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Hydrocarbons in particulate samples from wildfire events in central Portugal in summer 2010

Ana Vicente[1,*], *Ana Calvo*[2], *Ana P. Fernandes*[1], *Teresa Nunes*[1], *Cristina Monteiro*[1], *Casimiro Pio*[1], *Célia Alves*[1]

1. *Centre for Environmental and Marine Studies (CESAM), Department of Environment, University of Aveiro, 3810-193 Aveiro, Portugal*
2. *Department of Physics, IMARENAB, University of León, 24071 León, Spain*

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ABSTRACT

In summer 2010, twenty eight (14 $PM_{2.5}$ samples plus 14 samples $PM_{2.5-10}$) smoke samples were collected during wildfires that occurred in central Portugal. A portable high-volume sampler was used to perform the sampling, on quartz fibre filters of coarse ($PM_{2.5-10}$) and fine ($PM_{2.5}$) smoke samples. The carbonaceous content (elemental and organic carbon) of particulate matter was analysed by a thermal–optical technique. Subsequently, the particulate samples were solvent extracted and fractionated by vacuum flash chromatography into three different classes of organic compounds (aliphatics, polycyclic aromatic hydrocarbons (PAHs) and carbonyl compounds). The organic speciation was performed by gas chromatography–mass spectrometry (GC–MS). Emissions were dominated by the fine particles, which represented around 92% of the PM_{10}. A clear predominance of carbonaceous constituents was observed, with organic to elemental carbon (OC/EC) ratios ranging between 1.69 and 245 in both size fractions. The isoprenoid ketone 6,10,14-trimethyl-2-pentadecanone, a tracer for secondary organic aerosol formation, was one of the dominant constituents in both fine and coarse particles. Retene was the most abundant compound in all samples. Good correlations were obtained between OC and both aliphatic and PAH compounds. Pyrogenic processes, thermal release of biogenic compounds and secondary processing accounted for 97% of the apportioned $PM_{2.5}$ levels.

Introduction

Every year, a considerable area of the Portuguese territory is burned and some wildfires last several days, emitting to the atmosphere huge amounts of gases and particles. Smoke plumes consist of particulate matter and gaseous compounds from the combustion processes. Specific studies on biomass smoke indicate a consistent relationship between exposure and increased respiratory symptoms, increased risk of respiratory illness, and decreased lung function (World Health Organization, 1999). Inhalable coarse particles ($PM_{2.5-10}$), which are able to pass through the upper respiratory tract and deposit in the airways, and fine particles ($PM_{2.5}$), which can be inhaled deeply into the lungs and deposit in the gaseous exchange region of terminal bronchi and alveoli (Finlay et al., 2012), are emitted by wildfires. In earlier studies, it was observed that $PM_{2.5}$ particles emitted from wildfires represented about 80% of PM_{10} (Vicente et al., 2012, 2013). Emission inventories by the United States Environmental Protection Agency (USEPA) estimate that approximately 20%

* *Corresponding author*. E-mail: anavicente@ua.pt (Ana Vicente).

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of the total annual fine particle emissions to the atmosphere come from biomass combustion sources. Biomass combustion sources include energy conversion for cooking and heating, forest bush and weed removal for land clearing and fire safety, agricultural, municipal, and industrial waste incineration, cigarette smoke, charcoal production, structural fires and wildfires (Cass et al., 2001).

Polycyclic aromatic hydrocarbons (PAHs) are typical compounds emitted in biomass burning processes (Hata et al., 2014) and most of them are associated with fine particles (Tekasakul et al., 2008). PAHs comprise compounds that are considered carcinogenic, mutagenic and teratogenic (IARC, 2010; Kim et al., 2013; and references therein). Aliphatic compounds, also a product from biomass burning, comprise the homologous series of *n*-alkanes and *n*-alkenes. *n*-Alkanes with higher carbon chain (C_{25}–C_{33}) have been assigned to epicuticular waxes. The *n*-alkene homologous series do not represent major compounds in plant waxes. It has been assumed that *n*-alkenes are primarily formed by thermal dehydration of *n*-alkanols and, to a minor extent, from *n*-alkanes by oxidation during incomplete combustion (Oros and Simoneit, 2001a). Aliphatic compounds have also been proposed as precursors of straight chain ketones from partial combustion (Oros and Simoneit, 2001a).

The wood smoke composition depends on multiple factors, including the fuel type and moisture content, fire temperature, wind conditions and other weather-related influences (U.S. Environmental Protection Agency, 2008). Therefore, it is of the utmost importance the measurement in real conditions. These results are extremely useful for generating chemical fingerprint databases for different biomass combustion conditions. Lavoué et al. (2000) developed an algorithm to build an inventory of burned biomass and its carbonaceous aerosol emissions by wildfires at boreal and temperate latitudes. The final goal was to produce information to be used to evaluate emissions in future climate change scenarios. The study revealed that the lack of information about biomass burning emissions made the development of the work difficult.

The aim of the present study is to characterise the particulate matter emitted by wildfires in central Portugal. The results now obtained complement the extensive dataset already published, with gaseous compounds and particulate phase constituents (water soluble ions, elements and polar organic tracers) for the same wildfires (Vicente et al., 2013). Additional datasets obtained for wildfires in the previous year, representing distinct combustion stages and forest biomes, can be found elsewhere (Vicente et al., 2011, 2012). The information generated may represent an important contribution to climate and atmospheric chemistry models, to better understand the impact of wildfires on the human health, to improve emission inventories and to refine source apportionment methodologies.

1. Methodology

1.1. Sampling details

Smoke samples were collected from six wildfires that occurred in central Portugal between July and August of 2010 (Table 1).

In order to collect sequentially coarse ($PM_{2.5–10}$) and fine ($PM_{2.5}$) smoke particles from the plumes, a tripod high-volume sampler (TE-5200, Tisch Environmental Inc.) operating at a flow of 1.13 m^3/min was used. The impaction system for removing PM_{10} was designed at the University of Aveiro in accordance with the Marple and Rubow's (1986) theory. All the quartz fibre filters were previously baked at 500°C for 6 hr. A total of fourteen $PM_{2.5}$/$PM_{2.5–10}$ sample pairs were obtained. Tedlar bags previously flushed with N_2 were used to collect gas samples, in parallel and simultaneously with aerosol sampling. Sampling was performed at 1.5 m above ground, downwind from the burning area, at distances of 10–100 m from the fires. The sampling was normally conducted to obtain samples from the core of the smoke plume. However, due to the unpredictable behaviour of the wildfires and the very tricky field conditions, the plume cannot be sampled

Table 1 – Details of samples of smoke plumes from wildfires in the summer of 2010 in central Portugal.

Sampling locations	Latitude/ longitude	Altitude (a.s.l.)	Date	Major types of biomass	Number of samples ($PM_{2.5}$ + $PM_{2.5–10}$)	MCE
Dornelas (Sever do Vouga)	40°46′31″N/8°23′49″W	227	26 Jul.	*Eucalyptus globulus*/Furze/Grasses	2	0.87
Rebordelo (Santa Maria da Feira)	40°59′47″N/8°25′14″W	244	27 Jul.	Vineyards/*Castanea sativa*/Grasses/ *Eucalyptus globulus*/*Pterospartum tridentatum*/Gorse/*Ericaceae*	6	0.83–0.94
Albergaria-a-Velha	40°42′19″N/8°30′04″W	133	4 Aug.	Piles of *Pine* and *Eucalyptus* logs, sawdust, wood chips and giant roots	4	0.92
Albergaria-a-Velha	40°43′27″N/8°28′49″W	162	6 Aug.	*Pinus pinaster*/*Eucalyptus globulus*/Bush/ *Ericaceae* and forest litter	2	0.89
Junqueira (Vale de Cambra)	40°48′38″N/8°20′38″W	246	11 Aug.	*Pinus pinaster*/*Eucalyptus globulus*/*Cytisus striatus*	4	0.87–0.91
Vila Nova de Tazem (Gouveia)	40°30′56″N/7°41′48″W	374	13 Aug.	*Pinus pinaster* and *pinea*/*Cytisus striatus*/ *Acacia saligna*/*Quercus suber*/*Rubus fruticosus*/*Arbustus unedo*/*Olea europaea* L.	12	0.64–0.84

MCE = modified combustion efficiency = ($\Delta[CO_2]$) / ($\Delta[CO_2]$ + $\Delta[CO]$), where $\Delta[CO_2]$ and $\Delta[CO]$ are background subtracted concentrations in carbon equivalents. a.s.l. - above sea level.

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