

# Composition and source apportionment of atmospheric aerosols in Portugal during the 2003 summer intense forest fire period

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## Abstract

The summer of 2003 was characterized by an intense heat wave across Europe that resulted in a large number of deaths and intense and extended forest fires. In Portugal, during this period more than 300000 ha of forests were destroyed by fire, during a short period, emitting enormous quantities of pollutants to the atmosphere. These emissions have presumably important effects in terms of regional human health and on the atmospheric radiation balance. During the summer of 2003 aerosol samples were taken in the Aveiro region, Portugal, and analysed for total mass and a series of inorganic and organic compounds, including tracers of biomass burning such as potassium and levoglucosan. Based on air mass trajectories, the aerosol size distribution, the levels of particulate mass and the aerosol composition, observed during periods with and without forest fires, the contribution of forest fires to the regional aerosol load is inferred. The absolute and relative variability of the aerosol inorganic and organic components are used to evaluate the importance of forest fire emissions as sources responsible for the presence in the summer atmosphere of compounds such as particulate tracers. The results permit also to have, at least, a semi quantitative estimation of the emission factors of biomass burning tracers such as potassium and levoglucosan to the organic aerosol load in air mass plumes resulting from forest fires. The calculation of emission factors from natural forest fires (without the bias of laboratory and prescribed burnings) is a useful complement for a correct inventory of the impact of these nowadays common summer events on the contamination of regional and global atmosphere.

*Keywords: atmospheric aerosols, carbonaceous content, forest fires, levoglucosan, potassium.*



## 1 Introduction

Aerosols are minute particles suspended in the atmosphere. The major aerosol components include inorganic substances such as sulphates and carbonaceous species, which are divided into organic carbon (OC) and elemental carbon (EC). On a global basis, the major source of carbonaceous aerosols is biomass burning, due to forest fires and to the widespread use as fuel for heating homes and cooking [1–4]. Smoke aerosols perturb regional, and probably global, radiation budgets by their light-scattering effects and by their influence on cloud microphysical processes. Fine particles and the associated organic compounds are also of current apprehension because of their recognized health effects.

Substantial investigation on the contribution of biomass smoke to ambient aerosol levels has been executed for rain forests (e.g., [5–10]), smoked impacted areas in North America and Canada (e.g., [3, 4, 11–13]), and the aerosol outflow from the Asian continent (e.g., [14–16]). In Europe, data on detailed characterisation of atmospheric aerosols impacted by biomass burning are rather inexistent. Because of the specific weather conditions and the greater diversity of vegetation types burned in forest fires, regional differences in smoke impacted aerosol composition almost certainly exist. Accurate quantification of the amounts of particulate constituents emitted from forest fires and other sources of biomass burning on a regional and global basis is required by a number of users, including scientists studying a wide range of atmospheric processes, national governments who are required to report atmospheric emissions, and those interested quantifying the sources of air pollution that affect human health at regional scales.

In Portugal, it was estimated that, in the last decade, fires have destroyed around 110000 ha/year of forest, what corresponds to an annual loss of biomass of approximately 400000 ton [17]. Major forest fires raged across the country in 2003. Nearly 300000 ha of forest land were burnt, with cork and oak coverts particularly affected. The total area burned represented almost 5 times the average of the last two decades. The aerosol samples collected during the wildfire season of 2003 constituted an opportunity to evaluate the impact on background aerosol composition of emissions by extensive forest fires during drought conditions and a heat wave that has baked much of Europe for weeks.

## 2 Experimental

Integrated in the EU project CARBOSOL, during the summer of 2003, atmospheric aerosol samples were collected, continuously, on a weekly basis, on pre-fired quartz fibre filters. Aiming to separate particles into two size fractions (aerodynamic diameter,  $dp < 2.5 \mu\text{m}$  and  $2.5 < dp < 10 \mu\text{m}$ ), a  $\text{PM}_{2.5}$  impactor (*Tisch TE – 231F*) and a  $\text{PM}_{10}$  size selective inlet (*Sierra SSI 1220*) were used. The sampling site was located in Moitinhos, Portugal ( $40^\circ 35' \text{N}$ ;  $8^\circ 38' \text{W}$ ). It represented a rural area, situated 6 km southeast of the small coastal city of Aveiro with approximately 50000 inhabitants. The region is characterised by patches of maritime pine and eucalyptus mixed forests and by small scale



agricultural fields used for horticulture and maize growing. Filter samples were characterised at the University of Aveiro (carbon analyses), Laboratory of Glaciology in Grenoble (inorganic ions), University of Veszprem, Hungary (humic like substances – HULIS), and Technical University of Vienna (levoglucosan, cellulose and water soluble organic carbon – WSOC).

The carbonaceous content was analysed by means of home-made thermal-optical equipment [18, 19]. Controlled heating was performed to separate OC into four fractions of increasing volatility. The first fraction corresponds to the volatilisation at  $T < 150^{\circ}\text{C}$  of lower molecular weight organics (OC1). Second and third fractions are related to decomposition and oxidation of higher molecular weight species at temperatures ranging from  $150\text{--}350^{\circ}\text{C}$  (OC2) and  $350\text{--}600^{\circ}\text{C}$  (OC3), respectively. The last fraction of OC is identified by transmittance and corresponds to pyrolysed organic carbon.

The analytical procedure for the determination of cellulose in atmospheric aerosols was subdivided into three main steps: (i) an alkaline peroxide pre-treatment to improve the enzymatic accessibility by removing parts of hemicellulose and lignin; (ii) enzymatic conversion of cellulose to D-glucose and (ii) photometric detection of D-glucose [20]. The determination of levoglucosan and other sugars was performed by high performance liquid chromatography with an electrochemical detector [21]. For the determination of soluble potassium and its non-sea-salt and non-dust fraction, small parts of the filters were extracted with ultra pure Milli-Q water. The liquid extract was analysed for cations by ion chromatography with conductivity detection, using a Dionex 500 chromatograph. Determination of WSOC included soaking a spot of filter in Milli-Q water. The total carbon contents of the extracted filter spot were analysed by an Astro 2100 TOC analyser in the solid mode [22]. HULIS concentrations were determined by measuring the absorbance of the MilliQ water extracts with a UV-VIS spectrophotometer [25].

### 3 Results and discussion

#### 3.1 Meteorological conditions, air quality and particulate carbonaceous content

The summer of 2003 was one of the hottest on record in Europe. In Portugal, the heat wave fanned the country's worst forest fires in more than 20 years. Air mass back-trajectories computed using the HYSPLIT (Hybrid Single-Particle Lagrangian Integrated Trajectory) model (not shown) indicate continental transport of the smoke from different inland regions of the Iberian Peninsula, depending on the days, to the western coastal sampling site of Moitinhos. Forest fires occurred, in particular, when the atmospheric circulation formed an important ridge associated with south-easterly conditions, and a strong advection of hot and dry air from northern Africa that was additionally heated when passing through central Iberia [24]. Meteorological results obtained for the Aveiro region over periods of large scale forest fires confirm an abrupt increase in the temperature, and a significant drop in the relative humidity records.



Between July 29 and August 13, all districts in Portugal experienced unusually high temperatures. At least 8 of the 18 mainland Portuguese districts had daily maximum temperatures above 32°C during all this period. Four districts, corresponding to the non-coastal interior of Portugal, had daily maximum temperatures above 35°C during the entire interlude (maximum temperature ever registered of 47.6°C in Alentejo). This time interval, and several days after September 11 were the most affected by fire activity. During these episodes, in the Aveiro region, particulate matter levels were elevated 2- to 3-fold above the prior and post smoke baseline periods. However, PM<sub>10</sub> hourly-averaged concentrations reached values higher than 300 µg m<sup>-3</sup>, and even sporadic levels around 500 µg m<sup>-3</sup> at some air quality monitoring stations closest to the forest fire fronts. The results show that the smoke layers and the reduced UV may have lowered the photochemical activity, reducing the ozone produced, during the first few days of the plumes' history (Figure 1).

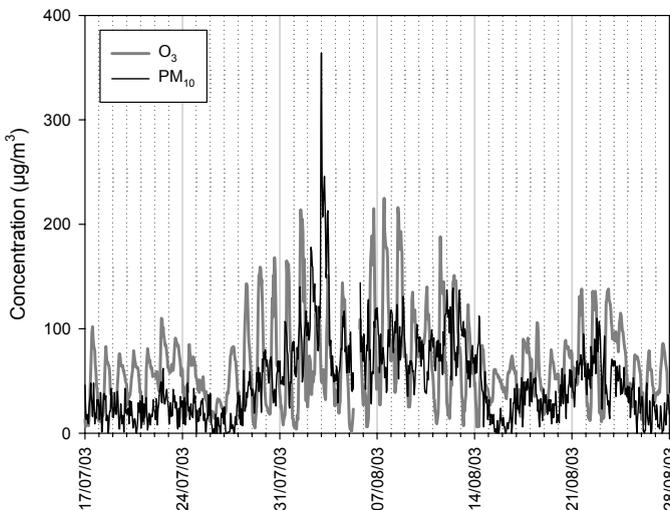


Figure 1: Particulate matter and ozone levels registered in the city of Coimbra, located about 50 km southeast of Moitinhos.

Average weekly PM<sub>10</sub>/PM<sub>2.5</sub> ratios of 1.6 and 1.7 were obtained during the smoke events and for baseline periods before and after the fire episodes, respectively. Comparatively, Ward et al. [13] calculated a ratio of 1.3 during smoke events and of 2.4 for all other days throughout the summer of 2003 in Montana. A PM<sub>10</sub>/PM<sub>2.5</sub> ratio of 1.7 was found in an airshed greatly impacted by residential wood burning with wintry conditions in Libby, Montana [25]. Ratios of 1.5 and 2.0 were measured in Seattle for the heating and non-heating seasons, respectively [26].

Elemental and organic carbon accounted for 17 to 39% of the PM<sub>2.5</sub> mass. The light-absorbing soot-like structures contributed to 12-26% of the carbonaceous material. Compounds that evaporate at lower temperatures

(<150°C) represented 6-10% of OC, indicating that the contribution of semi volatile species to the organic particulate loading is small. Higher molecular weight species evolving above 350°C in the thermograms constituted 12 to 21% of the OC mass. Pyrolysed carbon dominated the OC fraction, signifying 52-63% of its mass (Figure 2). The carbonaceous content in the aerosol from Moitinhos is lower than values obtained with biomass burning aerosols over Amazonia (Graham [7]) and of the same range than levels measured in aerosol samples from the Lower Fraser Valley, Canada, impacted by forest fires [11]. Usually, more OC than EC is emitted by forest fires compared with other anthropogenic sources, resulting in a relatively higher OC/EC ratio during the smoke events.

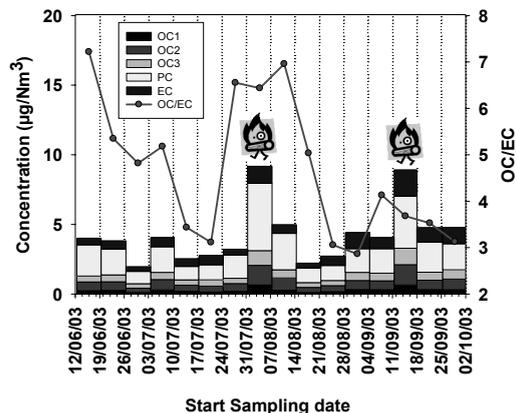


Figure 2: Variation of various carbon fractions and the ratio between organic and elemental carbon.

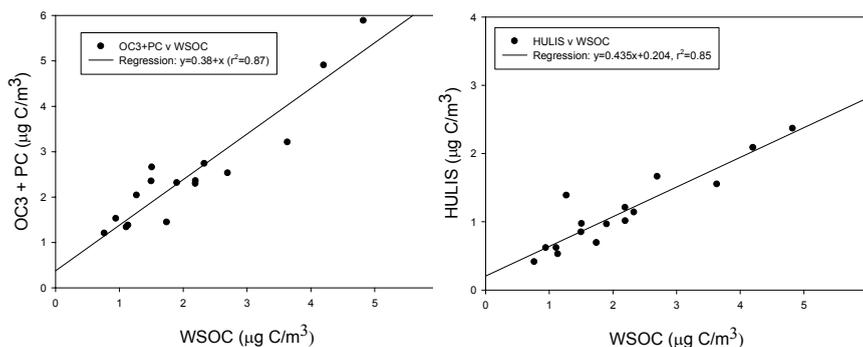


Figure 3: Linear correlations between OC fractions and water soluble organic compounds and between these and humic-like matter.

The WSOC content of the samples represented 43-83% of OC, which indicates the ability of the aerosol particles to act as cloud condensation nuclei and, as a consequence, influence cloudiness and climate. Its variation between

the biomass burning and cleaner periods is considerable, showing concentrations around  $4\text{--}5\ \mu\text{g m}^{-3}$  and less than  $1\ \mu\text{g m}^{-3}$ , respectively. The good correlation between the heavier molecular weight fraction plus pyrolysed carbon (OC3+PC) and WSOC (Figure 3) suggests that the biomass burning aerosol was mainly affected by flaming combustion, which may also have contributed to the water soluble refractory matter (soluble fraction of HULIS).

### 3.2 Anhydrosugars and potassium

Three anhydrosugars (levoglucosan, mannosan and galactosan) were identified in the aerosol samples. Levoglucosan and the related degradation products from cellulose can be utilised as specific and general indicator compounds for the presence of emissions from biomass burning in samples of atmospheric fine particulate matter [27]. These compounds accounted for 1.1-4.0% and 1.3-6.5% of OC and WSOC, respectively. As expected, the anhydrosugars were confined chiefly to the fine fraction, since smoke aerosol consists, for the most part, of accumulation mode particles. Levoglucosan presented levels between a minimum of  $17\ \text{ng m}^{-3}$  and an upper limit of  $105\ \text{ng m}^{-3}$ , which was achieved during a vast wildfire period. Much higher average levels of 1200 and 2500  $\text{ng m}^{-3}$  have been reported for forest and pasture sites, respectively, in 1999, during the burning season in R ndonia (southwest Amazonia) [7]. Cellulose itself experienced an augment in concentrations during the periods of increased smoke plumes, while a slight drop of its contribution to OC is observed at the same time (Figure 4). Cellulose decomposes on heating or on exposure to an ignition source, giving rise to diverse breakdown products [27].

Based on the average value between the OC/levoglucosan ratio of 12.3 measured for the fine dry season aerosol in R ndonia [7] and the ratio of 10.5 obtained for a pine forest fire in southeast USA [28], a smaller than expected contribution (11-36%) of wood combustion to the amount of OC throughout the summer CARBOSOL campaign (Figure 5). Thus, unrealistically, it seems that the major fraction of OC measured in both fine and coarse aerosols during the present study was chiefly related to other primary anthropogenic and biogenic sources, as well secondary formation processes. In spite of a significant raise in OC levels during the two weeks with strongest impact from the forest fire smoke plumes, the levoglucosan concentrations and the estimated contribution of wood burning to OC did not increase as expected. However, if the average levels of OC and levoglucosan measured during the 3 weeks less affected by wildfires are taken as baseline values and if these values are subtracted from the corresponding concentrations during the intense forest fire periods, then an OC/levoglucosan ratio of 80 is obtained. This analysis make evident that the OC/levoglucosan relationships proposed in the literature for deriving the amount of OC from wood or biomass combustion in ambient aerosols should be taken with precaution. Since the ratios are quite variable for different burning conditions and wood types, it has yet to be estimated more specific factors with application to wildfires under extreme weather conditions (dryness and high temperatures) in Mediterranean countries.



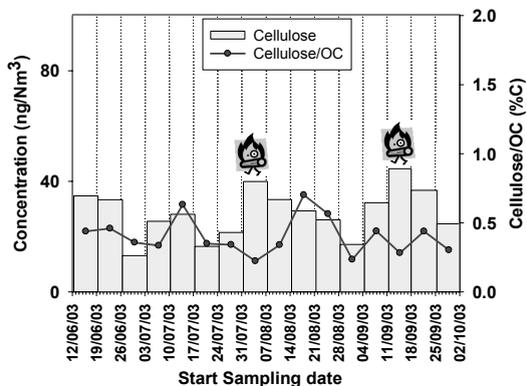


Figure 4: Concentrations of cellulose and its contribution to OC levels in atmospheric aerosols.

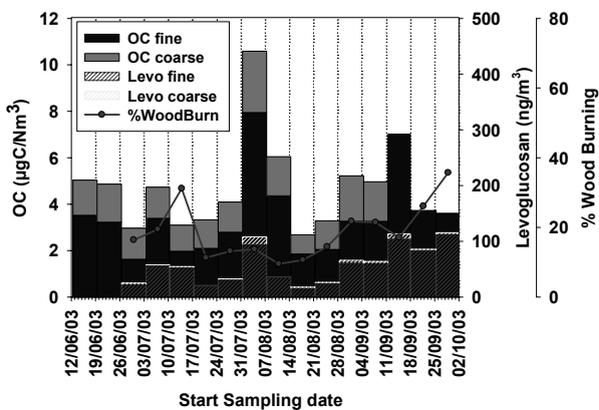


Figure 5: Variation of organic carbon and levoglucosan concentrations in both the fine and coarse aerosol fractions and contribution of smoke particles to the OC content.

It should also be mentioned that the emission of particulate matter constituents is quite different during the main combustion phases: flaming and smoldering [29, 30]. During smoldering combustion or in the initial thermal decomposition large quantities of levoglucosan are formed. During the flaming phase at higher temperatures (>400°C) levoglucosan re-polymerizes into polysaccharides, which then further react to form organic solids containing conjugated double bonds and carbonyl groups, as can be found in HULIS [31]. Another possibility is that some or all the HULIS is just humic matter from soil and/or putrefying leaf litter lofted during combustion [8]. Significant correlations between both HULIS fractions and biomass combustion tracers support the

hypothesis of biomass combustion emissions as precursors for a sizeable fraction of atmospheric HULIS in aerosols from Moitinhos.

Potassium is an important major emission from biomass burning [32]. The fraction of soluble potassium not related to sea-salt and soil dust (K<sub>nsnd</sub>) has been used as a qualitative tracer for biomass combustion [33]. The K<sub>nsnd</sub> was estimated by subtracting, from the soluble potassium determined on bulk aerosol filters, the sea-salt contribution, considering the mass ratio of potassium to sodium in seawater (0.038) and the marine sodium levels [34]. Since the dust material contains leachable potassium, its contribution was also subtracted by using non sea-salt calcium levels and assuming a mean K/Ca ratio of 0.36, which corresponds to the minimum value obtained over a year long period of measurements in the Aveiro region. Based on this estimation, it was found that the fraction of soluble potassium not related to sea-salt and soil dust constituted 38%-85% of the total. The modest correlation between the levoglucosan and K<sub>nsnd</sub> ( $r^2=0.37$ ) and K/levoglucosan ratios up to several units are indicative of additional potassium inputs from other sources. It should be remembered that typical K/levoglucosan ratios reported in the literature for different types of biomass combustion do not exceed 0.5 [21, and references therein]. However, higher relationships have been observed by Schkolnik et al. [30] during a biomass burning experiment in R ndonia. These researchers attributed the higher values to a more extensive oxidation during the biomass burning process. It is also probable that an important part of the potassium found in our atmospheric aerosol derive from soil lofted during combustion. This hypothesis is corroborated by the parallel increment in concentrations of potassium and calcium (a crystal trace element) during forest fires events (Figure 6) and a clear positive correlation between them.

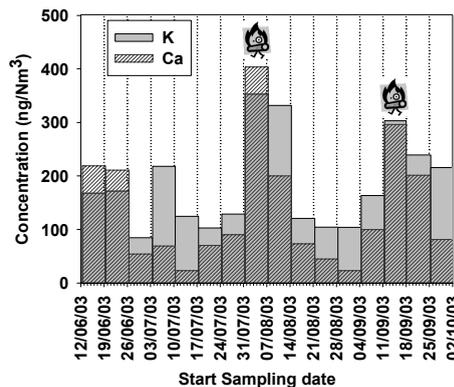


Figure 6: Summer variation in concentrations of potassium and calcium detected in atmospheric aerosols.

### 3.3 Sugars and sugar alcohols

Total sugar alcohol and monosugar concentrations ranged from about 40 to 100 ng m<sup>-3</sup> with maximum level found in a sample less affected by the passage

of the smoke plume from the forest fires. The majority of the sugar polyols identified (arabitol, sorbitol and mannitol) were found to be most prevalent in the coarse fraction. Saccharide alcohols are known components of bacteria, fungi, lichens, invertebrates and lower plants, acting as osmoregulators, stress inhibitors or carbohydrate suppliers [12, 35]. A general lack of correlation with various biomass burning tracers and higher coarse fraction concentrations were taken as indication that these compounds may be part of the natural background aerosol with a likely association with the primary biological particles. An exception should be referred for xylitol, which presented a fine/coarse ratio between 2 and 4 during the weeks of intense forest fires, inverting the proportion over periods with less influence of smoke.

The dominant primary monosaccharides in aerosols from Moitinhos are comprised of glucose, mannose, fructose, arabinose, with minor quantities of galactose. There are several sources of these constituents, including microorganisms, vascular plants and animals [12]. Simoneit et al. [36] suggested soil and associated microbiota as the main source of saccharides to the atmosphere. According to these researchers, all these compounds derive mainly from soil resuspension into the atmosphere, though emissions of considerable amounts may occur by thermal stripping during biomass burning events. Contrarily to the majority of sugar alcohols, the monosaccharide constituents presented higher fine fraction concentrations and a moderate correlation ( $r^2=0.42-075$ ) with levoglucosan. The proportion between the fine and the coarse fraction increases during periods of severe forest fires, indicating an origin from biomass burning. This observation is in accordance with the results presented by Medeiros et al. [12], who registered enrichments by factors of 2-5 in samples collected under the influence of smoke plumes from Quebec forest burning, indicating that wildfires also enhance emissions of uncombusted saccharides. Moreover, good correlations were generally obtained between pairs of sugars within each group, suggesting a common origin. Xylitol constitutes an exception, since it is better correlated with monosaccharides than with other polyols. Thus, microbiota or other primary biological sources may have not contributed to the observed xylitol levels, resulting probably from the forest fire emissions. Curiously, an investigation by Simoneit et al. [36] of the saccharide content of various representative agricultural soils and both paved and unpaved road dusts revealed that glucose was a dominant constituent in samples of all types, while xylitol was only detected in some samples of paved road dust, indicating a different origin than its relative compounds.

## 4 Conclusions

During the wildfire episodes, in the Aveiro region, particulate matter levels were elevated 2- to 3-fold above the prior and post smoke baseline periods. The carbonaceous material accounted for 17 to 39% of the PM<sub>2.5</sub> mass and was noticeably represented by high molecular weight organic matter. Evidence of biomass burning as a significant source is supported by the presence of anhydrosugars and potassium in atmospheric aerosols. On the basis of typical



OC/levoglucosan ratios reported in the literature, it was estimated that smoke particles accounted for 11-36% of the OC content, manifesting a smaller than expected impact. The OC/levoglucosan relationships proposed in the literature for deriving the amount of OC from wood or biomass combustion in ambient aerosols should be taken with precaution. Since the ratios are quite variable for different burning conditions and wood types, it has yet to be estimated more specific factors with application to wildfires under extreme weather conditions in Mediterranean countries. Identical conclusion is achieved when using typical K/levoglucosan ratios. It is probable that part of the potassium (and other elements) found in atmospheric aerosols derives from soil lofted under extreme combustion conditions.

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