values of $87.1 \pm 18.2 \text{ g kg}^{-1}$ (MCE=0.924±0.016), $79.3 \pm 18.1 \text{ g kg}^{-1}$ (MCE=0.930±0.016), and $103 \pm 29.3 \text{ g kg}^{-1}$ (MCE=0.908±0.027) for tropical forest, savanna and temperate forest, respectively. An EF_{CO} of 459 g kg^{-1} (MCE=0.59) was measured for feathermoss/lichen in Scotch pine forests of Central Siberia.

The EF_{CO_2} obtained for wildfires in Portugal (2010) ranged between 1029 and a maximum of 1655 g kg^{-1} biomass (dry basis) burned, representing the most important fraction of carbon emitted ($78.3 \pm 8.1\%$). CO_2 emission factors of $1657 \pm 39.0 \text{ g kg}^{-1}$, $1660 \pm 39.0 \text{ g kg}^{-1}$ and $1603 \pm 64.4 \text{ g kg}^{-1}$ were estimated by Yokelson et al. [20] for tropical forest, savanna and temperate forest for predominant flaming conditions. Similar values were registered by Andreae and Merlet [32], with values of 1613 ± 95

g kg⁻¹ and 1580±90 g kg⁻¹ for savannah and tropical forest, respectively. As expected, EF_{CO} and EF_{CO2} were negatively correlated ($r = -0.95$) (Table 3a).

In this study, total hydrocarbons represented 1.3±1.4% of the total carbon emitted. EF_{THC} reached a maximum of 28 g kg⁻¹ (dry basis), averaging 8.1±9.0 g kg⁻¹. Total hydrocarbon emission factors ranging between 0.4-10.4 g kg⁻¹ and 1.2-125 g kg⁻¹ have been found by Chen et al. [31] for flaming and smouldering combustions, respectively.

The emission factors ranges registered for the gases studied reflect the different contribution from flaming and smouldering combustions.

Emission factors registered in summer 2009 for wildfires in Portugal ranged between 53-488 g kg⁻¹, 1000-1697 g kg⁻¹ and 6-350 g kg⁻¹ for CO, CO₂ and THC, respectively [22]. In 2009, MCE values ranged between 0.52 and 0.97 with a predominance of smouldering combustion.

An important difference between 2009 and 2010 wildfire emissions is registered for total hydrocarbons. The reason could be related to a higher presence of flaming conditions in 2010.

Correlation between EFs and MCE for CO, CO₂ and total volatile hydrocarbons have been represented (Fig. 3). The predominance of flaming

or smouldering phase in estimating the emission factors is indicated by the slope of the regressions. Positive slopes are registered when emissions are promoted by flaming combustion, while negative slopes suggest that emission of the species is favored by the smouldering phase. When the steep of the slope increases, the dependence of the type of combustion also increases [18]. CO is a very important parameter in the development of emission inventories for several pollutants [22]. As expected, EF_{CO} correlates very well with MCE (EF_{CO}=1062-1058xMCE, $r = 0.99$). The negative slope indicates that it is an indicator of smouldering combustion. On the other hand, EF_{CO2} shows a positive slope (EF_{CO2}=-121+1851xMCE) given that it is emitted mainly during flaming combustion, in which a more complete oxidation is involved. Total hydrocarbons don't show a clear tendency.

3.2 Particulate matter

PM_{2.5} and PM₁₀ concentrations reached 25.2 mg m⁻³ and 27.0 mg m⁻³, with average values of 5.78±6.67 mg m⁻³ and 6.69±7.46 mg m⁻³, respectively. PM_{2.5} constitutes an important fraction of PM₁₀, with a PM_{2.5}/PM₁₀ average ratio of 0.91±0.05.

Table 2. MCE and emission factors for gases (g kg⁻¹), PM, OC and EC (for PM_{2.5} and PM₁₀) for the different wildfires studied during summer 2010 in Portugal

Forest Fire	MCE	CO	CO ₂	THC	PM ₁₀	OC _{PM10}	EC _{PM10}	PM _{2.5}	OC _{PM2.5}	EC _{PM2.5}
Mangualde	0.65	383.23	1132.28	2.19	9.54	5.27	0.05	7.94	4.52	0.05
Sever	0.79	225.43	1328.21	7.87	23.90	15.15	0.09	21.02	13.55	0.07
	0.78	235.18	1341.99	15.33	6.35	1.71	0.01	4.36	1.52	0.01
Dornelas	0.87	143.37	1498.00	3.65	15.36	6.32	0.96	14.03	6.30	0.95
	0.83	191.00	1429.22	bdl	22.50	7.46	0.89	20.12	7.00	0.87
Rebordelo	0.83	180.53	1356.79	bdl	51.87	31.73	0.86	47.88	30.76	0.85
	0.93	76.30	1622.63	1.19	13.53	5.49	2.26	12.84	5.33	2.17
Albergaria-a-Velha	0.85	155.97	1372.47	25.33	31.78	19.44	0.40	29.65	18.90	0.35
Fontanheiras	0.81	203.59	1348.61	22.61	12.40	7.86	0.13	11.37	7.23	0.12
Albergaria-a-Velha	0.89	118.85	1552.14	2.48	9.60	3.81	0.08	8.20	3.46	0.08
Chão do Coto (Oliveira de Frades)	0.79	235.81	1361.26	bdl	20.96	7.31	0.38	19.73	7.01	0.37
	0.77	249.42	1335.43	6.46	7.10	3.95	0.10	6.63	3.79	0.10
Sobrosa (São Pedro do Sul)	0.85	171.87	1477.73	0.33	6.30	2.99	0.08	5.83	2.84	0.08
	0.78	240.54	1348.11	5.90	8.21	4.79	0.03	7.62	4.50	0.03
	0.76	257.83	1318.57	6.20	8.53	5.16	0.08	7.96	4.88	0.08
	0.77	256.29	1316.41	7.48	8.46	5.50	0.03	8.07	5.29	0.03
Junqueira (Vale de Cambra)	0.78	248.15	1347.39	5.19	4.64	2.21	0.08	4.30	2.11	0.07
	0.91	101.58	1570.16	bdl	16.01	7.94	0.30	14.89	7.55	0.30
Vila Nova de Tazem	0.87	147.38	1512.38	bdl	7.16	4.28	0.09	6.48	3.98	0.08
	0.84	168.70	1417.95	14.57	25.48	9.54	0.52	24.10	9.33	0.51
	0.64	364.31	1029.20	11.70	72.14	32.76	1.64	67.52	31.99	1.60
	0.68	345.32	1135.77	bdl	47.40	21.12	1.13	44.32	20.60	1.12
	0.84	166.63	1403.36	19.89	17.21	10.42	0.51	16.03	9.94	0.46
	0.78	227.97	1265.85	28.08	24.47	14.96	1.05	22.35	13.83	0.93
	0.84	172.65	1373.08	23.43	22.90	13.57	0.39	21.70	13.06	0.37

bdl- below detection limit

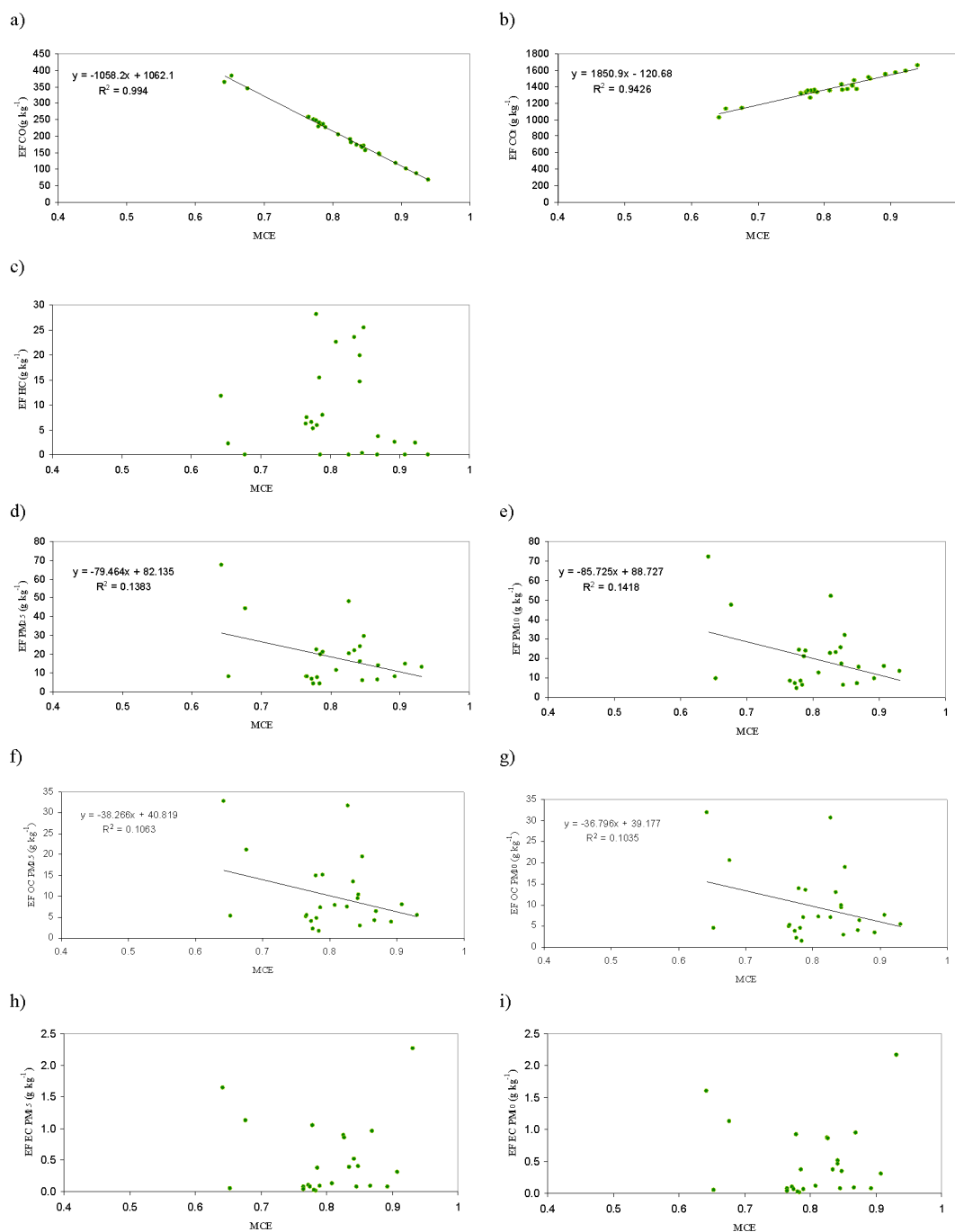


Fig. 3. Emissions factors as a function of MCE for a) CO, b) CO₂, c) THC, d) PM_{2.5}, e) PM₁₀, f) OC_{PM2.5}, g) OC_{PM10}, h) EC_{PM2.5} and i) EC_{PM10}.

The EF ranged between 4 and 68 g kg⁻¹ for PM_{2.5} and between 5 and 72 g kg⁻¹ (dry basis) for PM₁₀ (Table 2).

Emission factors for PM_{2.5} and PM₁₀ presented a significant correlation ($r=1.00$), but they were negatively correlated with EF for CO₂ (Table 3a). The highest emissions of particles occurred during smouldering conditions (Fig. 3d, e).

The linear regression between MCE and PM₁₀ (Fig. 3e) obtained in this study ($EF_{PM10}=88.7-85.7 \times MCE$) is in good agreement with Alves et al.'s [22] relationship, who obtained $EF_{PM10}=$

$81.4-76.6 \times MCE$. Particle emission factors depend on the plume dilution; at high levels of dilution, such as in atmospheric conditions, the concentration of semivolatile species is reduced, shifting this material to the gas phase in order to maintain phase equilibrium. Temperature and background organic aerosol concentrations are two parameters that strongly influence the partitioning of the emissions [33], [34].

A clear predominance of carbonaceous aerosol was observed, with OC concentrations always remaining higher than EC in both size ranges

(OC/TC ratios ranged between 0.99 and 0.71 for both sizes). OC mass fraction of PM₁₀ ranged between 26.8% and 65.0% with an average ratio of 50.8±11.0%. This fraction increase when MCE decrease, showing average ratios of 45.1±6.37% for samples with MCE>0.90 and 51.4±11.5% for samples with MCE<0.90. In the case of EC/PM₁₀, these differences were even more pronounced. The EC/PM₁₀ ratios were much higher for samples with MCE>0.90 (9.31±10.5% vs 1.78±1.45% for MCE higher and lower than 0.90, respectively). The same behavior was observed for the relationships between the carbonaceous constituents and PM_{2.5}. OC/PM_{2.5} and EC/PM_{2.5} ratios of 52.6±10.3 and 2.43±3.28, respectively, were obtained in the smouldering derived samples.

Similar OC/PM_{2.5} ratios were obtained for cerrado [35] and temperate forest [35] with percentages of 57% and 50%, respectively.

Battye and Battye [36] pointed out that the ratio of OC to total PM_{2.5} is very similar for smouldering and flaming conditions. Thus, OC appears to correlate well with total PM_{2.5} over the full range of combustion. In this study, a good correlation between EF_{OC/PM_{2.5}} and EF_{PM_{2.5}} was obtained ($r=0.96$). EF for OC and EC for both sizes are highly correlated with EF for PM_{2.5} and PM₁₀ with $r>0.59$ (Table 3a).

The concentrations of water-soluble inorganic ions are listed in Table 4. They represented, on average, 3.6% and 2.6% of PM_{2.5} and PM_{2.5-10} mass, respectively. Focusing on average concentrations, highest values are registered for Na⁺, NH₄⁺, Cl⁻ and NO₃⁻ for the fine fraction (PM_{2.5}), and K⁺, Mg²⁺, Ca²⁺ and SO₄²⁻ for PM_{2.5-10}. The correlations between ion mass concentrations (μg mg⁻¹ PM) are presented in Table 3b.

Table 3. Pearson correlation coefficients (r) for a) emissions factor of gases and particles and b) ion concentrations (μg mg⁻¹ PM) during wildfires in summer 2010 in Portugal

a)

	CO	CO ₂	HC	PM _{2.5}	PM ₁₀	OC _{PM10}	EC _{PM10}	OC _{PM2.5}	EC _{PM2.5}
CO	1.00								
CO ₂	-0.95**	1.00							
HC	-0.01	-0.22	1.00						
PM _{2.5}	0.31	-0.52**	0.10	1.00					
PM ₁₀	0.31	-0.52**	0.10	1.00**	1.00				
OC _{PM10}	0.26	-0.50*	0.20	0.96**	0.96**	1.00			
EC _{PM10}	-0.08	-0.04	-0.03	0.60**	0.59**	0.50*	1.00		
OC _{PM2.5}	0.26	-0.50*	0.19	0.96**	0.96**	1.00**	0.50*	1.00	
EC _{PM2.5}	-0.08	-0.04	-0.06	0.60**	0.60**	0.50*	1.00**	0.51**	1.00

b)

	Na ⁺	NH ₄ ⁺	K ⁺	Mg ²⁺	Ca ²⁺	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻
<i>a) Fine fraction components</i>								
Na ⁺	1.00							
NH ₄ ⁺	-0.10	1.00						
K ⁺	0.25	-0.10	1.00					
Mg ²⁺	0.14	-0.40*	0.65**	1.00				
Ca ²⁺	-0.07	-0.53**	0.39*	0.77**	1.00			
Cl ⁻	0.05	0.75**	0.36	-0.06	-0.40*	1.00		
NO ₃ ⁻	-0.10	-0.36	0.16	0.51**	0.57**	-0.34	1.00	
SO ₄ ²⁻	0.06	-0.26	0.39*	0.64**	0.47*	-0.02	0.74**	1.00
<i>b) Coarse fraction component</i>								
NH ₄ ⁺		1.00						
K ⁺		0.04	1.00					
Mg ²⁺		0.45*	0.20	1.00				
Ca ²⁺		-0.05	0.34	0.50**	1.00			
Cl ⁻		0.40*	0.44*	0.15	-0.28	1.00		
NO ₃ ⁻		-0.21	-0.23	-0.21	-0.04	-0.11	1.00	
SO ₄ ²⁻		0.19	.46*	0.52**	0.36	0.20	0.14	1.00

*Significant at the 0.05 level

**Significant at the 0.01 level

Table 4. Concentration ranges (and averages) for water-soluble ions ($\mu\text{g mg}^{-1}$ PM) in smoke particles.

Wildfire		Na ⁺	NH ₄ ⁺	K ⁺	Mg ²⁺	Ca ²⁺	Cl	NO ₃ ⁻	SO ₄ ²⁻
Mangualde	PM _{2.5}	bdl	bdl	bdl	0.80	4.70	bdl	1.51	1.83
	PM _{2.5-10}	bdl	0.59	2.53	bdl	bdl	8.13	bdl	3.30
Sever do Vouga	PM _{2.5}	bdl	4.11-9.31 (6.71)	bdl	0.10-0.82 (0.46)	0.99-3.36 (2.17)	6.17-6.67 (6.42)	bdl-0.46 (0.23)	1.59-2.95 (2.27)
	PM _{2.5-10}	bdl	0.53-1.49 (1.01)	0.20-1.37 (0.79)	bdl-1.17 (0.59)	bdl-1.36 (0.68)	1.06-1.77 (1.42)	bdl	0.75-2.86 (1.80)
Dornelas	PM _{2.5}	10.06	6.30	13.72	2.74	3.45	14.75	2.33	5.53
	PM _{2.5-10}	bdl	0.72	22.05	bdl	7.08	6.91	bdl	14.16
Rebordelo	PM _{2.5}	bdl-8.13 (2.71)	bdl-11.23 (5.02)	2.65-8.38 (5.36)	1.47-2.73 (2.02)	1.41-7.55 (4.58)	bdl-20.46 (8.16)	2.02-12.86 (8.03)	6.06-6.90 (6.49)
	PM _{2.5-10}	bdl	0.69-2.05 (1.27)	1.94-5.78 (3.33)	bdl-4.69 (1.56)	bdl-5.75 (3.82)	bdl-7.81 (2.60)	bdl-3.17 (1.06)	6.12-11.47 (9.39)
Alb.-a-Velha	PM _{2.5}	bdl-3.66 (1.83)	4.38-4.69 (4.53)	5.22-8.45 (6.84)	0.28-0.97 (0.62)	1.85-6.39 (4.12)	5.90-6.36 (6.13)	1.33-1.82 (1.58)	2.78-4.40 (3.59)
	PM _{2.5-10}	bdl	0.39-0.80 (0.60)	5.96-7.81 (6.89)	1.33-1.96 (1.65)	3.62-9.93 (6.78)	2.32-2.92 (2.62)	0.77-0.91 (0.84)	6.91-8.44 (7.68)
Fontanheiras	PM _{2.5}	bdl	0.79	bdl	0.48	3.74	bdl	0.76	0.97
	PM _{2.5-10}	bdl	bdl	2.53	1.66	6.89	bdl	bdl	3.24
Alb.-a-Velha	PM _{2.5}	bdl	2.29	bdl	1.48	7.10	4.65	7.49	7.96
	PM _{2.5-10}	bdl	0.41	1.25	1.79	6.84	2.48	3.58	8.09
Chão do Coto (Ol. de Frades)	PM _{2.5}	bdl	bdl	9.19	3.80	12.50	7.57	4.91	4.18
	PM _{2.5-10}	bdl	1.08	6.72	7.73	20.69	bdl	bdl	11.05
Sobrosa (S. Pedro do Sul)	PM _{2.5}	bdl-22.42 (10.59)	4.79-14.62 (8.67)	bdl-3.45 (1.36)	0.45-2.08 (0.93)	1.82-5.45 (3.00)	4.45-13.05 (7.66)	1.95-5.27 (2.97)	2.73-4.40 (3.46)
	PM _{2.5-10}	bdl	0.89-2.07 (1.38)	2.12-4.56 (3.73)	1.37-5.04 (3.23)	4.07-9.85 (6.61)	bdl-2.85 (1.75)	bdl	5.27-14.73 (9.36)
Junqueira (V. de Cambra)	PM _{2.5}	bdl	4.30-9.01 (6.65)	bdl-1.68 (0.84)	0.61-1.65 (1.13)	2.51-5.12 (3.81)	bdl-5.12 (2.56)	3.60-3.74 (3.67)	3.91-5.25 (4.58)
	PM _{2.5-10}	bdl	0.73-1.18 (0.96)	3.73-3.91 (3.82)	1.41-2.24 (1.83)	3.80-6.83 (5.32)	bdl-1.21 (0.61)	bdl	5.02-7.11 (6.07)
V. N. de Tazem	PM _{2.5}	bdl-40.25 (6.71)	1.74-35.92 (13.18)	3.58-11.38 (7.03)	0.56-2.83 (1.36)	1.41-8.42 (4.53)	5.47-18.44 (12.19)	0.71-8.37 (3.64)	2.32-5.63 (3.96)
	PM _{2.5-10}	bdl	0.54-2.38 (1.15)	5.40-17.30 (10.41)	bdl-5.59 (2.56)	4.21-16.19 (10.06)	bdl-7.85 (3.00)	bdl	bdl-12.70 (5.83)

bdl- below detection limit

The highest levels of Mg²⁺ and Ca²⁺ were registered in smoke particles from Chão do Coto for both fine and coarse fractions. The mass concentrations in this smoke plume were 3.8 $\mu\text{g mg}^{-1}$ PM_{2.5} and 7.73 $\mu\text{g mg}^{-1}$ PM_{2.5-10} for Mg²⁺ and 12.5 $\mu\text{g mg}^{-1}$ PM_{2.5} and 20.7 $\mu\text{g mg}^{-1}$ PM_{2.5-10} for Ca²⁺. A significant Pearson correlation (at a significant level of 0.01) between these two cations was observed ($r=0.77$ for PM_{2.5} and $r=0.50$ for PM_{2.5-10}) (Table 3b).

Since there is a higher concentration in the coarse fraction and a significant correlation between these two ions, a possible entrainment of soil dust is suggested.

Potassium concentrations reached values up to 13.7 $\mu\text{g mg}^{-1}$ PM_{2.5} and 22.1 $\mu\text{g mg}^{-1}$ PM_{2.5-10} with mean values of 4.02±4.10 $\mu\text{g mg}^{-1}$ and 5.88±5.10 $\mu\text{g mg}^{-1}$, for the fine and, coarse particles, respectively. These concentrations represent 0.6% of the total mass for both fractions. Low potassium concentrations were also registered by Alves et al., [21], [22] in 2009 wildfires in Portugal and in prescribed burnings.

A wide range of potassium emission factors was found by Chen et al. [31] burning several wildland fuels under laboratory conditions. Mass percentages of potassium were higher than 20% for sagebrush and less than 1% for certain shrubs, grasses and softwood. Potassium shows a significant correlation with magnesium ($r=0.65$) for PM_{2.5}.

Ammonium and chlorine, present mainly in the fine fraction, with concentrations up to 35.92 $\mu\text{g mg}^{-1}$ and 20.46 $\mu\text{g mg}^{-1}$ respectively, show a good correlation ($r=0.75$) with each other in this fraction. NH₄Cl is a typical compound observed in inorganic fine particles emitted during fires (mainly in flaming fires) and, since it is very soluble in water, this compound is expected to be active as cloud condensation nuclei. Sulphate shows mass concentrations between 0.97 and 7.96 $\mu\text{g mg}^{-1}$ for PM_{2.5} and up to 14.7 $\mu\text{g mg}^{-1}$ for PM_{2.5-10}. The process responsible for the presence of SO₄²⁻ in smoke samples can be related to the adsorption of SO₂ on black carbon particles through a catalytic effect in the gas-to-particle

conversion of SO₂ to sulphate [22]. Sulphate shows a significant correlation with magnesium for both size fractions, with *r* values of 0.64 and 0.52, respectively, suggesting the presence of these compounds in the form of magnesium sulphate.

Sodium was below the detection limit for the majority of the samples in both fractions. A high concentration was registered for one of the samples taken in Vila Nova de Tazem, in which this cation registered a concentration higher than 40 µg mg⁻¹ PM for fine fraction (PM_{2.5}).

Nitrate concentrations showed mean concentrations of 3.53±3.05 µg mg⁻¹ PM_{2.5} and 0.32±0.93 µg mg⁻¹ PM_{2.5-10}. It is likely produced in reactions of NO_x emitted during burning. Furthermore, it has been pointed out that burning enhances the biogenic emissions of nitric and nitrous oxides from soil. Nitrate shows a significant correlation (at 0.01 level) with Mg²⁺ and Ca²⁺ in fine fraction, with *r* values of 0.51 and 0.57, respectively. This suggests that nitrate ions could be associated with Ca²⁺ and Mg²⁺ in the form of Ca(NO₃)₂ and Mg(NO₃)₂ in the fine fraction of aerosols.

Levogluconan was always present at higher concentrations than those of galactosan and mannosan. Ratios of OC to levogluconan, galactosan and mannosan were similar to those registered during summer 2009 wildfires in Portugal [23].

4 CONCLUSIONS

Trace gases and aerosol particle emissions from several wildfires occurring in Portugal were sampled in summer 2010. The CO and CO₂ emission factors (EF) were around 67-383 and 1029-1655 g kg⁻¹ biomass (dry basis) burned, respectively. The EF for PM_{2.5} and PM₁₀ ranged between 4 and 68 g kg⁻¹ for PM_{2.5} and between 5 and 72 g kg⁻¹ (dry basis) for PM₁₀. For THC, EF reached values up to 28 g kg⁻¹ (dry basis).

PM_{2.5} constitutes an important fraction of PM₁₀, with a PM_{2.5}/PM₁₀ average ratio of 0.91±0.05. A clear predominance of carbonaceous aerosol was observed, with OC concentration always remaining much higher than EC in both size ranges (OC/TC ratios ranged between 0.99 and 0.71 for both sizes). The relationship between MCE and the pollutant emission factors has been established.

Water-soluble inorganic ions represented less than 4% of the aerosol mass with highest values registered for Na⁺, NH₄⁺, Cl⁻ and NO₃⁻ for fine fraction (PM_{2.5}), and K⁺, Mg²⁺, Ca²⁺ and SO₄²⁻ for PM_{2.5-10}. As in other studies, low potassium concentrations were registered (up to 13.7 µg mg⁻¹ PM).

Ratios of OC to levogluconan, galactosan and

mannosan were similar to those registered during summer 2009 wildfires in Portugal.

This study is potentially useful for source apportionment models and for evaluating, using numerical simulations, the impact of wildfires on the microscale to regional scale atmosphere in the Mediterranean region, which is not well studied. The understanding of processes that regulate atmospheric composition during and after wildfires is critical to the establishment of a sustainable development strategy in the Mediterranean region. There is an absolute need for further field studies in order to investigate emissions and associated transformation mechanisms resulting from wildfires.

ACKNOWLEDGMENT

This work was supported by the Centre for Environmental and Marine Studies (CESAM) and the Portuguese Science Foundation (FCT) through the project "Contribution of biomass combustion to air pollutant emissions", PTDC/AMB/65706/2006 (BIOEMI). Ana I. Calvo and Ana Vicente acknowledge the Post-Doc and PhD grants SFRH/BPD/64810/2009 and SFRH/BD/48535/2008, respectively, from FCT.

REFERENCES

- [1] J.S. Reid, R. Koppmann, T.F. Eck, and D.P. Eleuterio. "A review of biomass burning emissions part II: intensive physical properties of biomass burning particles". *Atmos. Chem. Phys.*, vol. 5, pp. 799–825, 2005.
- [2] D. Spracklen, J. Logan, L. Mickley, R. Park, R. Yevich, A. Westerling, and D. Jaffe. "Wildfires drive interannual variability of organic carbon aerosol in the western U.S. in summer". *Geophys. Res. Lett.*, 34 (L16816), doi:10.1029/2007GL030,037, 2007.
- [3] J. Zhang, J.L. Jimenez, M.R. Canagaratna, J.D. Allan, H. Coe, I. Ulbrich, M.R. Alfarra, A. Takami, A.M. Middlebrook, Y.L. Sun, K. Dzepina, E. Dunlea, K. Docherty, P.F. De- Carlo, D. Salcedo, T. Onasch, J.T. Jayne, T. Miyoshi, A. Shimojo, S. Hatakeyama, N. Takegawa, Y. Kondo, J. Schneider, F. Drewnick, S. Borrmann, S. Weimer, K. Demerjian, P. Williams, K. Bower, R. Bahreini, L. Cottrell, R.J. Griffin, J. Rautiainen, J.Y. Sun, Y.M. Zhang, and D.R. Worsnop. "Ubiquity and dominance of oxygenated species in organic aerosols in anthropogenically-influenced Northern Hemisphere midlatitudes". *Geophys. Res. Lett.*, 34, L13801, doi:10.1029/2007GL029979, 2007.
- [4] Ö. Gustafsson, M. Kruså, Z. Zencak, R.J. Sheesley, L. Granat, E. Engström, P.S. Praveen, P.S.P. Rao, C. Leck, H. Rodhe. "Brown Clouds over South Asia: Biomass or Fossil Fuel Combustion?" *Science*, vol. 323, pp. 495, 2009.
- [5] S. Janhäll, M.O. Andreae and U. Pöschl. "Biomass burning aerosols emissions from vegetation fires: particles number and mass emission factors and size distribution". *Atmos. Chem. Phys.* vol. 10, pp. 1427-1439, 2010.
- [6] G. Adler, J.M. Flores, A. Abo Riziq, S. Borrmann, Y. Rudich. "Chemical, physical and optical evolution of biomass burning aerosols: a case study". *Atmos. Chem. Phys.*, vol. 11, pp. 1491–1503, 2011.

- [7] R.Koppmann, K von Czapiewski., and J.S. Reid. "A review of biomass burning emissions, part I: gaseous emissions of carbon monoxide, methane, volatile organic compounds, and nitrogen containing compounds", *Atmos. Chem. Phys. Discuss.*, 5, 10455– 10516, doi:10.5194/acpd-5-10455-2005, 2005.
- [8] L.-W.A. Chen., P. Verburg, A. Shackelford, D. Zhu, R. Susfalk, J.C. Chow, and J.G. Watson. "Moisture effects on carbon and nitrogen emission from burning of wildland biomass". *Atmos. Chem. Phys.*, vol. 10, pp. 6617–6625, 2010.
- [9] Portuguese Ministry of Agriculture, Rural Development and Fisheries. www.afn.min-agricultura.pt, 2011.
- [10] M.G. Pereira, R.M. Trigo, C.C. da Camara, J.M.C. Pereira, and S.M. Leite. "Synoptic patterns associated with large summer forest fires in Portugal". *Agr. Forest Meteorol.*, vol. 129, pp. 11-25, 2005.
- [11] A. Carvalho, M.D. Flannigan., K. Logan, A.I. Miranda, and C. Borrego. "Fire activity in Portugal and its relationship to weather and the Canadian FIRE weather index system". *Int. J. Wildland Fire*, vol. 17, pp. 328-228, 2008.
- [12] A. Carvalho, M.D. Flannigan, K. Logan, L. Gowman, A.I. Miranda, and C. Borrego. "The impact of spatial resolution on area burned and fire occurrence projections in Portugal under climate change". *Climatic change*, vol. 98, pp. 177-197, 2010.
- [13] G.R. van der Werf, J.T. Randerson, L. Giglio, G.J. Collatz, M. Mu, P.S. Kasibhatla, D.C. Morton, R.S. DeFries, Y. Jin and T.T. van Leeuwen. "Global fire emissions and the contribution of deforestation, savanna, forest, agricultural, and peat fires (1997–2009)", *Atmos. Chem. Phys. Discuss Vol. 10*, 16153–16230, 2010.
- [14] V. Arora, and G.J. Boer. "A parameterization of leaf phenology for the terrestrial ecosystem component of climate models", *Glob. Change Biol.*, vol. 11(1), pp. 39-59, 2005.
- [15] S. Kloster, N.M. Mahowald, J.T. Randerson, P.E. Thornton, F.M. Ho man, S. Levis, P.J. Lawrence, J.J. Feddema, K.W. Oleson and D. M. Lawrence. "Fire dynamics during the 20th century simulated by the Community Land Model", *Biogeosciences*, vol. 7, pp. 1877- 1902, 2010.
- [16] R.J. Yokelson, S. Urbanski, E. Atlas, D.W. Toohey, E.C. Alvarado, J.D. Crouse, P.O. Wennberg, M.E. Fisher, C.E. Wold, T.L. Campos, K. Adachi, P.R. Buseck, and W. M. Hao. "Emissions from forest fires near Mexico City", *Atmos. Chem. Phys.*, vol. 7, pp. 5569– 5584, 2007.
- [17] R.J. Yokelson, T.J. Christian, T.G. Karl and A. Guenther. "The tropical forest and fire emissions experiment: laboratory fire measurements and synthesis of campaign data" *Atmos.Chem. Phys.*, vol. 8, pp. 3509–3527, 2008.
- [18] P. Sinha, P.V. Hobbs, R.J. Yokelson, I.T. Bertschi, D.R. Blake, I.J. Simpson, S. Gao, T.W. Kirchstetter and T. Novakow. 2003. "Emissions of trace gases and particles from savanna fires in southern Africa". *J. Geophys. Res.*, 108, 8487, doi: 10.129/2002JD002325, 2003.
- [19] G.R. McMeeking, S.M. Kreidenweis, S. Baker, C.M. Carrico, J.C. Chow, J.L. Collett, W.M.K. Hao, A.M. Holden, T.W. Kirchstetter, W.C. Malm, H. Moosmüller, A.P. Sullivan, C.E. Wold. "Emissions of trace gases and aerosols during the open combustion of biomass in the laboratory". *J. Geophys. Res.* 114 (D19210). Doi:10.1029/2009JD011836, 2009.
- [20] R.J. Yokelson, I.R. Burling, S.P. Urbanski, E.L. Atlas, K. Adachi, P.R. Buseck, C. Wiedinmyer, S.K. Akagi, D.W. Toohey and C.E. Wold. "Trace gass and particle emissions from open biomass burning in Mexico", *Atmos. Chem. Phys. Discuss.*, vol. 11, pp. 7321-7371, 2011.
- [21] C.A Alves., C. Gonçalves, C. Pio., F. Mirante, A. Caseiro L. Tarelho, M.C. Freitas, and D.X.Viegas. "Smoke emissions from biomass burning in a Mediterranean shrubland". *Atmos. Environ.* 44, 3024-3033, 2010.
- [22] C. Alves, A. Vicente, T. Nunes, C. Gonçalves, A.P. Fernandes, F. Mirante, L. Tarelho, A.M. Sánchez de la Campa, X. Querol, A. Caseiro and C. Monteiro, M. Evtugina, and C. Pio. "Summer 2009 wildfires in Portugal: Emission of trace gases and aerosol composition". *Atmos. Environ.*, vol. 45, pp. 641-649, 2011.
- [23] C.A Alves., A. Vicente, C. Monteiro, C. Gonçalves, M. Evtugina and C. Pio. "Emission of trace gases and organic components in smoke particles from a wildfires in a mixed-evergreen forest in Portugal". *Sci. Total Environ.*, vol. 409, pp. 1466-1475, 2011.
- [24] V.A. Marple and K.L. Rubow. Chapter 4: theory and design guidelines. In: Lodge JP, Chan TL, editors. *Cascade impactors: sampling & data analysis*. Akron, OH: *American Industrial Hygiene Association*; 1986.
- [25] A. Carvalho, C. Pio, C. Santos, and C. Alves. "Particulate carbon in the atmospheric of a Finnish forest and a German antropogenically influenced grassland". *Atmos. Res.*, vol. 80, pp. 133-150, 2006.
- [26] J.J.F. Silva, E.M.S.R. Oliveira, A.P.D. Gomes and L.A.C Tarelho. "Leaching of shrub biomass collected in Eucalyptus forest of Central Portugal for use as a biofuel" 16th European Biomass Conference & Exhibition; 2008. pp. 499–503. June, Valencia, Spain.
- [27] R.J. Yokelson, D.E. Ward, R.A. Susott, J. Reardon, and D.W.T. Griffith. "Emissions from smoldering combustion of biomass measured by open-path Fourier transform infrared spectroscopy" *J. Geophys. Res.*, vol. 102, pp. 18865-18877, 1997.
- [28] S.P. Urbanski, W.M. Hao, and S. Baker. "Chemical composition of wildland fire emissions, in: *Wildland Fires and Air Pollution*", edited by: Bytnerowicz, A., Arbaugh, M., Riebau, A., and Andersen. *Developments in Environmental Science, Wildland Fires and Air Pollution*, vol. 8, Elsevier, The Netherlands, pp. 79-107, 2009.
- [29] D.E. Ward, and W.M. Hao. "Air toxic emissions from burning of biomass globally-preliminary estimates", in: *Proceedings: Air & Waste Management Assoc. 85th Annual Meeting & Exhibition*, 1992.
- [30] R.J. Yokelson. SAFARI 2000 "Gas Emissions from Biofuel Use and Production". September 2000. Data set Available on-line. Oak Ridge National Laboratory Distributed Active Archive Center, Oak Ridge, Tennessee, U.S.A. doi:10.3334/ORNLDAAC/753. <http://daac.ornl.gov>, 2004.
- [31] L.W.A. Chen, H. Moosmüller, W.P. Arnott, J.C. Chow, J.G. Watson, R.A. Susott, R.E. Babbitt, C.E. Wold, E.N. Lincoln, W.M. Hao. "Emissions from laboratory combustion of wildland fuels: emission factors and source profile", *Environ. Sci. Technol.*, vol. 41, pp. 4317–25, 2007.
- [32] M.O. Andreae and P. Merlet. "Emission of trace gases and aerosols from biomass burning". *Global Biogeochem. Cycles*, vol. 15, pp. 995-966, 2001.
- [33] N.M. Donhahe, A.L. Robinson, C.O. Stanier, and S.N. Pandis. "Coupled partitioning dilution, and chemical aging of semivolatile organics". *Environ. Sci. Tech.*, vol. 40, pp. 2635-2643, 2006.
- [34] M.K. Shrivastava, E.M. Lipsky, C. Stainer and A.L. Robinson. "Modelling semivolatile aerosol mass emissions from combustion systems". *Environ. Sci. Tech.*, vol. 40, pp. 2671-2677, 2006.
- [35] D.E. Ward, R.A. Susott, J.B. Kauffman, R.E. Babbitt, D.L. Cummings, B. Dias, B.N. Holben, Y.J. Kauffman, R.A. Rasmussen and A.W. Setzer. "Smoke and fire characteristics for cerrado and deforestation burns in Brazil: BASE-B experiment". *J. Geophys. Res.*, vol. 97, pp. 14601-14619, 1992.
- [36] W. Battye and R. Batty. "Development of emissions inventory Methods for Wildland Fire U.S. Environmental Protection Agency", Chapell Hill, NC, 91pp, 2002.