

# Hydrocarbons in smoke samples from wildfire events in central Portugal in summer 2010

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In summer 2010, smoke samples were collected from six wildfires occurring over central Portugal.

In order to collect sequentially, on pre-fired quartz fibre filters, coarse (PM<sub>2.5-10</sub>) and fine (PM<sub>2.5</sub>) smoke particles from the plumes, a tripod high volume sampler operating at a flow of 1.13 m<sup>3</sup> min<sup>-1</sup> was used. Sampling was performed at 1.5 m above ground, downwind from the burning areas, at distances of 10-100 m from the fire fronts. The organic and elemental carbon content (OC and EC) of particulate matter was analysed by a thermal-optical transmission technique. The detailed speciation of organic compounds in smoke samples was carried out by gas chromatography-mass spectrometry (Alves *et al.*, 2011).

The chromatographically resolved organics, object of this study, are *n*-alkanes, *n*-alkenes, polycyclic aromatic hydrocarbons (PAHs), carbonyl compounds and acid methyl esters.

The smoke particle concentrations were in the ranges 0.69-12 mg m<sup>-3</sup> for PM<sub>2.5</sub> and 0.085-0.66 mg m<sup>-3</sup> for PM<sub>2.5-10</sub>. Fine particles represented 92±4.1% of the PM<sub>10</sub> mass. On average, 47±13% of the PM<sub>2.5</sub> emissions consisted of organic carbon, whilst the OC mass fraction obtained for coarse particles was 27±13%.

Aliphatic compounds comprised the *n*-alkane homologous series from C<sub>10</sub> to C<sub>34</sub> without a clear odd-to-even carbon number predominance. The homologues with the highest concentrations (C<sub>max</sub>) were C<sub>22</sub>, for fine particles, and C<sub>29</sub>, for coarse particles. The *n*-alkene homologous series ranged from C<sub>14</sub> to C<sub>30</sub>, with C<sub>max</sub> at C<sub>20</sub>, for both size fractions, showing an even-to-odd carbon number predominance. *n*-Alkenes derive mostly from the thermal dehydration of *n*-alkanols and, in smaller amounts, from the oxidation of *n*-alkanes during incomplete combustion (Oros and Simoneit, 2001). The *n*-alkane and *n*-alkene contents in the wildfire smoke particles were in the ranges 0.0022-1.2 mg g<sup>-1</sup> OC and 0.0035-0.37 mg g<sup>-1</sup> OC, respectively.

PAHs are formed as a result of incomplete combustion or thermal decomposition (pyrolysis) of the organic material. The OC-normalised concentrations of the dominant PAHs identified in coarse and fine smoke particles are presented in Figure 1. Retene was the dominant polyaromatic hydrocarbon found in both particle sizes. It is the fully aromatised thermal alteration product of the resin acids present in conifer woods (Ramdahl, 1983). Besides retene, fluoranthene and chrysene were the most abundant PAHs found in both size fractions. Benzo[a]anthracene, benzo[a]pyrene and benzo[e]pyrene, components with high mutagenic and

genotoxic potential (Medeiros and Simoneit, 2008), were also identified in smoke samples. PAHs in biomass burning emissions are common to those emitted by other combustion sources. Diagnostic ratios are used as a tool for assessing the possible contribution of different sources (Alves, 2008). The ratios obtained in this study are listed in Table 1.

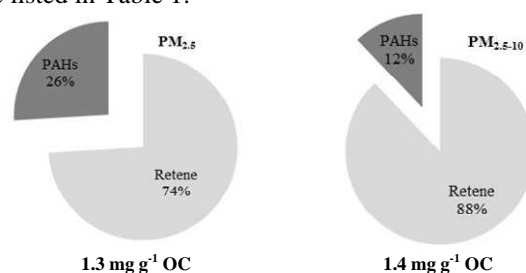


Figure 1. OC-normalised concentrations of PAHs detected in fine and coarse particles.

The dominant carbonyl compound in the wildfire aerosols was 6,10,14-trimethyl-2-pentadecanone. Alkanoates and vanillin were also found to be abundant in the majority of samples.

Table 1. PAH diagnostic ratios obtained in this study.

	PM <sub>2.5</sub>	PM <sub>2.5-10</sub>
Flu/(Flu+Pyr)	0.46-0.60	0.50-0.73
IcdP/(BghiP+IcdP)	0.74-0.84	0.75-0.82
BFs/BghiP	2.4-5.7	3.8-4.9
BeP/(BeP+BaP)	0.33-0.57	0.37-0.51
BghiP/BaP	0.29-0.66	0.41-0.63
Phe/(Phe+Ant)	0.47-0.80	0.53-1.0

Flu – Fluoranthene; Pyr – Pyrene; IcdP – Indeno[1,2,3-cd]pyrene; BghiP – Benzo[ghi]perylene; BFs – Benzo[fluoranthene]; BeP – Benzo[e]pyrene; BaP – Benzo[a]pyrene; Phe – Phenanthrene; Ant – Anthracene

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