

Emissions of trace gases and aerosols from wildfires in Portugal in summer 2009 - Experimental results from ground base measurements

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Abstract

In summer 2009, emissions of trace gases and aerosols from several wildfires registered in Portugal were sampled. A portable high-volume sampler was used to collect sequentially, on quartz fibre filters, coarse (PM_{2.5-10}) and fine (PM_{2.5}) smoke particles. Tedlar air sampling bags have been used for complementary chemical characterisation of the gaseous phase. Total hydrocarbons and carbon oxides (CO₂ and CO) were measured using automatic analysers with flame ionisation and non-dispersive infrared detectors, respectively. The carbonaceous content (elemental and organic carbon, EC/OC) of particulate matter was analysed by a thermal-optical transmission technique. Emission factors of species that are favoured by the smouldering phase (e.g. CO) were above the values reported in the literature for biomass burning in other ecosystems. Emission factors for CO were 231±117 g kg⁻¹ biomass (dry basis) burned. Compounds whose emissions are promoted in fresh plumes and during the flaming burning phase, such as CO₂, produced emission factors generally lower than those proposed for savannah and tropical forest fires. The emission factors for CO₂ were in the range from about 1000 to 1700 g kg⁻¹. Total hydrocarbons, PM_{2.5}, PM₁₀ and OC presented variable emissions, but in general substantially higher than values reported for wildfires in African and Amazonian biomes. The emission factors obtained in Portugal were as follows (in g kg⁻¹ biomass, dry basis): 6-350 for total hydrocarbons, 0.5-42 for PM_{2.5}, 1-60 for PM₁₀, and 0.2-42 for OC (in PM₁₀). The organic carbon-to-elemental carbon ratios measured in the present study largely exceed those obtained by other researchers.

Keywords: wildfires, trace gases, particles, organic and elemental carbon, emission factors

1. Introduction

Hot and dry conditions over the Mediterranean countries, Australia, California, or in many other regions, have contributed to increasingly wildfires. When wildfires rage out of control, tons of gaseous and particulate pollutants are released into the atmosphere with a strong effect at the regional scale (Jaffe et al., 2008; McMeeking et al., 2006; Balasubramanian and See, 2008; Liu et al., 2009) and also at sites thousands of kilometres from the source (Lewis et al., 2007; Duck et al., 2007; Petzold et al., 2007; Jaffe et al., 2004). Future climate changes are expected to result in more frequent and intense wildfires with far reaching consequences for visibility, air quality and the global carbon cycle. Using a chemical transport model, Spracklen et al. (2009) calculated that climate change will increase summertime organic carbon (OC) aerosol concentrations over the western United States by 40% and elemental carbon (EC) concentrations by 20% from 2000 to 2050. Most of this increase (75% for OC, 95% for EC) will be caused by larger wildfire emissions. While OC aerosols are known as important light scattering atmospheric components contributing to atmospheric cooling, EC has more recently gained attention as major light

absorbing aerosol species exerting a positive radiative forcing and reinforcing the atmospheric warming due to increases in the greenhouse gases (Chung and Seinfeld, 2005; Chen and Bond, 2010). The eventual climate effects from carbon aerosols will depend on their physical and chemical composition, as well as their lifetime and distribution in the atmosphere (Jacobson, 2001). Besides the climate interactions, wildland forest fire smoke can have profound adverse health effects at local and regional scales (Jayachandran, 2009; Potera, 2009).

Current global estimates of gas and particulate emissions from biomass burning are largely varying (NASA, 2009): 220-13500 Tg CO₂ yr⁻¹, 120-680 Tg CO yr⁻¹, and 11-53 Tg CH₄ 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).

There are still many unknown aspects related to the emissions of trace gases and aerosol from wildfires. Part of this is due to the unpredictability of fires, which hampers systematic field studies. Since emissions vary with type of fuel burned and combustion stage (flaming versus smouldering) (Alves et al., 2010), and taking also into account that atmospheric photochemistry, source apportionment and climate change models require detailed reliable emission factor inputs, it is necessary to obtain emission databases reflecting the distinct fuel and burning conditions.

2. Methodology

In summer 2009, emissions of trace gases and aerosols from several wildfires registered in Portugal (Table 1) were sampled. A portable high-volume sampler (TE-5200, Tisch Environmental Inc.) operating at a flow of 1.13 m³ min⁻¹ was used to collect sequentially, on pre-fired quartz fibre filters, coarse (PM_{2.5-10}) and fine (PM_{2.5}) smoke particles. The sampler was connected only when impacted by the smoke plumes. In parallel, Tedlar bags previously flushed with N₂ were used for the collection of gas samples. Pre-removal of particulate matter and water vapour from the air stream was carried out in quartz filter and a U glass tube filled with glass spheres, immersed in an ice bath, respectively. The sampling set up also included a Teflon diaphragm pump connected to a needle valve and a calibrated rotametre operating at a flow rate of 1 L min⁻¹. The different elements were connected with Teflon tube.

Total hydrocarbons and carbon oxides (CO₂ and CO) in the Tedlar bags were measured using automatic analysers with flame ionisation (Dyna-FID, 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 concentration/emission of hydrocarbons is presented in methane-equivalents.

The carbonaceous content (EC and OC) of particulate matter was analysed by a thermal-optical technique after a previous sample acidification to remove carbonates, following a short multi-step temperature protocol, first in an inert (N₂) and then in an oxidising atmosphere (N₂/O₂). Two 9 mm diameter filter punches, in the case of PM_{2.5} samples, or strips representing 1/20 of the total area, in the case of PM_{2.5-10} samples, were used in each analytical run. For each filter, two or three replicate analyses were done. The CO₂ released during sample heating is measured by a non-dispersive infrared analyser. The anoxic heating conditions (OC quantification) follow a two-step temperature profile: 200°C for 200 seconds and 600°C for 600 seconds, respectively. After these steps, the anoxic gas stream is replaced by an oxidising atmosphere (4% O₂) (EC quantification), and the sample is heated up to 850°C. However, thermally unstable organic compounds pyrolyse in the N₂-

mode to form pyrolytic carbon (PC), which then usually desorbs off the filter in the oxidising atmosphere, like native EC. To correct for pyrolysis, the optical properties of the sample are monitored during the analysis with a laser beam. During anoxic mode heating light transmission decrease while OC chars in the N₂-mode. When PC and EC are released from the filter in the N₂/O₂-mode, transmission increase again and the point at which the transmission reaches the pre-pyrolysis value is used to discriminate OC and EC (split point). Carbon carbonate present in aerosol samples was analysed throughout the release of CO₂ when a punch of filter is acidified with orthophosphoric acid in a free CO₂ gas stream.

Table 1. Location of wildfires episodes over Portugal in summer 2009 where smoke samples were collected.

Sampling locations	Latitude/Longitude Altitude (a.s.l.)	Date	Major types of biomass/Fire characteristics
Sever do Vouga	40°35'59"N/8°22'10"W 255 m	31 May	<i>Acacia melanoxylon</i> / <i>Eucalyptus globulus</i>
Ovar	40°51'56"N/8°37'47"W 25 m	17 Jul.	<i>Acacia/Eucalyptus globulus</i>
Penedono	40°56'25"N/7°23'52"W 810 m	21 Jul.	<i>Pinus pinaster</i> / <i>Cytisus striatus</i> / <i>Rubus fruticosus</i>
Montemor-o-Velho	40°12'50"N/8°41'38"W 51 m	11 Aug.	<i>Pinus pinaster/Eucalyptus globulus</i>
Nariz (Aveiro)	40°32'52"N/8°35'30"W 25 m	27 Aug.	<i>Pinus pinaster</i> / <i>Acácia sp./Eucalyptus globulus</i>
Cinfães (Viseu)	40°59'04"N/8°07'12"W 619 m	30 Aug.	Creeping fire in an <i>Eucalyptus globulus</i> forest. Biomass burned: fallen twigs, <i>Erica</i> shrubs, <i>Eucalyptus</i> bark and dried leaves
Farejinha (Castro Daire)	40°55'55"N/7°51'03"W 822 m	31 Aug.	<i>Pinus pinaster</i> / <i>Cytisus striatus</i>
Quinta da Póvoa (Sabugal)	40°20'40"N/7°14'30"W 500 m	01 Sept.	<i>Cytisus striatus</i> (dominant); some isolated pine trees
Pendilhe (V. N. de Paiva)	40°53'34"N/7°49'48"W 825 m	06 Sept.	<i>Cytisus striatus</i> / <i>Pinus pinaster</i>

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: CO₂, CO, hydrocarbons, and total particulate carbon (TC=OC+EC). 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):

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

It has been estimated that the dominant 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. 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 CO₂ 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:

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

Pure smouldering usually has MCE below 0.85 (Yokelson, 2004). The flaming combustion usually exhibits the highest MCE (0.9–1) (Reid et al., 2005).

3. Results and Discussion

The PM_{2.5} and PM_{2.5-10} smoke samples presented concentrations up to 45400 µg m⁻³ and 4330 µg m⁻³, respectively. The gravimetric mass concentration data confirmed that the PM₁₀ mass was dominated by PM_{2.5} mass concentrations. PM_{2.5} represented 86±8.8% of the PM₁₀ mass. Mass percentages of the same order have been obtained in previous works (Alves et al., 2010; McMeeking et al., 2009). Carbonates represented 0.15 to 3.1% (average = 0.83%) of PM_{2.5-10}, whereas its contribution to the mass of fine particles was negligible (Table 2). On average, 50±18% of the PM_{2.5} mass emissions was composed of organic carbon, whilst the mass fraction in PM_{2.5-10} was 36±18%. The OC mass fractions were in the range of values reported for biomass burning in grasslands, savannah, cerrado, boreal and tropical forests (Reid et al., 2005). On average, the OC concentrations were 10 times higher in PM_{2.5} than in PM_{2.5-10}. The carbonaceous fraction of smoke samples from any of the fires in this study was clearly dominated by organic carbon. A wide range of OC/EC ratios were obtained. Most of the values are much higher than those reported for other biomass burning events (Andreae and Merlet, 2001; Reid et al., 2005). Very high OC/EC ratios were also determined for intense flaming fires in a Mediterranean shrubland (Alves et al., 2010). The high OC production in fire plumes has been attributed 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). It could be argued that some differences between values of the current study and those reported in the literature may be a consequence of the utilisation of different methodologies for the OC and EC determination. It should be noted, however, that 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) gave similar results for OC and EC, without significant differences at a 95% confidence level (Nunes et al., 2010). Good results were also obtained by the University of Aveiro in an international round robin test (Schmid et al., 2001).

Table 2. Mass fraction of carbonates, organic carbon and total carbon (TC=OC+EC) in the particulate matter, and organic-to-elemental carbon ratios.

Particle size	CO ₃ ²⁻ /PM (%)	OC/PM (%)	TC/PM (%)	OC/EC
PM _{2.5}	0.15-3.1 (avg = 0.83)	50±18	52±20	5-924 (avg = 90)
PM _{2.5-10}	---	36±18	37±18	10-111922 (avg = 12275)

The PM_{2.5} emission factors obtained for wildfires in Portugal were 19.3±15.1 g kg⁻¹, lying in the ranges reported in the literature for other fires. Considering that MCE values higher or lower than 90% are characteristic of flaming or smouldering combustion, respectively, Reid et al. (2005) obtained EF_{PM_{2.5}} around 9 g kg⁻¹ for flaming combustion measurements, while an approximate value of 34 g kg⁻¹ was derived for smouldering stages. Yokelson et al. (2008) estimated a fine aerosol emission factor of 9.93 g kg⁻¹ dry fuel, with global values ranging from 2.17 to 16.61 g kg⁻¹ for MCEs between 0.88 and 0.979. Ward and Hardy (1991) suggested an EF_{PM_{2.5}} of 10 g kg⁻¹ for cured grasses, 15 g kg⁻¹ fuel for chaparral and palmetto/gallberry fires and 20-50 g kg⁻¹ for long-needled conifer fires. From open combustion of biomass in the laboratory, McMeeking et al. (2009) obtained EF_{PM_{2.5}} g kg⁻¹ dry fuel of 29.4±25.1 for montane, 18.9±13.9 for rangeland, 11.6±15.1 for chaparral, 23.4±18.7 for coastal plain and 12.7±11.3 for boreal forest ecosystem species. In their review paper, Andrea and Merlet (2001) presented EF_{PM_{2.5}} (dry fuel) of 5.4±1.5 g kg⁻¹ (savannah and grassland), 9.1±1.5 g kg⁻¹ (tropical forest) and 13.0±7.0 g kg⁻¹ (extratropical forest). However, Yokelson et al. (2008) derived an Amazon-average EF_{PM_{2.5}} of 16.8 g kg⁻¹, which represents 85% more PM_{2.5} emissions for the region than using the Andreae and Merlet (2001) recommendation of 9.1 g kg⁻¹. The physical basis for this increase was the inclusion of a larger contribution from smouldering combustion. Thus, taking into account the discrepancies observed, more measurements would be valuable. Kasischke and Bruhwiler (2002) argued that most of the ground-layer organic matter is consumed during smouldering combustion, and this has to be accounted for when estimating forest fire emissions.

Figure 1 shows the relationship between MCE and the pollutant emission factors. MCE values ranged from 0.52-0.97, but most of the values correspond to a greater predominance of smouldering than flaming combustions. The linear regression between MCE and PM_{2.5} is in good agreement with Ward and Hardy's relationship, who obtained EF_{PM_{2.5}}=67.4-66.8×MCE for prescribed fires in the Pacific Northwest. It also approaches the empirical relationship estimated by Babbitt et al. (1994) for wildfires in Montana, Idaho and Oregon (EF_{PM_{2.5}}=62.6-61.4×MCE). However, the correlation (EF_{PM_{2.5}}=336-341×MCE) developed by McMeeking et al. (2009) in laboratory experiments with different types of biofuels differs significantly from the above-mentioned relationships. The discrepancy may be due to the inherent variability of emissions coupled with different fuels and burning conditions, as well as different ranges of MCE covered by the measurements. The lack of data in the literature over a broad range of MCE may result in biased estimates of particle emissions and properties. If smouldering emissions are underestimated, the total PM_{2.5} emissions attributed to biomass combustion in current inventories are likely to be undervalued.

The average PM_{2.5}/CO emission ratio was 0.08±0.06 g g⁻¹. Janhäll et al. (2010) reported emission ratios of PM/CO=(0.13±0.05) g g⁻¹ for forest, PM/CO=(0.08±0.03) g g⁻¹ for savannah, and PM/CO=(0.07±0.03) g g⁻¹ for grass. The PM/CO emission ratio has low MCE dependence and can be used to predict the level of one pollutant in a plume, when the concentration of the other is known.

As perceived in previous studies (McMeeking et al., 2009), the significance of the relationship between EC and MCE was weak. While OC increases considerably under smouldering conditions, EC emissions seem similar for flaming and smouldering conditions. This observation is in accordance with the inferences by Battye and Battye (2002) based on the compilation of several emission databases. However, it deviates from

the reasoning that EC emissions enhance with flaming-phase combustion, consistent with temperature and oxidant-dependent soot formation mechanisms (Chen et al., 2007; McMeeking et al., 2009).

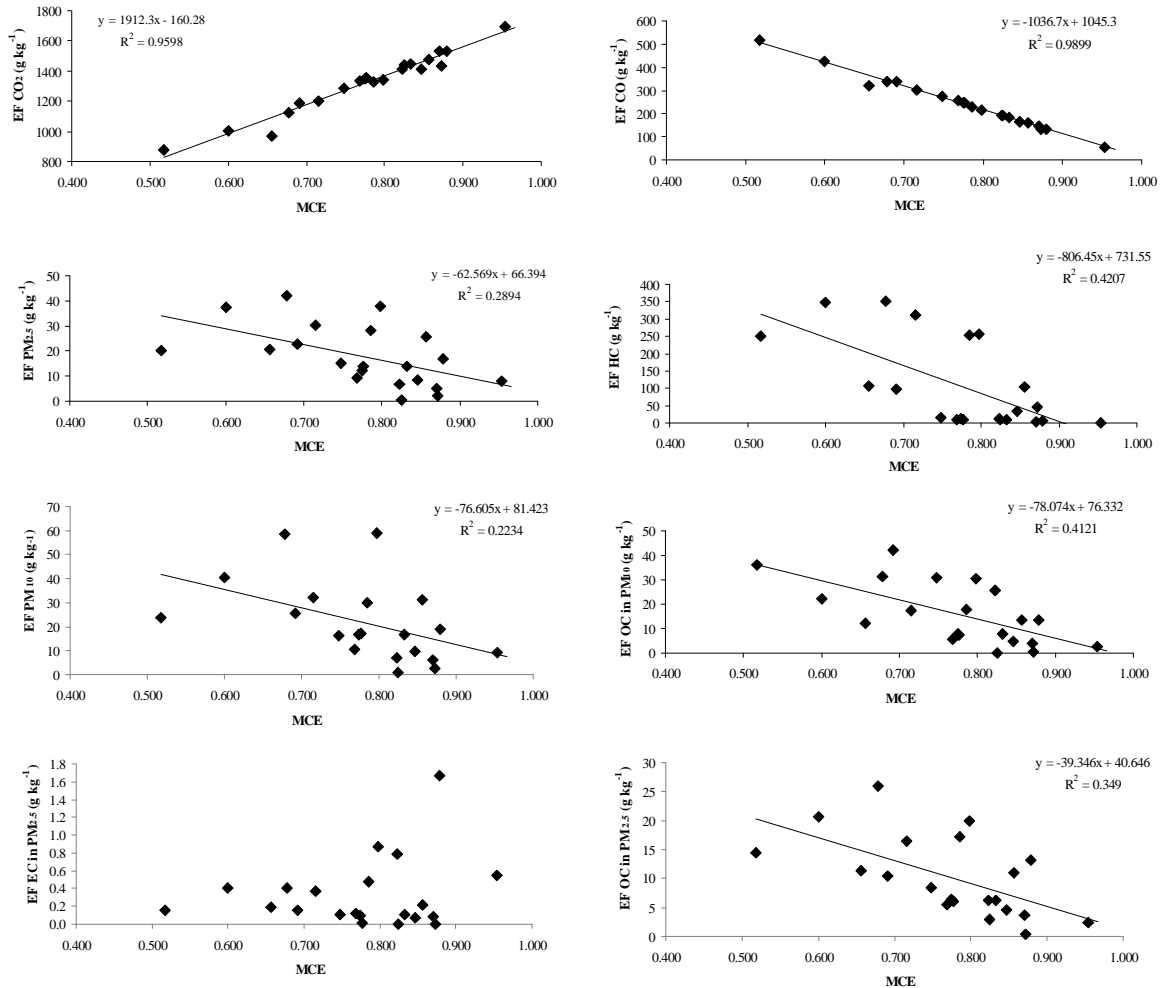


Figure 1. Emission factors as a function of MCE

EC/TC ratios in PM_{2.5} were less than 4% for MCE values below 0.90, and increased strongly for higher MCE values. The extreme EC/TC ratios were 0.012 for a sample collected during only the smouldering phase of the fire (MCE = 0.52) and 0.18 for a sample collected during the flaming phase (MCE = 0.97). Battye and Battye (2002) reported EC/TC ratios of 0.06 (flaming) and 0.16 (smouldering) for airborne field studies with Ponderosa pine, while for chaparral species the ratios were 0.11 (smouldering) and 0.11-0.22 (flaming). McMeeking et al. (2009) obtained an EC/TC ratio of ~0 for a sample collected during only the smouldering phase of the fire (MCE = 0.80) and 0.5 for a sample collected during the flaming phase (MCE = 0.99).

In accordance with the results presented by Battye and Battye (2002), 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 efficiencies

($EF_{OC}=1.94 \times EF_{PM_{2.5}}$; $r^2=0.87$). Emission factors ranged from 0.16 to 42 g kg⁻¹, averaging 15.8 g kg⁻¹. Andreae and Merlet (2001) reported EF_{OC} of 3.4±1.4 g kg⁻¹ (savannah), 5.2±1.5 g kg⁻¹ (tropical forest) and 8.6-9.7 g kg⁻¹ (extratropical forest). Battye and Battye (2002) gathered mean values from 1.96 to 25.6 g kg⁻¹ for different US forest biofuels and burning stages.

On average, 75.1±11.5% of the carbon was emitted in the form of CO₂, followed by CO (20.6±10.4%), hydrocarbons (3.37±3.04%), OC (1.15±1.09%), and EC (0.04± 0.02%). CO is very important in the development of emissions inventories for many pollutants. Because CO is an indicator of smouldering combustion, its emission factor is often used to estimate emission factors for many other products of incomplete combustion (Battye and Battye, 2002). The EF_{CO} obtained for wildfires in Portugal (231±117 g kg⁻¹) are higher than the 65±20, 104±20 and 107±37 g kg⁻¹ dry fuel compiled by Andreae and Merlet (2001) for fires in savannah, tropical and extratropical forests, respectively. Battye and Battye (2002) reported CO emission factors for different fire types in the ranges 99-232 g kg⁻¹ and 22-78 g kg⁻¹ smouldering and flaming combustions, respectively, suggesting EF_{CO} of 125 g kg⁻¹ biomass consumed for both canopy fuel and shrubs and 158 g kg⁻¹ for duff. A high CO emission factor (459 g kg⁻¹) was measured for feathermoss/lichen in Scotch pine forests of Central Siberia with a low MCE of 0.59 (McRae et al., 2006).

The CO₂ emission factors obtained in this study ranged between a few values around 1000 and a maximum of 1697 g kg⁻¹, reflecting the different contributions from smouldering and flaming fires. In laboratory experiments, McMeeking et al. (2009) obtained EF_{CO_2} from 1311±325 g kg⁻¹ (boreal forest fuels) to 1632±150 g kg⁻¹ (coastal plain fuels). Andreae and Merlet (2001) suggested EF_{CO_2} of 1613±95 g kg⁻¹ (savannah), 1580±90 g kg⁻¹ (tropical forest) and 1569±13 g kg⁻¹ (extratropical forest).

Total hydrocarbon (HC) emission factors ranged from about 6 to 350 g kg⁻¹, averaging 102 g kg⁻¹. Chen et al. (2007) obtained average emission factors for HC from laboratory combustion of wildland fuels of 0.4-10.4 g kg⁻¹ (flaming) and 1.2-125 g kg⁻¹ (smouldering). These researchers observed higher and more variable emission factors for total hydrocarbons during the smouldering phase, especially for fuels containing substantial moisture.

4. Conclusions

This study covers a comprehensive set of measurements that include gas-phase and particulate-phase emissions, along with an indicator of combustion conditions, for several wildfires that occurred in Portugal during the 2009 summer season. Parameterizations for the CO₂, CO, total hydrocarbons, particulate matter and OC emission factors as a function of modified combustion efficiency were obtained: EF_{CO_2} (g kg⁻¹) = (1912×MCE-160), EF_{CO} (g kg⁻¹) = (-1037×MCE+1045), EF_{HC} (g kg⁻¹) = (-806×MCE+73), $EF_{PM_{2.5}}$ (g kg⁻¹) = (-63×MCE+66) and $EF_{OC_{PM_{2.5}}}$ (g kg⁻¹) = (-39×MCE+41). Our results consolidate previous argumentations that smouldering emissions make a significant contribution to the total emissions. When emission factors account for this combustion phase, the overall emissions largely exceed the estimates based on widely used recommendations. 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. Since EC is an aerosol component that plays a key role in radiative forcing, and taking into account the discrepancies between the various studies, the magnitude of the emission factor for EC

remains a significant uncertainty in estimates of the climate impacts of biomass burning and deserves further investigation.

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References

- Alves, C.A., Gonçalves, C., Pio C.A., Mirante, F., Caseiro, A., Tarelho, L., Freitas, M.C., Viegas, D.X., 2010. Smoke emissions from biomass burning in a Mediterranean shrubland. *Atmospheric Environment* In Press.
- Andreae, M.O., Merlet, P., 2001. Emission of trace gases and aerosols from biomass burning. *Global Biogeochemical Cycles* 15, 955-966.
- Babbitt, R.E., Ward, D.R., Susott, R.A., Hao, W.M., Baker, S.P., 1994. Smoke from western wildfires, 1994. In: *Proceedings of 1994 Annual Meeting of Interior West Fire Council*, Coeur d'Alene, Idaho, November.
- Balasubramanian, R., See, S.W., 2006. Impact of forest fires on regional air quality in Southeast Asia. *Chinese Journal of Geochemistry* 25(S1), 221-222.
- Battye, W., Battye, R., 2002. Development of emissions inventory methods for wildland fire, 91 pp, U.S. Environmental Protection Agency, Chapel Hill, NC.
- Cavalli, F., Viana, M., Yttri, K. E., Genberg, J., Putaud, J.P., 2009. Toward a standardised thermal-optical protocol for measuring atmospheric organic and elemental carbon: the EUSAAR protocol. *Atmospheric Measurement Techniques* 3, 79-89.
- Chen, L.W.A., Moosmüller, H., Arnott, W.P., Chow, J.C., Watson, J.G., Susott, R.A., Babbitt, R.E., Wold, C.E., Lincoln, E.N., Hao, W.M., 2007. Emissions from laboratory combustion of wildland fuels: Emission factors and source profiles. *Environmental Science and Technology* 41, 4317-4325.
- Grieshop, A.P., Logue, J.M., Donahue, N.M., Robinson, A.L., 2009. Laboratory investigation of photochemical oxidation of organic aerosol from wood fires 1: measurements and simulation of organic aerosol evolution. *Atmospheric Chemistry and Physics* 9, 1263-1277.
- Jaffe, D., Bertschi, I., Jaegl, L., Novelli, P., Reid, J., Tanimoto, H., Vingarzan, R., Westphal, D., 2004. Long-range transport of Siberian biomass burning emissions and impact on surface ozone in western North America. *Geophysical Research Letters* 31, L16106, doi:10.1029/2004GL020093.
- Jaffe, D., Hafner, W., Chand, D., Westerling, A., Spracklen, D., 2008. Influence of fires on O₃ concentrations in the western US. *Environmental Science and Technology* 42, 2812-2818.
- Janhäll, S., Andreae, M.O., Pöschl, U., 2010. Biomass burning aerosol emissions from vegetation fires: particle number and mass emission factors and size distributions. *Atmospheric Chemistry and Physics* 10, 1427-1439.
- Jayachandran S., 2009. Air quality and early-life mortality. *Journal of Human Resources* 44, 916-954.
- Kasischke, E. S., Williams, D., Barry, D., 2002. Analysis of the patterns of large fires in the boreal forest region of Alaska. *International Journal of Wildland Fire* 11, 131-144.
- Lewis, A., Evans, M., Methven, N., Watson, J., Lee, J., Hopkins, J., Purvis, R., Arnold, S., McQuaid, J., Whalley, L., Pilling, M., Heard, D., Monks, P., Parker, A., Reeves, C., Oram, D., Mills, G., Bandy, B., Stewart, D., Coe, H., Williams, P., Crosier, J., 2007. Chemical composition observed over the mid-Atlantic and the detection of pollution signatures far from source regions *Journal of Geophysical Research* 112, D10S39, doi:10.1029/2006JD007584.
- Liu Y., Kahn R.A., Chaloulakou A., Koutrakis P., 2009. Analysis of the impact of the forest fires in August 2007 on air quality of Athens using multi-sensor aerosol remote sensing data, meteorology and surface observations. *Atmos. Environ.* 43, 3310-3318.
- McMeeking G., Kreidenweis S., Lunden M., Carrillo J., Carrico C.M., Lee T., Herckes P., Engling G., Day D.E., Hand J., Brown N., Malm W.C., Collett J.L., 2006. Smoke-impacted regional haze in California during summer 2002. *Agr. Forest Meteorol.* 137, 25-42.

- McMeeking, G.R., Kreidenweis, S.M., Baker, S., Carrico, C.M., Chow, J.C., Collett, J.L., Hao, W.M., Holden, A.M., Kirchstetter, T.W., Malm, W.C., Moosmüller, H., Sullivan, A.P., Wold, C.E., 2009. Emissions of trace gases and aerosols during the open combustion of biomass in the laboratory. *Journal of Geophysical Research* 114, D19210, doi:10.1029/2009JD011836.
- McRae, D., Conard, S., Ivanova, G., Sukhinin, A., Baker, S., Samsonov, Y., Blake, T., Ivanov, V., Ivanov, A., Churkina, T., Hao, W., Koutzenogij, K., Kovaleva, N. 2006. Variability of fire behavior, fire effects, and emissions in Scotch pine forests of Central Siberia. *Mitigation and Adaptation Strategies for Global Change* 11, 45-74.
- NASA (National Aeronautics and Space Administration), 2009. Global Fire Monitoring. URL: <http://earthobservatory.nasa.gov/Features/GlobalFire/printall.php>. Accessed June 2009.
- Nunes, T., Mirante, F., Almeida, E., Pio, C., 2010. Comparison of methods for the quantification of the different carbon fractions in atmospheric aerosol samples. *Geophysical Research Abstracts*, Vol. 12, EGU2010-11595.
- Petzold, A., Weinzierl, B., Huntrieser, H., Stohl, A., Real, E., Cozic, J., Fiebig, M., Hendricks, J., Lauer, A., Law, K., Roiger, A., Schlager, H., Weingartner, E., 2007. Perturbation of the European free troposphere aerosol by North American forest fire plumes during the ICARTT-ITOP experiment in summer 2004. *Atmospheric Chemistry and Physics* 7, 5105-5127.
- Potera, C., 2009. Air pollution: the oxidative punch of wildfires. *Environ. Health Perspect.* 117, A58.
- Randerson, J.T., van der Werf, G.R., Giglio, L., Collatz, G.J., Kasibhatla, P.S., 2006. Global Fire Emissions Database, Version 2 (GFEDv2). Data set. Available on-line [<http://daac.ornl.gov/>] from Oak Ridge National Laboratory Distributed Active Archive Center, Oak Ridge, Tennessee, U.S.A. doi:10.3334/ORNLDAAAC/834.
- Reid, J. S., Koppmann, R., Eck, T.F., Eleuterio, D.P., 2005. A review of biomass burning emissions part II: intensive physical properties of biomass burning particles. *Atmospheric Chemistry and Physics* 5, 799-825.
- Schmid, H., Laskus, L., Abraham, H.J., Baltensperger, U., Lavanchy, V., Bizjak, M., Burba P., Cachier H., Crow, D., Chow, J., Gnauk, T., Even, A., Ten Brink, H.M., Giesen, K.P., Hitzemberger, R., Hueglin, C., Maenhaut, W., Pio, C., Carvalho, A., Putaud, J.P., Toom-Sauntry, D., Puxbaum, H., 2001. Results of the ‘‘carbon conference’’ international aerosol carbon round robin test stage I. *Atmospheric Environment* 35, 2111-2121.
- Silva, J.F., Oliveira, E.M.S.R., Gomes, A.P.D., Tarelho, L.A.C., 2008. Leaching of shrub biomass collected in eucalyptus forest of central Portugal for use as biofuel. In: *Proceedings of the 16th European Biomass Conference & Exhibition*, Valencia, Spain, pp. 499-503.
- Spracklen, D.V., Mickley, L.J., Logan, J.A., Hudman, R.C., Yevich, R., Flannigan, M.D., Westerling, A.L., 2009. Impacts of climate change from 2000 to 2050 on wildfire activity and carbonaceous aerosol concentrations in the western United States. *Journal of Geophysical Research* 114, D20, doi:10.1029/2008JD010966.
- Ward, D.E., Hardy, C.C., 1991. Smoke emissions from wildland fires. *Environmental International* 17, 117-134.
- Yokelson, R.J., 2004. SAFARI 2000 Gas Emissions from Biofuel Use and Production, September 2000. Data set. Available on-line [<http://daac.ornl.gov/>] from Oak Ridge National Laboratory Distributed Active Archive Center, Oak Ridge, Tennessee, U.S.A. doi:10.3334/ORNLDAAAC/753.
- Yokelson, R.J., Christian, T.J., Karl, T.G., Guenther, A., 2008. The tropical forest and fire emissions experiment: laboratory fire measurements and synthesis of campaign data. *Atmospheric Chemistry and Physics Discussions* 8, 4221-4266.