

Chemical composition of atmospheric aerosols during the 2003 summer intense forest fire period

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ABSTRACT

In Portugal, during summer 2003, unusually large forested areas (>300,000 ha) were destroyed by fire, emitting pollutants to the atmosphere. During this period, aerosol samples were collected in the Aveiro region, and analysed for total mass and a set of inorganic and organic compounds, including tracers of biomass burning. Comparisons of aerosol size distributions, levels of particulate mass and chemical aerosol composition between heavily smoke-impacted periods and the rest of the summer permit to evaluate the contribution of forest fires to the regional aerosol load. The absolute and relative variability of the particulate inorganic and organic constituents were used to evaluate the importance of wildfires as emission sources responsible for the presence of compounds such as molecular tracers in the summer atmosphere. From organic carbon to levoglucosan or to potassium ratios it was estimated that 40–55% of primary organic carbon could be attributed to wood smoke. The large fraction of secondary organic carbon suggested that forest fires may strongly contribute to gas-to-particle processes. It was found a better correlation of organic carbon with potassium than with levoglucosan, indicating that, during more complete combustive processes, potassium is possibly a more reasonable biomass burning tracer.

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1. Introduction

The major aerosol components include inorganic substances, such as sulphates and carbonaceous species. At the global scale, the major source of primary carbonaceous aerosols is biomass burning, due to forest fires and to the widespread use as fuel for heating homes and cooking (Sapkota et al., 2005; Ward and Smith, 2005; Zheng et al., 2002). Smoke aerosols are able, at least at regional scale, to influence the radiation budget by their light-scattering

effects and their influence on cloud microphysics (e.g. Lyamani et al., 2006). Epidemiological studies have suggested that a substantial part of the causes of mortality (21–38% of the total excess deaths) could be attributed to high ozone and aerosol levels encountered during large forest fire events following a heat wave (Stedman, 2004). In addition, long range transport of smoke particles can lead to redistributions of plant nutrients (e.g. NO_3^- , PO_4^{3-} and K^+), whereas deposition on leaves can affect rates of diffusion of CO_2 and O_2 between plant tissues and the atmosphere (Allen et al., 2004, and references therein).

Several investigations of the contribution of biomass smoke to ambient aerosol levels have been performed over rain forests (e.g., Andreae et al., 2002; Formenti et al., 2003;

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Graham et al., 2002; Mayol-Bracero et al., 2002; Reid et al., 1998; Zdráhal et al., 2002), smoke-impacted areas in North America and Canada (e.g., Leithead et al., 2006; Medeiros et al., 2006; Sapkota et al., 2005; Ward and Smith, 2005; Ward et al., 2006a, b), savanna fires over South Africa and in the aerosol outflow from the Asian continent (e.g., Abas et al., 2004; Novakov et al., 2000; Guazzotti et al., 2003). In Europe, data on detailed characterisation of atmospheric aerosols impacted by open biomass burning are rather rare and mainly from high northern latitudes (Saarikoski et al., 2007; Sillanpää et al., 2005). Because of the specific weather conditions and the greater diversity of vegetation types burned in forest fires, regional differences in smoke-impacted aerosol composition are expected. Accurate quantification of the amounts of particulate constituents emitted from forest fires and other sources of biomass burning on a regional and global scale 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 in quantifying the sources of air pollution that affect human health at regional scales.

In Portugal, it was estimated that, over the last decade, fires have destroyed around 110,000 ha per year of forest, which corresponds to an annual loss of biomass of approximately 400,000 ton (Dias, 2002). Major forest fires raged across the country in 2003. Nearly 400,000 ha of forest land were burnt, with cork and holm oak stands particularly affected. From July 31 to August 14 a total number of 6097 fire occurrences were recorded (MAI, 2003). The total area burned represented almost five times the average of the last two decades. In the framework of the EU CARBOSOL project, aerosol samples were continuously collected at Aveiro from July 1, 2002 to June 17, 2004. The set of aerosol samples collected during the wildfire season of 2003 represents 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

During the summer of 2003, atmospheric aerosol samples were collected, continuously, on a weekly basis, on pre-fired quartz fibre filters. The weekly sampling applied in the CARBOSOL project was not dedicated to the studies of sporadic events. Nevertheless, since in 2003 most wildfires spanned several days, it is possible to compare samples collected during significant smoke events with those obtained during non- or less-impacted periods (Table 1). The description of the full campaign, including detailed justification for sampling and analytical methodologies, can be found in Pio et al. (2007) and accompanying papers published in a special issue of the Journal of Geophysical Research (see Legrand and Puxbaum (2007) for a summary of the project). Here we concentrate on samples collected in 2003 in Portugal, the European country that was the most impacted by forest fires followed by France.

To separate collected particles into two size fractions, aerodynamic diameters (D_p) lower than $2.5 \mu\text{m}$ and $2.5 < D_p < 10 \mu\text{m}$, a $\text{PM}_{2.5}$ impactor (Tisch TE – 231F) and

Table 1
Identification of the sampling periods based on fire activity

Sampling period	Fire activity
June 12–June 19	Moderate fire activity
June 19–June 26	Intense fire activity
June 26–July 03	Low fire activity
July 03–July 10	Low fire activity
July 10–July 17	Baseline period
July 17–July 24	Moderate fire activity
July 24–July 31	Moderate fire activity
July 31–Aug 7	Very intense fire activity
Aug 7–Aug 14	Very intense fire activity
Aug 14–Aug 21	Intense fire activity
Aug 21–Aug 28	Moderate fire activity
Aug 28–Sept 4	Baseline period
Sept 4–Sept 11	Moderate fire activity
Sept 11–Sept 18	Very intense fire activity
Sept 18–Sept 25	Moderate fire activity
Sept 25–Oct 02	Moderate fire activity

a PM_{10} size selective inlet (Sierra SSI 1220) were deployed. The study of the size segregated composition of aerosol was conducted between July 31 and August 7 by using a high-volume sampling device (Sierra-Andersen) and a cascade impactor (Sierra – 235). The sampling site, Moitinhos, in Portugal ($40^{\circ}35' \text{N}$; $8^{\circ}38' \text{W}$), is located in a rural area, 6 km southeast of the small coastal city of Aveiro (50,000 inhabitants), 47 m above sea level. The region is characterised by patches of maritime pine and eucalyptus mixed forests and by small agricultural fields used for horticulture and maize growing.

Filter samples were analysed at the University of Aveiro for elemental and organic carbon (EC and OC, respectively), at the Laboratory of Glaciology in Grenoble for inorganic ions and dicarboxylates, at the University of Pannonia for water-soluble organic carbon (WSOC) and brown carbon that includes light-absorbing organic matter (other than soot) and humic like substances (HULIS), and at the Technical University of Vienna for saccharides (primary sugars, polyols and anhydrosugars) and cellulose.

The carbonaceous content was analysed by using home-made thermal-optical equipment (Castro et al., 1999; Carvalho et al., 2006; Pio et al., 2007). 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 to 350°C (OC2) and 350 to 600°C (OC3), respectively. The last fraction of OC is identified by transmittance and corresponds to pyrolysed organic carbon. The method has been tested with the NIST 8785 filter standard and in an inter-comparison experiment with real aerosol samples (Schmid et al., 2001), giving EC/OC ratios between the NIOSH and the IMPROVE protocols but more similar with the IMPROVE methodology. The analytical procedure for the determination of cellulose in atmospheric aerosols includes three main steps: an alkaline peroxide pre-treatment to improve the enzymatic accessibility by removing parts of hemicellulose and lignin, an enzymatic conversion of total cellulose to D-glucose and a photometric detection of D-glucose

(Puxbaum and Tenze-Kunit, 2003). The determination of levoglucosan, other sugars and polyols was performed by high-performance liquid chromatography with an electrochemical detector (Dionex ED40, pulsed amperometry with gold working electrode). The separation was performed on a high pH anion-exchange column for sugar analysis (Dionex CarboPac PA1, 250 × 4 mm) (Caseiro et al., 2007; Puxbaum et al., 2007). The filter aliquot to be analysed (about 4.5 cm² from a quartz fibre filter from a high-volume sampler) was extracted in 3 mL of Milli-Q water by ultrasonic bath agitation for 45 min. Undissolved sample material and filter debris were removed from the sample solution by centrifugation (3 min at 13.4 × 103 rpm) and in-line filtration (35 and 5 µm, Dionex®) prior to injection.

Apart from minimising the time between extraction and analysis (24 h at most) and keeping the extracts in closed recipients, no additional steps to prevent losses were taken. However, reproducibility studies over typical analysis run time showed no significant differences in the concentrations detected (see Caseiro et al., 2007).

For the determination of soluble inorganic ions and dicarboxylates, small parts of the filters were extracted with ultra pure Milli-Q water. For cations, a Dionex 500 chromatograph equipped with a CS12 separator column was used. For anions, a Dionex 600 equipped with an AS11 separator column was run with a quaternary gradient of eluents (H₂O, NaOH at 2.5 and 100 mM, and CH₃OH). As detailed in Legrand et al. (2007), these working conditions allow the determination of inorganic anions as well as C2–C5 dicarboxylates oxalate (–OOC(=O)–), malonate (–OOCCH₂COO–), succinate (–OOC(CH₂)₂COO–), malate (–OOCCH₂CHOHCOO–), tartarate (–OOC(CHOH)₂COO–), and glutarate (–OOC(CH₂)₃COO–), hereafter also referred as diacids. Determination of water-soluble organic carbon (WSOC) included soaking a spot of filter in 25 mL of Milli-Q water for 2 h. The total carbon contents of the extracted filter spot, as well as of a non-extracted spot of identical size, were analysed by an Astro 2100 TOC analyser in the solid mode. The determination involved catalytic burning at 680 °C in O₂, followed by non-dispersive infra-red detection of the evolved CO₂ (Varga et al., 2001). Brown carbon concentrations were determined by measuring absorbance of the Milli-Q water extracts with a UV-VIS spectrophotometer at the wavelengths of 250 and 350 nm (Lukács et al., 2007).

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 (Draxler and Hess, 1997) and satellite images (Fig. 1) indicate continental transport of the smoke from different inland regions of the Iberian Peninsula 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 flow, and a strong advection of hot and dry air from northern Africa that was additionally heated when passing over central Iberia (Pereira et al., 2005). Meteorological data for the Aveiro region over the 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 continuously experienced daily maximum temperatures above 32 °C during this period. Four districts located inland Portugal experienced daily maximum temperatures above 35 °C during this period (the highest temperature ever registered in Portugal of 47.6 °C in Alentejo). This period and several days after September 11 were the most affected by fire activity (Table 1).

During these episodes, in the Aveiro region, particulate matter levels were elevated 2- to 3-fold above the prior and post smoke baseline periods of ~30 µg m⁻³ (Fig. 2). PM₁₀ hourly-averaged concentrations reached values higher than 300 µg m⁻³, and sometimes 500 µg m⁻³ at some air quality monitoring stations closer to the forest fire fronts. As seen in Fig. 2, the smoke layers and the reduced solar radiation may have lowered the photochemical activity, reducing the ozone produced, during the first few days of the plumes' history. The O₃ production in the boundary layer may also be hindered by UV-B absorption by aerosols. It was calculated that soot particles and mineral dusts can reduce the O₃ photolysis rate by 6–11% (Liao et al., 1999).

Average weekly PM₁₀/PM_{2.5} ratios of 1.6 and 1.7 were observed during the smoke events and the baseline periods, respectively. In general, previous studies suggested that forest fires produce mainly fine-mode particles. For instance, Ward et al. (2006a) calculated a ratio of 1.3 during smoke events and a value of 2.4 for all other days throughout the summer of 2003 in Montana. A PM₁₀/PM_{2.5} ratio of 1.7 was found in an airshed greatly impacted by residential wood burning with wintry conditions in Libby, Montana (Ward et al., 2006b). Ratios of 1.5 and 2.0 were measured in Seattle for the heating and non-heating seasons, respectively (Liu et al., 2003). For wildfires in 2003 in Portugal the decrease in the PM₁₀/PM_{2.5} ratios was not as high as expected during extreme burning events. This is probably due to a co-emission of coarse particles composed by ash, partially burned foliage and lofted soil particles, which are entrained by the turbulent nature of the uncontrolled high-intensity fires under extreme drought conditions. It is also possible that emitted smaller particles have been scavenged by coagulation with larger particles in the smoke plume (Phuleria et al., 2005).

On average, the carbonaceous material accounted for 28 ± 8% of the PM_{2.5} mass. Excepting for the week of August 7–August 14, during which PM_{2.5} had a great contribution from inorganic constituents, the carbonaceous fraction was rather high (up to 43%) throughout very intense fire periods. The PM_{2.5} sample that was not dominated by carbon during the week ended August 14 may have had the contribution of intense fires closest to the sampling site, which promoted lofting of dust and ashes. A white deposit layer of ashes was observed over

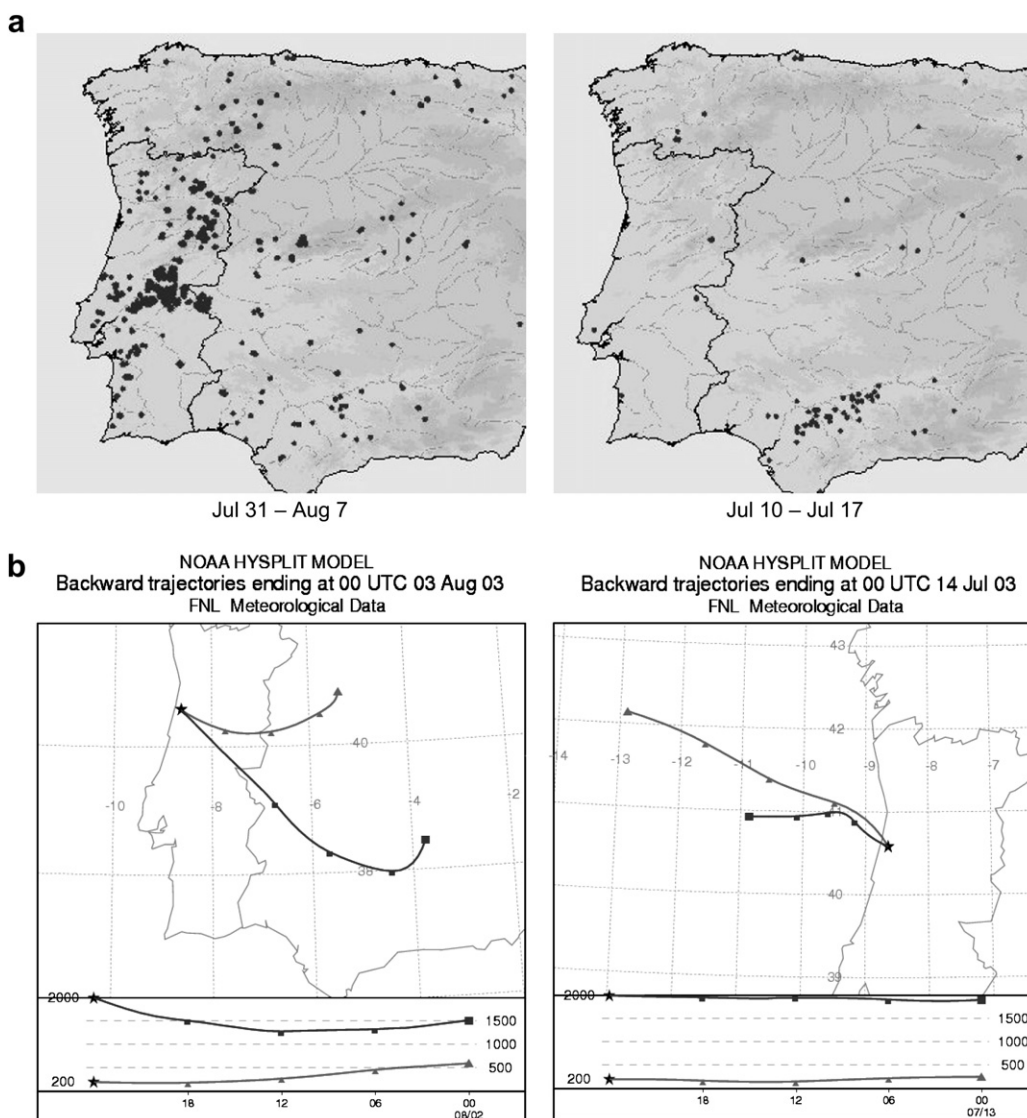


Fig. 1. (a) Web hotspot/fire maps (NASA/University of Maryland, 2002) taken on the event of greatest smoke and during a cleaner period; (b) one day back-trajectories of air parcels ending at Moitinhos from the HYSPLIT model.

ground surface at the sampling site as result of atmospheric transport and dry deposition during the most intensive fire period. The carbonaceous content in the aerosol from Moitinhos is lower than values obtained in biomass burning aerosols over Amazonia (Graham et al., 2002) and in the same range than that in aerosol samples from the Lower Fraser Valley, Canada, impacted by forest fires (Leithead et al., 2006).

The light-absorbing soot-like structures (EC) contributed to 12–26% of the particulate carbon content. 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 (Gelencsér et al., 2007; Watson et al., 2001). As seen in Fig. 3, the OC/EC ratio was consistently lower (~ 3) for baseline periods than over large smoke events (up to 7).

The OC concentrations changed from a mean baseline level of 2.6 to $6.4 \mu\text{g m}^{-3}$ in samples strongly impacted by smoke, which represents an increase of about 60% (Table 2). Compounds that evaporate during analysis at lower temperatures ($<150^\circ\text{C}$) represented 6–10% of OC, indicating that the contribution of semi-volatile species to the organic particulate loading is small regardless of the considered time period. Higher molecular weight species, or highly substituted low molecular weight constituents, evolving above 350°C in the thermogram constituted 12–21% of the OC mass. Pyrolysed carbon dominated the OC fraction (52–63% of OC, Fig. 3). Its average contribution to OC increased from 50% during baseline periods to 57% for the weeks more impacted by smoke plumes. Comparison between concentrations measured during the two periods of more intense fires and those obtained for the two

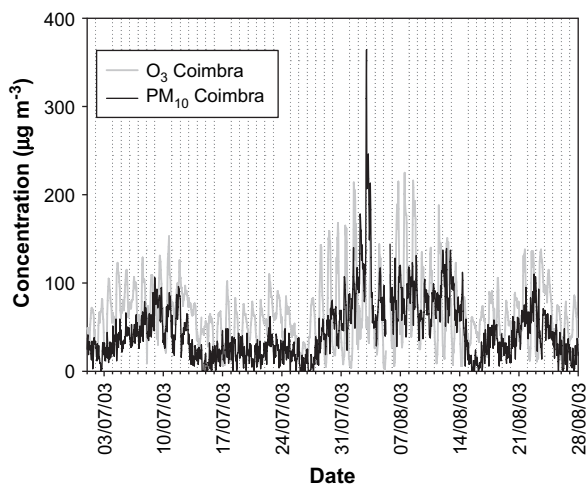


Fig. 2. Particulate matter and ozone levels recorded in the city of Coimbra, located about 50 km southeast of Moitinhos (Aveiro).

baseline weeks reveals increases of 45, 46, 48 and 44% in the OC1, OC2, OC3 and PC values, respectively.

During the 16-week sampling period, the WSOC content of the samples represented 43–83% of OC, which indicates the ability of aerosol to act as cloud condensation nuclei and, as a consequence, influence cloud physics and climate. Its variation between the biomass burning and cleaner periods is very significant, 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 higher molecular weight fraction plus pyrolysed carbon (OC3+PC) and WSOC (Fig. 4) suggests that the biomass burning aerosol may have contributed to the water-soluble refractory matter (soluble fraction of brown carbon). However, WSOC is also positively correlated with other OC fractions, which also increase in fire periods. Thus, it seems that there is no absolutely specific link between WSOC and soluble refractory matter.

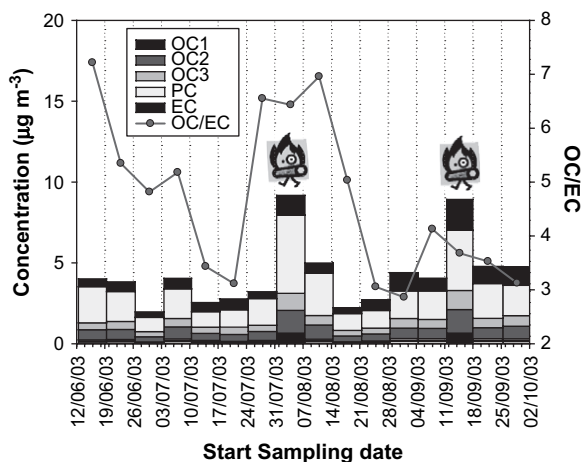


Fig. 3. Variations of various carbon fractions and of the ratio between organic and elemental carbon.

The size distribution of aerosol collected during the week of more intense forest fires (Fig. 5a) showed that the WSOC was concentrated in the $0.49\text{--}1.5\ \mu\text{m}$ size range, though a small mode skewed towards the larger size was also observed. This additional mode may be related with aging processes of the smoke aerosol.

3.2. Anhydrosugars and cellulose

Three anhydrosugars (levoglucosan, mannosan and galactosan) were identified in aerosol samples, showing high correlations with each other. Levoglucosan and the related degradation products from cellulose and hemicelluloses can be used as specific and overall indicator compounds for emissions from biomass burning (Simoneit et al., 1999). These compounds accounted for 0.8–4.0% and 1.3–6.5% of OC and WSOC, respectively, over the entire study period. Their total concentrations were in the range $130\text{--}145\ \text{ng m}^{-3}$ during the periods of peak smoke impact, decreasing to values between 20 and $85\ \text{ng m}^{-3}$ over the remaining weeks. Levoglucosan levels varied from a minimum of $17\ \text{ng m}^{-3}$ to a maximum of $105\ \text{ng m}^{-3}$, corresponding to the vast wildfire period. The average ratio of levoglucosan to mannosan was found to be 3.5 ± 0.8 . The ratio of levoglucosan to mannosan in wood smoke is different for deciduous and conifer trees, being on average 25 and 4.7 in US-studies (Fine et al., 2004, and related papers by the same authors), and around 15 and 3.7 in a mid-European study (Schmidl et al., 2008), respectively. The composition of the Portuguese aerosol is consistent with a greater input of coniferous than deciduous wood combustion.

As expected, the anhydrosugars were mainly present in the fine fraction (Fig. 5b), since smoke aerosol consists, for the most part, of accumulation mode particles (Schkolnik et al., 2005). On average, the $\text{PM}_{2.5}$ fraction contained 97% of the levoglucosan PM_{10} mass concentration. Interestingly, the size distribution of levoglucosan also exhibited a coarser peak probably due to ejection of levoglucosan containing-particles from the surfaces of plants and ground (e.g. soil, uncompleted burned vegetation detritus, ash, etc.) as a consequence of the strong turbulence associated with the very intensive combustion of these fires. In combustion experiments, Engling et al. (2006) also found the majority of the levoglucosan mass in the accumulation mode, although the anhydrosugar was also present in the coarse-particle fraction for some fuel types. The mass concentrations in the upper size classes were observed to be slightly higher for duff than for sage brush and oak wood. On the other hand, it is known that levoglucosan emissions vary greatly with burning conditions, but the impact of smouldering versus flaming conditions on size distribution is unsolved (Gao et al., 2003; Schkolnik et al., 2005). During smouldering combustion, or in the initial thermal decomposition, large quantities of levoglucosan are formed. During the flaming phase at higher temperatures ($>400\ ^\circ\text{C}$) levoglucosan re-polymerises into polysaccharides, which then further react to form organic solids containing conjugated double bonds and carbonyl groups, as can be found in HULIS (Kawamoto et al., 2003). Another possibility is that some or all the HULIS is just humic matter

Table 2

Averaged levels of PM_{2.5}, carbonaceous constituents, potassium related to biomass burning (see text) and anhydrosugars, and concentration range for diacids, during baseline conditions and very intense fires

	Baseline periods	Very intense fires	Fire input
PM _{2.5} (μg m ⁻³)	18.4	38.1	19.7
Total carbon (μg m ⁻³)	3.5	7.7	4.2
OC (μg m ⁻³)	2.6	6.4	3.8
EC (μg m ⁻³)	0.86	1.26	0.40
WSOC (μg m ⁻³)	1.6	4.2	2.6
Brown carbon (μg m ⁻³)	1.8	4.0	2.2
Cellulose (ng m ⁻³)	22.6	39.3	16.7
Diacids (ng m ⁻³)			
C5	11 ± 1 (13%)	39 ± 10 (19%)	27.8 (22%)
DhC4	1.3 ± 0.3 (1.5%)	7.5 ± 3.8 (3.6%)	6.2 (5%)
hC4	27 ± 5 (32%)	61 ± 14 (29%)	33.7 (27%)
C4	14 ± 1 (17%)	42 ± 11 (20%)	27.2 (22%)
C3	30 ± 5 (36%)	60 ± 15 (29%)	29.5 (23%)
C2	303 ± 75	611 ± 175	308
Mannosan (ng m ⁻³)	17.6	20.6	3.0
Levoglucosan (ng m ⁻³)	58	79	21
K _{BB} (ng m ⁻³)	102	285	182

The last column, obtained by subtracting baseline conditions from fire conditions, refers to the composition of the ambient aerosol strongly influenced by wildfire smoke. For C5–C3, values in parenthesis refer to the percentage of individual diacid to the sum of C3–C5 diacids. C2 is oxalic, C3 malonic, DhC4 tartaric, hC4 malic, C4 succinic, and C5 glutaric acid.

from soil and/or putrefying leaf litter lofted during combustion (Mayol-Bracero et al., 2002). Significant correlations between both brown carbon and biomass combustion tracers (not shown) support the hypothesis of biomass combustion emissions as precursors for a sizeable fraction of atmospheric HULIS in aerosols from Moitinhos.

Cellulose itself experienced somewhat enhanced concentrations during the periods of fire activity (Table 2), whereas a slight drop of its contribution to OC was observed at the same time. Cellulose decomposes on heating or on exposure to an ignition source, giving rise to diverse breakdown products, such as anhydrosugars (Simoneit et al., 1999). In wood combustion experiments also only low concentrations of cellulose were observed, i.e. around 1/100 of the levoglucosan value (Schmidl et al., 2008).

3.3. Monosugars and sugar alcohols

The terms “monosaccharides” and “monosugars” are going to be used interchangeably throughout the paper to refer to this class of compounds. In the same manner, the terms “sugar alcohols” and “polyols” will henceforth be considered as synonyms. Total sugar alcohol and monosugar concentrations ranged from about 40 to 100 ng m⁻³, with the maximum level found in a sample less affected by the smoke plumes. In general, sugar alcohols were found to be most prevalent in the coarse fraction (Table 3). Polyols are known components of bacteria, fungi, lichens, invertebrates and lower plants, acting as osmoregulators, stress inhibitors or carbohydrate suppliers (Graham et al., 2003; Medeiros et al., 2006). 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 primary biological particles, e.g. from fungal spores (Bauer et al., 2002, 2008). Xylitol is better correlated with monosaccharides than with other polyols and presents 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. This polyol was also detected in smoke aerosols from savanna fires by Gao et al. (2003). These researchers considered that xylitol may be a secondary species produced during the upward transport of aerosols, though the possibility that it constitutes a primary emission from biomass burning was not excluded.

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 (Medeiros et al., 2006). Simoneit et al. (2004) suggested soil and associated microbiota as the main source of saccharides to the atmosphere. According to these findings, the primary sugars derive from soil resuspension and from biogenic emissions into the atmosphere, though emissions of considerable amounts may occur by thermal stripping during biomass

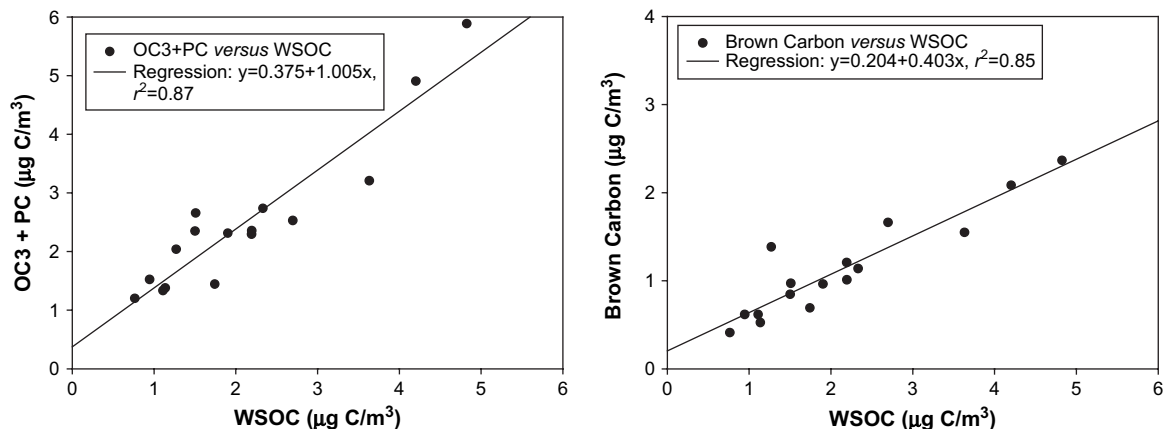


Fig. 4. Linear correlations between OC fractions and water-soluble organic compounds and between these and brown carbon.

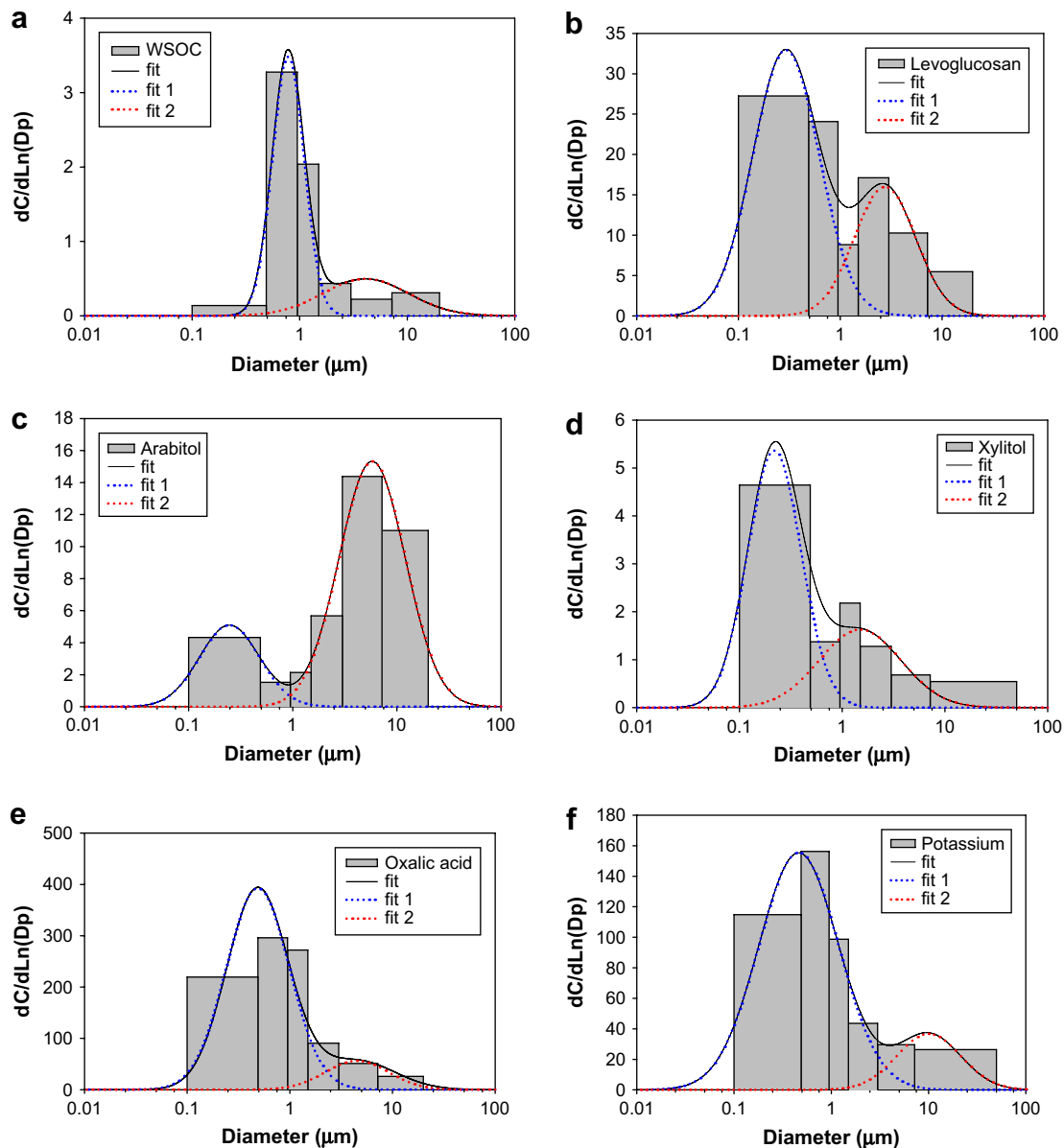


Fig. 5. Size segregated distributions of selected compounds in an aerosol sample strongly impacted by smoke from wildfires. Two-mode Lognormal curves that best-fit the experimental data are also shown.

burning events. Contrarily to the majority of sugar alcohols, the monosaccharide constituents presented higher fine fraction concentrations and a moderate correlation ($r^2 = 0.42\text{--}0.75$) with levoglucosan. The proportion between the fine and the coarse fraction increases during periods of severe forest fires, indicating an origin from biomass burning (Graham et al., 2002; Medeiros et al., 2006). In fact, it is possible that a number of these constituents are primary products, formed either through direct volatilisation from plant materials or as breakdown products of polysaccharides. Another formation pathway is the hydrolysis of the parent anhydrosugars under the acidic atmospheric conditions resulting from biomass burning

(Graham et al., 2002). The observation of higher sugar concentration ratios between the fine and the coarse aerosol sizes is in accordance with the results presented by Medeiros et al. (2006), 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.

The size-distributed sample taken during the week of more intense forest fires showed that polyols predominate in particles $>3\ \mu\text{m}$, suggesting that these compounds are

Table 3

Mass concentrations (range and average) of sugar alcohols, monosaccharides, dicarboxylic acids and inorganic ions in fine and coarse PM samples

	PM _{2.5} (ng m ⁻³)	PM _{2.5-10} (ng m ⁻³)	Fine/coarse ratios
Sugar alcohols			
Xylitol	0.30–3.74 (0.92)	0.44–1.90 (1.02)	0.24–4.83
Sorbitol	LOD–2.11 (0.47)	0.84–6.88 (2.43)	n.d.
Mannitol	0.98–13.93 (7.82)	5.90–21.57 (12.01)	0.17–0.95
Arabitol	1.54–11.41 (5.20)	9.82–27.25 (16.73)	0.12–0.72
Monosaccharides			
Glucose	1.78–13.04 (5.59)	1.21–6.12 (2.80)	0.78–4.65
Mannose	1.25–8.25 (4.12)	0.25–1.33 (0.58)	2.77–23.16
Fructose	2.03–8.45 (3.88)	0.30–3.26 (1.26)	n.d.
Arabinose	0.95–3.72 (2.27)	0.15–0.92 (0.46)	1.96–10.33
Galactose	0.27–1.60 (0.78)	0.08–0.79 (0.31)	1.05–15.05
Diacids			
Glutarate (C ₅)	2.0–47.5 (14.9)	0.3–2.0 (0.9)	7.4–57.0
Succinate (C ₄)	2.7–54.6 (19.1)	1.2–7.0 (2.7)	1.2–35.0
Malate (hC ₄)	5.1–76.8 (30.3)	0.6–4.0 (1.9)	8.4–34.2
Tartarate (dhC ₄)	0.3–10.4 (3.2)	LOD–0.8 (0.2)	3.5–58.0
Malonate (C ₃)	6.8–73.4 (31.3)	2.5–18.9 (8.4)	1.3–5.6
Oxalate (C ₂)	180.2–782.8 (359.5)	10.0–22.6 (17.3)	10.7–41.5
Ions			
SO ₄ ²⁻	2289–12,980 (5293)	135–1768 (885)	11.9–39.4
NH ₄ ⁺	608–4098 (1821)	0.2–23 (6.4)	120–6841
NO ₃ ⁻	71–1236 (401)	286–1450 (706)	0.08–3.07
Na ⁺	157–719 (372)	119–784 (502)	0.39–2.36
K ⁺	85–353 (183)	8–33 (22)	3.76–27.8
Ca ²⁺	45–404 (151)	74–414 (181)	0.32–1.95
Mg ²⁺	28–93 (53)	33–136 (83)	0.29–1.38
Cl ⁻	6–75 (29)	106–1768 (885)	0.01–0.71

LOD, limit of detection; n.d., not determined (not present in a significant number of PM_{2.5} or PM_{2.5-10} samples).

associated with primary biological material (Fig. 5c). Xylitol constitutes an exception, presenting a mass distribution that peaks for diameters smaller than 0.49 μm, as observed for the anhydrosugars (Fig. 5d). These small sizes resulted most likely from nucleation/condensation mechanisms of thermal decomposition products of biomass. Another mode was present for compounds in particles with diameters between 0.95 and 3 μm as a probable result of condensation on the surface of the pre-existing particles.

3.4. Dicarboxylates

Short chain dicarboxylic acids have been identified as ubiquitous aerosol components, which may have a primary origin from fossil fuel, biogenic sources or biomass combustion, or be formed in the atmosphere by photochemical reactions (Graham et al., 2002). The budget of these species was reviewed by Legrand et al. (2007) on the basis of their climatology established during the CARBOSOL project. It was shown that, in winter, European surface sites are influenced by fast production of C₂–C₅ diacids in wood burning plumes, and secondary aqueous phase production of oxalic acid from aldehydes formed by the rapid oxidation of toluene and ethene emitted by cars. Whereas C₃–C₅ diacids seem to come mainly from wood burning plumes, it was suggested that around two-thirds of C₂ are related to this source and one-third of C₂ to secondary production

from toluene and ethene vehicular emissions. In summer, the contribution of these anthropogenic processes is weakened but the contribution of biogenic emissions becomes important. It was suggested that 30–40% of C₂ are related to aqueous production from biogenic precursors (isoprene and acetic acid emitted by vegetation). The presence of C₃–C₅ diacids and of the left fraction of oxalic acid is less clear, likely related to other biogenic precursors (unsaturated fatty acids and oxygenated volatile organic compounds).

All diacids are mainly present in PM_{2.5} (Table 3; Fig. 5e), indicating that primary biogenic sources (e.g. fungi) mainly emitting coarse particles are insignificant and pointing out the secondary nature of diacids. The lowest partitioning ratios between the fine and the coarse fractions were obtained for malonic acid. This specie is more volatile than other diacids and can be transferred from fine to coarse sizes through evaporation and condensation onto larger particles.

The changing concentration of diacids between strongly impacted and baseline time periods reported in Table 2 clearly indicates that diacids were either emitted by fires or subsequently produced during aging of the plumes. Oxalic acid has been suggested to be formed in the atmosphere as a secondary product by the oxidation of aromatic hydrocarbons, which are known to be emitted during wildfires (Narukawa et al., 1999). It is also likely that other diacids are formed in the hazy atmosphere by gas-to-particle conversion of the volatile hydrocarbons emitted during forest fires (Narukawa et al., 1999; Gao et al., 2003). Graham et al. (2002) and Gao et al. (2003) have proposed a probable formation pathway of C₅–C₃ related to the breakdown of cellulose, hemicellulose and lignin. Considering aerosol samples collected at Aveiro in summers 2002 and 2003 over time periods during which no significant fires had taken place we found a y-intercept of the linear relationship between C₂ and C₃ of 124 ng m⁻³ (i.e. 40% of C₂). That suggests that for summertime period non-impacted by fires 40% of C₂ are not related to the oxidation of glyoxylic acid but to longer chain diacids. Doing the same for aerosols collected during fires the y-intercept remains similar (127 ng m⁻³), suggesting that most of C₂ produced by fires are related to aqueous phase oxidation of longer chain diacids.

As far as we know the most complete data set on C₂–C₅ diacids in wood burning plumes is from Gao et al. (2003) on savanna fires. Using potassium to account for the dilution of the plumes, Gao et al. (2003) showed that the concentrations of glutaric, succinic and oxalic acids strongly increased after 40 min of aging. For instance the glutarate to potassium ratio, close to 1% reached 15% after 40 min. A similar increase was observed for the oxalate to potassium ratio, 2% over the fire and 25% after 40 min. The chemical composition of the material related to the large smoke events at Aveiro indicates an oxalate to potassium ratio of 240% and a glutarate to potassium ratio of 20%. The rather high oxalate to potassium ratio seen in smoke reaching Aveiro suggests that during the transport of the plumes oxalic acid was formed from longer chain diacids. Even higher enrichment of diacids with respect to potassium has been observed in long range transported (a few days)

boreal wildfire smokes in summer with ratios of oxalate to potassium of 1000% (Sillanpää et al., 2005). In the case of Aveiro the aging of smoke plume was likely shorter (a day) as suggested by back-trajectories (Fig. 1).

Comparing the baseline and the peak fire periods (Table 2), it was observed that the increase of diacids was larger for long chain diacids (glutaric and C4) than for C3 and C2. C5 represents 19% of the C3–C5 total during fire events instead of 13% for baseline conditions. At the opposite C3 represents only 29% of the C3–C5 total during fire events instead of 36% for baseline conditions. This may suggest that, in addition to the aging of several plumes, the air mass was replenished with a fresh plume a few hours before its arrival at Aveiro. Gao et al. (2003) pointed out the singularity of malonic acid with respect to other diacids, being most of the time absent from the smoke plumes. That is not the case at Aveiro. Reversely, malonic acid was found to be the most abundant C3–C5 diacids emitted by pine wood burning (Rogge et al., 1998).

3.5. Inorganic ions

In this study, eight major water-soluble inorganic species were quantified (SO_4^{2-} , NH_4^+ , Cl^- , NO_3^- , Na^+ , K^+ , Ca^{2+} , and Mg^{2+}), of which SO_4^{2-} was the most abundant ion, followed by NH_4^+ and NO_3^- (Table 3). The mass concentrations of NO_3^- , SO_4^{2-} and NH_4^+ , i.e. typical species for inorganic secondary aerosols, reached their highest values during the intense fire events between July 31 and August 13. During this period, the fine/coarse ratios of these species increased by a factor of 2–4. In particular, sulphate peaked between August 7 and August 14 ($\sim 13 \mu\text{g m}^{-3}$), during the second week of intense fires, but showed a rather low value between September 11 and September 18 ($\sim 4 \mu\text{g m}^{-3}$), also a period of very intense fire activities. Therefore, the influence of fires on sulphate concentrations appears quite unclear. The study of the water-soluble components in aerosols from savanna fires by Gao et al. (2003) pointed out a rather very moderate impact for sulphate in plumes (median $10.5 \mu\text{g m}^{-3}$, range 1.5–35 $\mu\text{g m}^{-3}$) compared to background conditions (median $2.5 \mu\text{g m}^{-3}$, range 1–9 $\mu\text{g m}^{-3}$), although it was clear that SO_2 was emitted in substantial quantities.

Potassium is an important species emitted by biomass burning, since the combustion of plant matter, which contains K^+ as a major electrolyte within the cytoplasm, releases great quantities of K-rich particles. Biomass burning aerosols can be identified by the ratio of fine to coarse mode K^+ . The enrichment of K^+ in the fine mode was obvious during the intense forest fire periods (fine/coarse ratio of 14, instead of 4 for baseline periods) (Figs. 5f and 6). Contrarily to calcium, potassium is an easily volatilised element (Ca boiling point – 1484 °C; K boiling point – 759 °C). Thus, during the cooling of combustion emissions, potassium would condense on pre-existing particles in the accumulation size mode. The fraction of soluble potassium not related to sea-salt and soil dust has been used as a qualitative tracer for biomass combustion (Cachier et al., 1991). In an attempt to estimate the fraction of potassium related to biomass burning (K_{BB}^+), the sea-salt contribution was subtracted from the soluble potassium in fine aerosol

particles, considering the mass ratio of potassium to sodium in seawater (0.036) and the marine sodium levels (Pio et al., 2007). Since the dust material may contain leachable potassium, its contribution was also subtracted by using non sea-salt calcium levels and assuming a mean crustal $\text{K}^+/\text{Ca}^{2+}$ ratio of 0.12 as proposed by Pio et al. (2007) using the slope of the lower envelope of the relationship found between K_{nss}^+ and $\text{Ca}_{\text{nss}}^{2+}$ for concentration observed over 2 years in different CARBOSOL sites. In addition, since biomass burning may also emit calcium, its contribution should be subtracted, as follows, when calculating K_{BB}^+ :

$$K_{\text{BB}}^+ = K^+ - 0.036\text{Na}^+ - 0.12(\text{Ca}_{\text{nss}}^{2+} - \text{Ca}_{\text{BB}}^{2+}) \quad (1)$$

For deriving $\text{Ca}_{\text{BB}}^{2+}$, a mass ratio of 10 between K_{BB}^+ and $\text{Ca}_{\text{BB}}^{2+}$ was assumed. This ratio corresponds to the upper envelope (i.e. the maximum possible ratio) in the relationship between K_{nss}^+ and $\text{Ca}_{\text{nss}}^{2+}$ observed over the summer period. Since primary organic aerosol emission from biomass burning was found to represent the greatest single contributor to aerosol OC in winter over rural Europe (Gelencsér et al., 2007), the relationships between K_{nss}^+ and $\text{Ca}_{\text{nss}}^{2+}$ were also examined for the entire (winter and summer) data sets from Aveiro and other CARBOSOL sites (as well as for results gained in other studies carried out in Portugal - unpublished data), in order to evaluate the range of the upper envelopes. Whatever the considered data set, the upper envelopes of the relationship indicate potassium to calcium mass ratios ranging between 8 and 12, suggesting that a $K_{\text{BB}}^+/\text{Ca}_{\text{BB}}^{2+}$ value of 10 is reasonable.

Eq. (1) applied to periods with very intense fires and baseline periods can be used to calculate, by difference, fire inputs (see Table 2). The airborne particulate matter related to the most important fire inputs contained around 182 ng m^{-3} of fine potassium against 21 ng m^{-3} of levoglucosan. For savannah forest fires, Gao et al. (2003) found a potassium/levoglucosan ratio of 33.3 during flaming phase and from 0.2 to 0.6 for smouldering phase. The relatively high $K_{\text{BB}}^+/\text{levoglucosan}$ ratio over the fire period at Aveiro (8.7) tends to indicate the flaming character of the fires. The significant presence of a coarse and fine fraction of calcium in aerosol collected at Aveiro during fires also supports their flaming character, resulting probably from lofting of dust and soil by hot turbulent air. Comparatively, much lower $K_{\text{BB}}^+/\text{levoglucosan}$ ratios (less than 1) were obtained during the winter period, whether in Aveiro or K-puzsta on the Great Hungarian Plain, another CARBOSOL site also impacted by domestic wood burning in the cold season (see Fig. 7). Ratios lower than 0.25 and 0.1 have been obtained for $\text{PM}_{2.5}$ emissions for wood stove combustion of prevalent USA tree species (Fine et al., 2004) and prescribed burning in an USA pine forest (Lee et al., 2005), respectively. The variability of this ratio for distinct biomass combustion types stresses the need for further investigations to obtain more source-specific emission ratios.

3.6. Estimation of OC from biomass burning

Based on the average value between the OC/levoglucosan ratio of 12.3 measured for the fine dry season aerosol in Rondônia (Graham et al., 2002) and the ratio of 10.5

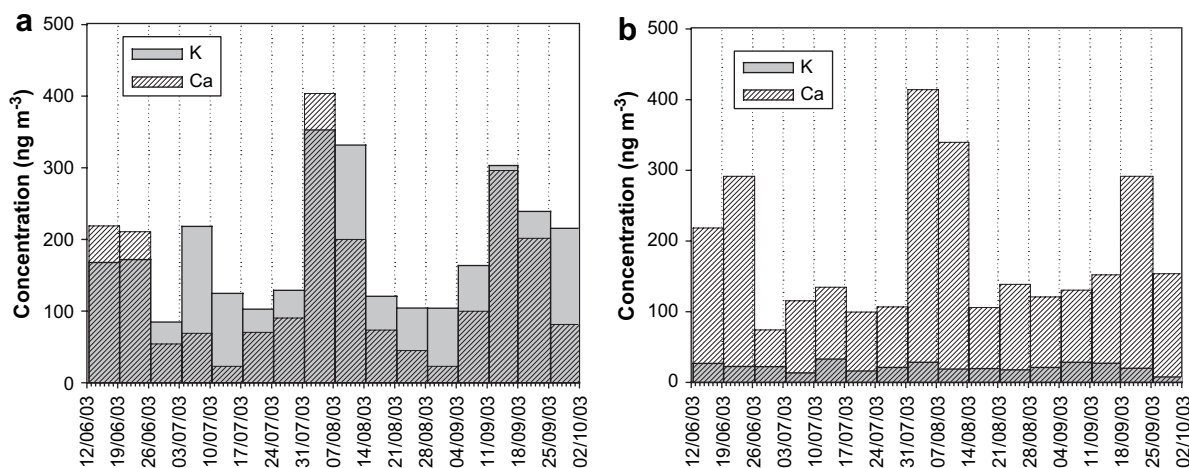


Fig. 6. Levels of potassium and calcium detected in the summer of 2003: (a) $\text{PM}_{2.5}$ and (b) $\text{PM}_{2.5-10}$.

obtained for a pine forest fire in southeast USA (Lee et al., 2005), a smaller than expected contribution (11–36%) of primary OC emissions from biomass combustion to the amount of OC throughout the summer Aveiro CARBOSOL campaign is obtained (Fig. 8). Despite 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. Thus, it seems that, in addition to biomass burning, a considerable fraction of OC measured in aerosols during the present study was also associated with other primary sources, as well as with secondary formation processes. However, it should be noted that the OC/levoglucosan relationships from studies (e.g. Rondônia and southeast US) for deriving the amount of OC from wood or biomass combustion in ambient aerosols are probably not appropriate for the wildfire conditions encountered in Portugal. Since the ratios are quite variable for different burning conditions and wood types, more specific factors with application to wildfires under extreme weather conditions (dryness and high temperatures), and Mediterranean vegetation need to be investigated. Our observation is consistent with the results presented by Jordan et al. (2006), who obtained a smaller than expected levoglucosan mass fraction in particulate matter (e.g. around 9 mg g^{-1} levoglucosan in PM_{10}) generated by bushfires in Australia.

To roughly estimate the OC derived from biomass burning, the carbonaceous fraction was divided into the following three classes:

$$\text{OC} = \text{OC}_{\text{FF}} + \text{OC}_{\text{BB}} + \text{OC}_{\text{sec}} \quad (2)$$

OC_{FF} represents the primary organic aerosol carbon related to fossil fuel combustion and is derived from EC by using an $(\text{OC}/\text{EC})_{\text{prim}}$ ratio of 1.1 for fossil fuel combustion (Pio et al., 2007), after subtracting the contribution of biomass burning from EC, which is estimated on the basis of an $(\text{OC}_{\text{BB}}/\text{EC}_{\text{BB}})$ ratio of 6.0, obtained by Gelencsér et al. (2007) for the CARBOSOL sites. It is calculated by the alternative subsequent equations:

$$\text{OC}_{\text{FF}} = 1.1(\text{EC} - 2.3\text{K}_{\text{BB}}^+) \quad (3)$$

$$\text{OC}_{\text{FF}} = 1.1(\text{EC} - 4.2 \text{ Levoglucosan}) \quad (4)$$

The $2.3 \text{ K}_{\text{BB}}$ factor in Eq. (3) represents the elemental carbon from biomass burning, which results from the mathematical combination of $\text{OC}_{\text{BB}}/\text{EC}_{\text{BB}} = 6.0$ and the slope of the lower envelope of the relationship found between the non-fossil fuel OC and K_{BB} ($\text{OC}_{\text{NFF}}/\text{K}_{\text{BB}} = 14 \text{ ng/ng}$). A similar reasoning was followed to derive Eq. (4) (Fig. 9).

OC_{BB} is the primary organic aerosol carbon from biomass burning derived from the minimum $\text{OC}_{\text{NFF}}/\text{K}_{\text{BB}}$ and $\text{OC}_{\text{NFF}}/\text{levoglucosan}$ ratios of 14 and 25, respectively. It should be mentioned that this procedure will give correct estimates if, in samples used to calculate minimum ratios, the amounts of secondary OC are negligible. This aspect seems to be fulfilled, since rather identical minimum ratios were observed at the different CARBOSOL sites and seasons.

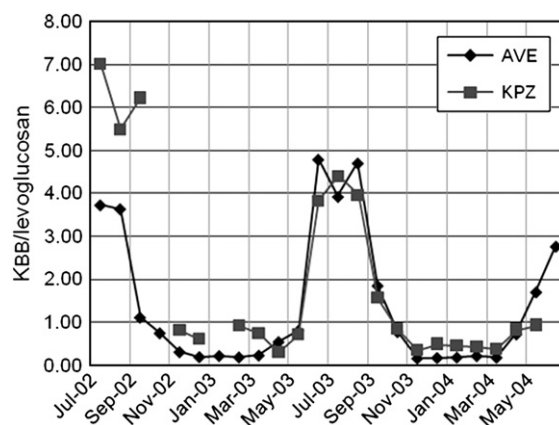


Fig. 7. Seasonal variability of $\text{K}_{\text{BB}}/\text{levoglucosan}$ ratios in $\text{PM}_{2.5}$ particles at Aveiro and K-pusztá during the entire CARBOSOL campaign.

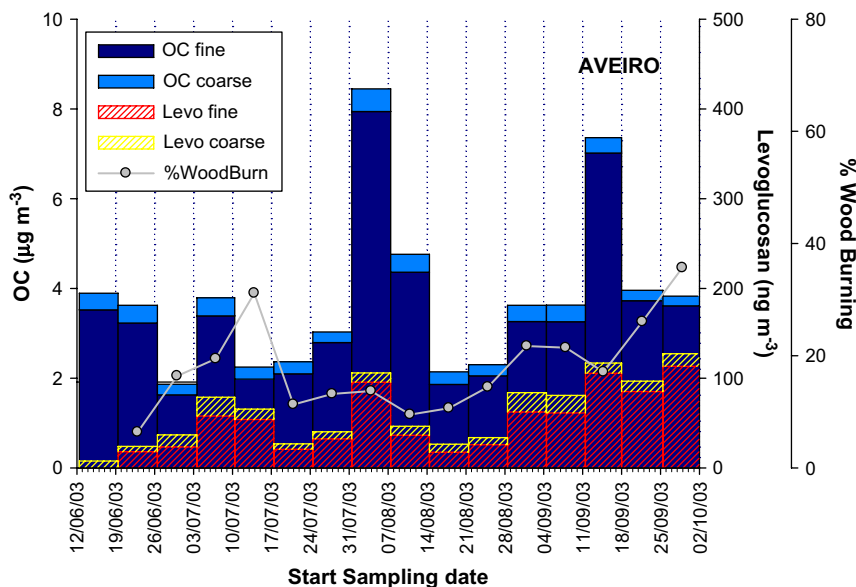


Fig. 8. Variation of organic carbon and levoglucosan concentrations in both the fine and coarse aerosol fractions and the contribution of smoke particles to the OC content based on typical marker-to-OC ratios from the literature (possibly underestimated, see text).

OC_{sec} is the secondary organic carbon, representing the difference between OC and the sum of the other fractions.

The input from natural biogenic sources to the primary fine OC was ignored, since it was previously estimated to represent less than 2% of the total carbon mass (Gelencsér et al., 2007). These rough calculations indicate that the contribution of OC_{BB} to total OC does not exceed 50% during wildfire events and point out that biomass burning emissions may significantly enhance the formation of OC_{sec} (Fig. 10). The secondary fraction represents 30–60% of total OC during the most critical fire episodes. Enhancement of HULIS and “brown carbon” levels as secondary products from wintry biomass combustion was also observed at rural sites during the CARBOSOL project (Lukács et al., 2007; Feczko et al., 2007).

The rough estimation of OC due to biomass burning, based on an $OC_{BB}/levoglucosan$ emission factor, was compared with that based on an OC_{BB}/K_{BB}^{+} emission factor (Fig. 10). The fraction of primary OC from biomass burning estimated from this later emission factor was found to be 2-fold higher than that obtained from levoglucosan, while the OC_{sec} was estimated to be approximately one half less than the corresponding calculations based on the anhydrosugar concentrations. Several authors have highlighted the helpfulness of levoglucosan as a source-specific tracer for biomass burning due to the fact that it cannot be formed by non-combustive processes (e.g. hydrolysis or microbial degradation of carbohydrates) and is resistant to degradation in the atmosphere. However, other studies demonstrate the decomposition of levoglucosan during multi-day

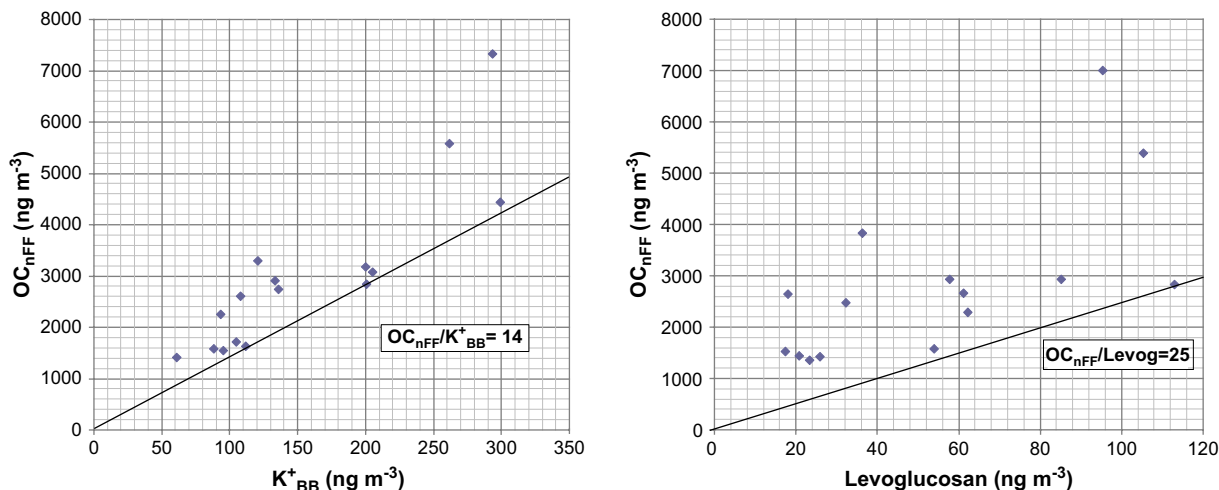


Fig. 9. Relationships between non-fossil fuel OC ($OC_{nFF} = OC - OC_{FF}$) and biomass burning tracers, at Aveiro, during the 2003 summer.

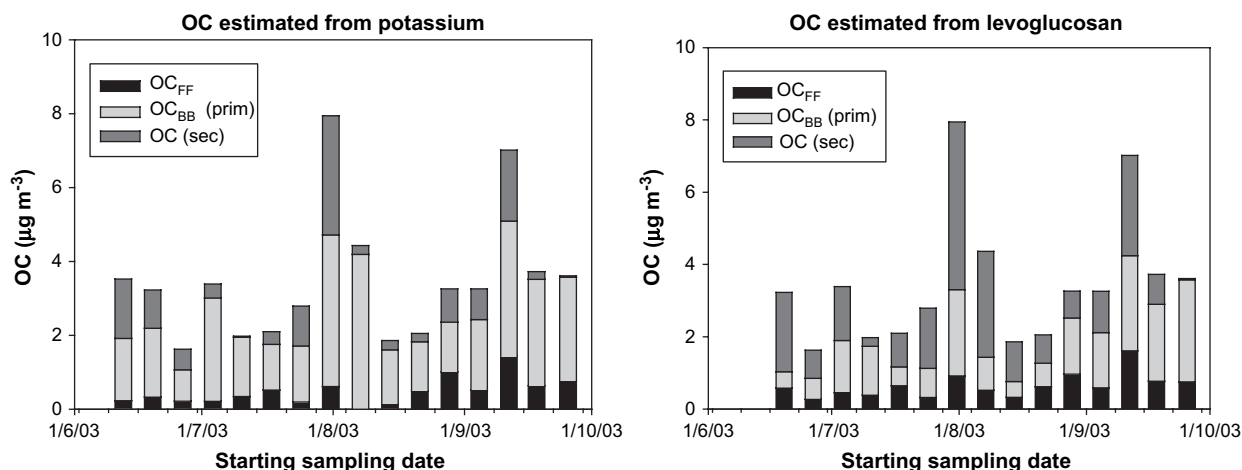


Fig. 10. Estimates of primary and secondary OC based on $OC_{BB}/levoglucosan$ (graph a) and OC_{BB}/K_{BB}^+ (graph b) ratios.

transport of the smoke plumes (Gao et al., 2003; Mochida et al., 2007). Acid hydrolysis could lead to its degradation during cloud processing. Laboratory investigations also reveal loss of levoglucosan likely due to biological degradation (Herckes et al., 2006; and references therein). In our study, the correlation of OC with levoglucosan ($r^2 = 0.53$) were found to be somewhat poorer compared with the correlation OC versus K^+ ($r^2 = 0.77$). The correlation is even worse when comparing the linear regression fit of OC_{nFF} versus levoglucosan ($r^2 = 0.38$) with that of OC_{nFF} versus K_{BB}^+ ($r^2 = 0.76$). These observations may indicate that, during more complete combusive processes at higher temperatures such as those occurring in the 2003 forest fire season, potassium is perhaps a more degradation-resistant tracer for wildfires biomass burning emissions.

4. Conclusions

During the wildfire episodes in the Aveiro region PM levels were elevated 2- to 3-fold above the prior and post smoke baseline periods. Evidence of biomass burning as a significant source is supported by the presence of anhydrosugars and potassium in atmospheric aerosols. The high potassium/levoglucosan ratio observed for the fire input (8.7), the presence of fine calcium, and the good correlation between the higher molecular weight fraction plus pyrolysed carbon ($OC_3 + PC$) and WSOC suggest that the biomass burning aerosol was mainly affected by flaming combustion. A rough estimate of OC derived from biomass burning based on $OC/levoglucosan$ and OC/K_{BB}^+ ratios indicated that smoke particles accounted for about 40–55% of the primary OC content. Smaller contributions are obtained when applying published ratios for other sites with quite different climatic and forested environments. Since these ratios are quite variable for different burning conditions and wood types, more specific factors with application to wildfires under extreme weather conditions, such as those observed in the Mediterranean countries have to be assessed. 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. The data set we got on C2–C5 diacids is more complete than those presently available in the literature. Data indicate enhancement of their levels by a factor of 2–3 during fire events. They also support the assumption that the degradation of cellulose during fires rapidly produces the C5 diacid subsequently oxidised into C4–C2 diacids.

Our results suggest that forest fire events may strongly contribute to gas-to-particle processes. The secondary fraction of OC may represent a mass fraction equivalent to that of primary OC from biomass burning. A poorer correlation of OC with levoglucosan compared with the corresponding relationship between OC and K^+ , and a smaller than expected biomass burning contribution to OC based on the anhydrosugar emission factors, led us to conclude that, during more complete combusive processes such as those occurring in the 2003 summer, K^+ is a degradation-resistant tracer, while the levoglucosan/OC ratio was around an order of magnitude lower than observed in smoke from wildfires at more humid sites.

Good correlations of diacids with K^+ and sulphate can be explained by in-cloud secondary formation of dicarboxylic species and SO_4^{2+} from cloud condensation nuclei (CCN) derived from biomass burning. The role of smoke aerosol particles in the secondary formation of diacids through in-cloud processes is worthy of further investigation. A better characterisation of the WSOC fraction and its effects on CCN activity is needed.

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