

Tracers and impact of open burning of rice straw residues on PM in Eastern Spain

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Abstract

Biomass burning emissions of rice straw residues may be carried out near urban agglomerations and may present a potential health risk for the population. Thus, tracers of these emissions should be clearly identified. We present a detailed chemical characterization, including inorganic and organic tracer species, of PM₁₀ aerosol at a rural site located close to the urban agglomeration of Valencia (Eastern Spain) during the rice straw burning season in 2006. Our results show that open burning of rice field residues increased daily PM₁₀ concentrations on a regional-scale (approx. 17,400 ha) by 10-15 µg/m³ on average, with a maximum of 30 µg/m³ on peak episodic days. PM₁₀ levels during open burning events were especially enriched in oxalate, fluoranthene, C₃₁ n-alkane, levoglucosan, K, water-soluble organic carbon (WSOC), oleic acid, Cl⁻, Na, NO₃⁻, and V. High enrichments were also obtained for Zn, Pb, Cr, Cd, and Na, probably as a consequence of the bioaccumulation of trace metals in rice straw and the influence of sea spray and brackish waters on the crops. Anthropogenic contributions from lubricant oil residues, probably from agricultural machinery or nearby traffic emissions, were also detected in the levels of n-alkanes (C₁₉). The high Carbon Preference Index (CPI, >3.5) obtained for n-alkanoic acids confirmed their mostly biogenic origin. Organic tracers were more sensitive than inorganic species to the influence of indirect (regional scale or long-range transported) biomass burning emissions. Source apportionment of the PM₁₀ mass by means of PCA-MLRA showed that rice straw burning reached maximum contributions up to 40% of the PM₁₀ mass during peak episodes.

Keywords: agricultural biomass, open fire, PM₁₀, WSOC, levoglucosan, oxalate, potassium, chlorine, CPI.

Introduction

Open burning of agricultural biomass is a known source of atmospheric particulate matter (PM) during specific periods of the year in the Valencia region, along the Eastern coast of Spain. The main biomass residues come from orange-tree plantations and rice fields, and are generated every year during the months of April-May and September-October, respectively. Despite the controls carried out by the local authorities regarding the specific dates and meteorological conditions under which the agricultural rice fires may be started, it is almost inevitable that the emissions from these fires will exert an impact on the levels and chemical composition of PM in nearby urban agglomerations. Consequently, biomass burning emissions in this region should

be monitored in order to be able to assess their impact on air quality and potentially on health by means of acute PM episodes.

On the global scale, biomass burning represents an important source of atmospheric aerosols and greenhouse gases, with a large interannual variability and carbon emissions of up to 3.2 Pg C year⁻¹ in 1998 (Van der Werf et al., 2006). Biomass burning emissions have demonstrated positive and negative effects on climate. Smoke and aerosol particles scatter sunlight or reflect it directly back to space, thereby having a cooling effect on the atmosphere. Black carbon particles, however, have a warming effect due to absorption of incoming radiation. Smoke particles are also a major source of cloud condensation nuclei (CCN) (Kaufman & Nakajima, 1993). Clouds, which consist of a higher number of smaller droplets reflect more radiation back into space, and as the clouds are less likely to produce rain, cloud coverage may also increase (Crutzen & Andreae, 1990). However, smoke emissions do not only have a cooling effect on the atmosphere, but a warming one as well. Some of the gases emitted by biomass burning (e.g., CO₂, CH₄) are greenhouse gases and thus contribute to the greenhouse effect which heats the atmosphere through absorption of thermal radiation (Kaufman et al., 1992). Other than these direct effects, indirect and semi-direct effects of biomass burning emissions have also been detected, whereby aerosols modify the microphysical and hence the radiative properties and amount of clouds (e.g., the increase in cloud coverage due to the larger number of CCN, or its decrease due to the increase in temperature resulting from the absorption of incoming radiation by EC particles, Haywood & Boucher, 2000; IPCC, 2001).

Biomass burning emissions from diverse sources have been studied by a number of authors: cookstoves (Kim Oanh et al., 2005), wildfires (Simoneit et al., 1999; Andreae & Merlet, 2001; Sillanpää et al., 2005; Ward et al., 2006; Saarikoski et al., 2007), or agricultural biomass (Simoneit et al., 1999; Hays et al., 2005). These studies show the relevance of organic tracer species such as levoglucosan or oxalate, and inorganic tracers such as potassium, for the interpretation of the impact of biomass burning emissions on ambient PM levels, as well as the significance of the ratios between tracers such as levoglucosan/mannosan (Fine et al., 2001) or levoglucosan/potassium (Schkolnik et al., 2005) to describe the properties of the type of biomass (e.g., coniferous vs. deciduous) or the type of combustion (e.g., smoldering vs. flaming). The growing use of biomass as a fuel, not only in the developing but also in the developed world (Tilman et al., 2001; Pio, et al., 2007; Gelencsér et al., 2007) has led to a need to characterise the different types of fuels utilised, as well as the conditions in which combustion is carried out (controlled open fires, uncontrolled natural wildfires, etc.). In this framework, the yearly periodical combustion of rice straw residues in Eastern Spain presented an opportunity to characterise in detail the chemical profile of the emissions from rice straw burning under controlled, open fire conditions. Studies focusing on the chemical profiles of rice straw emissions are relatively scarce (Hays et al., 2005), especially within Europe. Furthermore, most studies capture PM aerosols close to the emission source, aiming to characterise the emission profiles (Conde et al., 2005) but therefore eluding the characterisation of the aerosol at receptor sites, which represent the aerosol mix that the population is exposed to. In our case, the Valencia urban area with 2,464,000 inhabitants (INE, 2006) is located at approximately 10 km from the monitoring site and is thus influenced by biomass burning emissions.

The aims of this study spread in three main directions: a) the chemical characterisation of PM₁₀ aerosols under the influence of biomass burning emissions at a receptor site, including the identification and quantification of tracer species; b) the comparison between the observed chemical profile of rice straw burning emissions and literature data; and c) the assessment of the impact of such biomass burning emissions on the levels and chemical composition of PM₁₀, by comparison with periods of time when no

open fires were allowed. In sum, we aim to carry out the chemical characterisation of PM episodes which originated from open burning of agricultural biomass (rice straw) and to provide a series of tracer species or ratios which will aid in the future identification of this type of PM episodes in the region.

Methodology

The study area

The study area is situated in the region of Valencia in the east of Spain and extends over an area of approximately 6 to 10 km wide by 40 km long south of the city, in the mouth of the Turia Valley. The area includes a coastal pine forest and a coastal lake surrounded by continuous rice fields, which are the main agricultural crop (17,400 ha). The valley is dominated by sea-breeze circulations during warm periods (Pérez-Landa et al., 2007). The samples were collected at the Saler monitoring site in the nursery of the Natural Park of L'Albufera (9 km south of Valencia), see Figure 1, at less than 300 m of the rice fields located north of the lake.

PM10 sampling and analysis

PM10 sampling was carried out between 11/09/06 and 19/10/06. Open burning of rice straw residues was officially allowed after 27/09/06, but due to the forecasts of precipitation for 24-26/09/06, some early open fires were detected on 19-21/09/06 (straw was burnt before it would get wet by the rains). Sampling was carried out over 24-hour periods by means of a high-volume sampler (30 m³/h, DH80-Digitel), using 15-cm diameter quartz fibre filters as collection substrates (Schleicher & Schuell QF20). The campaign resulted in a total of 38 valid PM10 samples.

PM mass was determined by gravimetry after the filters had acclimatised for at least 24h. After mass determination, filters were cut in four sections for analysis:

- ¼ of the filter was acid digested in a sequence of acids (HF, HNO₃, HClO₄) for the determination of major and trace elements by inductively-coupled plasma mass and atomic emission spectrometry (ICP-MS and ICP-AES), according to the methodology described in Querol et al. (2001).
- ¼ of the filter was leached for the extraction of water-soluble ions (sulphate, nitrate, chloride, ammonium and oxalate) and subsequent analysis by ion chromatography (IC) and flow injection analysis (FIA). The anions were measured with a Dionex DX-120 ion chromatograph, using an AG4A-SC precolumn and an AS4A-SC column. The method was isocratic and the eluent was a solution 1.8 mM sodium carbonate and 1.7 mM sodium bicarbonate. Ammonium was measured by FIA.
- ¼ of the filter was used for the determination of organic carbon (OC) and elemental carbon (EC) by a thermal-optical transmission (TOT) technique (Birch and Cary, 1996) using a Sunset Laboratory OCEC Analyser with the temperature programme described in Schmid et al. (2001). Organic matter plus elemental carbon (OM+EC) was calculated by applying a factor of 1.6 to convert OC to OM (Turpin et al., 2000). Water-soluble organic carbon (WSOC) was measured using a Shimadzu TOC-V CPH high-sensitivity Total Organic Carbon Analyzer. Total water-soluble organic carbon was calculated by difference between total water-soluble carbon and inorganic water-soluble carbon ($TOC_{WS} = TC_{WS} - IC_{WS}$), and was used as WSOC.
- A portion of 11.34 cm² of the total area of the filters was used for the determination of organic species: these portions were ultrasonically extracted twice with dichloromethane/methanol (2:1), each time for 15 min; the extracts were combined and filtered through a glass fibre filter. The filtrates were concentrated by a rotary evaporator and then evaporated to dryness by a stream of N₂. The extracts were derivatised with 50 µL of N,O-bis-(trimethylsilyl)trifluoroacetamide (BSTFA) with 1% of

trimethylchlorosilane (TMCS) and using 10 μL of pyridine as catalyst at 70°C during 3 hours. The derivatised extracts were redissolved in 1 mL of n-hexane, and analysed by gas chromatography / mass spectrometry (Wang et al., 2006). p-Terphenyl was used as internal standard. The chromatograms were acquired in full scan mode (range: 50-500 m/z) and the compounds were quantified using their respective characteristic m/z (n-alkanes: 57; n-alkanols: 97; n-alkanoic acids: 117; erythritol: 147; levoglucosan: 204; dehydroabietic acid: 239; cholesterol: 329; naphthalene (Naph): 128; acenaphthylene (Acy): 152; acenaphthene (Ace): 153; fluorene (Fl): 166; phenanthrene (Phe) and anthracene (Ant): 178; fluoranthene (Ft) and pyrene (Pyr): 202; benz(a)anthracene (BaA) and chrysene (Chry): 228; benzo(b)fluoranthene (BbFt), benzo(k)fluoranthene (BkFt) and benzo(a)pyrene (BaP): 252; dibenz(a,h)anthracene (DBahA): 278; benzo(ghi)perylene (BghiP) and indene(1,2,3-cd)pyrene (IP): 276). Also, limits of detection for each group of compounds were quantified (0.007-0.044 ng/m^3 for n-alkanes, 0.002-0.022 ng/m^3 for PAHs, 0.019-0.333 ng/m^3 for n-alkanols, 0.008-0.228 ng/m^3 for n-alkanoic acids, 0.026 ng/m^3 for dehydroabietic acid, 0.047 ng/m^3 for levoglucosan, 0.007 ng/m^3 for cholesterol and 0.005 ng/m^3 for erythritol).

More information about blank filters, standards and validations used in the methodology regarding to the inorganic fraction can be found in previous publications such as Querol et al. (2001) and Minguillón et al. (2007).

Isentropic back-trajectory analysis modelling vertical velocity was carried out using the Hysplit model (<http://www.arl.noaa.gov/ready/hysplit4.html>, Draxler and Rolph, 2003), to interpret the origin of the air masses during 5 days of transport (120 h). Trajectories were calculated for 3 starting heights (750, 1500 and 2500 m a.s.l.). Meteorological data (wind speed and direction, precipitation) were obtained from a nearby micrometeorological flux tower (CARBOERUPE IP EU project, rice field station from CEAM).

Statistical analysis of the chemistry dataset was carried out by receptor modelling using Principal Component Analysis – Multi-Linear Regression Analysis (PCA-MLRA, Thurston & Spengler, 1985). This analysis was performed to identify the sources contributing to the PM₁₀ levels, as well as to determine the contributions of the identified sources. PCA builds on the variability of the PM components at the receptor site and seeks to determine the matrices A and S in the equation $C = A \cdot S$, where C represents the concentrations of the various PM constituents, S the source contributions and A the source profiles. A Varimax normalised rotation was applied to maximise (or minimise) the component loadings of the measured compounds in each rotated principal component. Quantification of the source contributions is then performed by MLRA, using the absolute principal component scores as source contribution indicators. Examples of its application may be found in Henry and Kim (1990) and Chueinta et al. (2000). In this study PCA-MLRA was applied with the software package STATISTICA 4.2.

Results and discussion

Chemical properties of PM₁₀ and tracers of open fire episodes

Figure 2 shows the time series of PM₁₀ levels during the study period. Mean daily PM₁₀ levels ranged from 10 to 62 $\mu\text{g}/\text{m}^3$, and were on average 26 $\mu\text{g}/\text{m}^3$. Such mean levels may be considered representative of the regional background, characteristic of the study area during this season. Three different types of periods were defined within the study period, as a function of PM₁₀ levels and the data available on open fires in the region (Figure 1 and Table 1):

- P1: no open fires detected in the surroundings of the monitoring site. These periods include the time before open fires were allowed or detected (11/09-17/09/06) and the period when precipitation prevented open fires from being started (24-26/09/06). However, it is not possible to discard the possible influence of biomass burning emissions from agricultural fields located farther away from the monitoring site, where open fires may have been allowed on different dates.
- P2: open fires detected in the surroundings of the monitoring site. There were two such periods, one when open fires were detected before the rains (19-22/09/06) and the other when open fires were allowed by the local authorities (27-30/09/06). Biomass burning probably continued after 01/10/06 and until 15/10/06, but the impact of these emissions on PM10 levels could not be ascertained (based on the PM10 chemical records and on the data on open fires) and consequently these samples were not included in the P2 means. By doing so, we aimed to ensure the representativity of the levels and composition of the open fire periods.
- P3: impact of biomass burning emissions on PM10 levels was not clearly identifiable. The sample from 03/10/06 must be highlighted owing to the high levels recorded of PM10 ($62 \mu\text{gPM}_{10}/\text{m}^3$), WSOC ($5.5 \mu\text{g}/\text{m}^3$) and K ($1.6 \mu\text{g}/\text{m}^3$), which initially seemed to indicate an impact from biomass burning emissions. However, levoglucosan concentrations did not show an increase for this sample and, on the contrary, relatively high levels of Al_2O_3 and other crustal components were detected, coinciding with a possible African origin of the air masses according to back-trajectory analysis (African dust transport). As a result, this sample was not included in the P2 averages.

The interpretation of the origin of the air masses is shown in Figure 2. During the biomass burning periods, the dominant meteorological scenarios were determined by anticyclonic conditions and regional-scale recirculation of the air masses, which favoured the stagnation of pollutants and prevented their dispersion. Long-range air mass advections such as those observed between 14-18/09/06 or on 23-26/09/06 coincided with lower PM10 levels, due to air mass renovation. Precipitation was registered on 12/09/06 (6.6 mm) and 23/09/06 (27.8 mm). Finally, regional recirculation episodes which did not coincide with biomass burning periods (13-19/10/06), but they resulted in PM10 mass increases as a consequence of air mass stagnation. The interpretation of back-trajectory analyses proved very useful for the definition of the limits of periods P1 and P2, and thus to clearly separate the biomass burning chemical profiles.

Table 1 presents the chemical speciation of PM10 aerosols during the different sampling periods, as well as the mean values for the entire study period. The P3 period presents a mixture of contributions which was not clearly interpreted, and consequently this period was not compared with P1 and P2. P2/P1 ratios represent the enrichment of each species during open fires with respect to non-open fire periods, and the enrichment was considered significant when the P2/P1 ratio was larger than 2.

PM10 mass concentrations were markedly higher during P2 (open fires, $32 \mu\text{g}/\text{m}^3$, Table 1) than during P1 periods (no open fires, $17 \mu\text{g}/\text{m}^3$). As expected, PM10 levels during P2 open fire episodes were enriched in WSOC and bulk K (P2/P1 = 2.0 and 2.2, respectively) given that these are some of the main tracers of biomass combustion (Jaffrezo et al., 1998; Simoneit et al., 1999), with levels reaching on average $1.6 \mu\text{gWSOC}/\text{m}^3$ and $0.4 \mu\text{gK}/\text{m}^3$. Cl⁻ has been identified as one of the main elements emitted from biomass combustion in Helsinki (Sillanpää et al., 2005) and this seems to be the case also here, as suggested by its enrichment (P2/P1 = 2.7). Furthermore, high concentrations and enrichments were also obtained for Na (2.6) and NO_3^- (3.2), less

frequently described as tracers of biomass burning but usual markers of sea water and vegetation. Due to the proximity of our site to the Mediterranean coast, sea breeze can carry significant amounts of sea spray, which may be deposited onto the rice fields (in addition to Na contributions from the use of brackish waters for watering the rice fields). The formation of NaNO_3 by reaction of HNO_3 with sea salt is also well-known (Harrison & Pio, 1983). As a result, the rice straw burning may have generated high Na and NO_3^- concentrations in PM10. However, the higher P2/P1 ratio obtained for NO_3^- than for Na indicates that sea-spray is not the only source of enriched NO_3^- levels during P2 episodes. One possible explanation for this could be the contribution from the emissions from agricultural vehicles during burning episodes, given that V and Ni show similar enrichments (P2/P1 = 2.7-2.9) during P2 periods. Finally, a higher enrichment was obtained for OC (1.6) than for EC (1.3), although, on average, these ratios were lower than expected, when compared with those obtained for other common tracers of biomass burning such as K (2.2) or WSOC (2.0).

Regarding inorganic trace species (Table 1), substantially higher concentrations were obtained during open fire periods for V (16 ng/m^3 , P2/P1 = 2.9), Ni (5 ng/m^3 , 2.7) and Zn (49 ng/m^3 , 2.6), and high enrichments without markedly high levels were observed for Cr (P2/P1 = 2.3), Se (2.9), Cd (2.1) and Pb (2.5). The emission of Zn during rice straw burning could be explained by the bioaccumulation of this element in rice plantations (Abbas et al., 2007; Zafar et al., 2007), and bioaccumulation has also been reported for Mn, Fe and Cu, and sometimes Ni. The high enrichment for Mn ($1.9, 9 \text{ ng/m}^3$) confirms the biogenic origin of these elements (through bioaccumulation). The enrichment was not so clear for Fe (P2/P1 = 1.3). In the case of Cu, the bioaccumulation in rice plants originates from commonly used Cu-enriched fertilisers (Abbas et al., 2007), which are, however, not widely employed in the study region. Finally, the high V and Ni P2/P1 ratios (2.9 and 2.7, respectively) could be related to the influence of the emissions from agricultural machinery (farm tractors, etc.). Above ground biomass was collected in the rice fields before burning and it is on the way of being analysed to confirm if there are high levels due to heavy metal bioaccumulation.

A wide range of organic compounds was also measured, including n-alkanes (C_{16} to C_{37}), polycyclic aromatic hydrocarbons (PAHs), n-alkanols ($\text{C}_{14}\text{-OH}$ to $\text{C}_{34}\text{-OH}$) and n-alkanoic acids ($\text{C}_{8:0}$ to $\text{C}_{32:0}$) and two n-alkenoic acids (oleic acid $\text{C}_{18:1}$ and linoleic acid $\text{C}_{18:2}$). Table 2 summarises the results obtained for commonly used tracers of biomass combustion (levoglucosan, oxalate, dehydroabietic acid) (Simoneit et al., 1999; Hays et al., 2005) as well as for a selection of organic compounds. Levoglucosan concentrations obtained for P2 periods (129 ng/m^3) were clearly higher than during P1 periods (P2/P1 = 2.2), indicating that this compound effectively traces biomass burning emissions. These results highlight the importance of knowing the type of biomass combusted in order to identify pollution episodes, as the mean levels registered during our P2 periods (rice straw burning) are markedly lower than the values reported by Ward et al., 2006 (1337 ng/m^3) for forest fires. The levels of oxalate also increased significantly during open fire episodes (P2/P1 = 3.2, 373 ng/m^3), as was the case for the n-alkane C_{31} (P2/P1 = 2.3) and for oleic acid (5.2). The levels of dehydroabietic acid (DHAA, 3.2 ng/m^3 , P2/P1 = 0.9) were similar during P1 and P2 periods owing to the fact that this compound is considered a tracer for *coniferous* or softwood burning, but not for burning of rice straw residues (Hays et al., 2005, Leithead et al., 2006). A significant increase in the levels of DHAA was only detected in one sample (17/10/2006, 27 ng/m^3), suggesting the point impact of some sort of combustion emissions (wood, garbage, etc.) on that date, as will be discussed in the following sections.

As a result of this analysis, Figure 3 summarises the main species identified as tracers of rice straw burning emissions in this study:

- P2/P1 >2 (major tracers): oleic acid, indene(1,2,3-cd)pyrene, NO₃⁻, oxalate, Se, V, Ni, Cl⁻, Na, Zn, Pb, fluoranthene, Cr, C₃₁ n-alkane, levoglucosan, K, Cd, WSOC. These species and elements showed a marked enrichment in PM10 during open fire events. Short-chain PAHs such as fluorene are known as tracers of open fires given that temperature does not increase high enough to produce longer-chain compounds. Consequently, the high P2/P1 ratio for indene(1,2,3-cd)pyrene (long-chain PAH) was unexpected. As regards n-alkanes, high and odd numbers of C-atoms are linked to biogenic emissions, as is the case for C₃₁ (P2/P1 = 2.3). In sum, these tracers may be grouped as follows: a) Biomass burning: oxalate, fluoranthene, C₃₁ n-alkane, levoglucosan, K, WSOC, oleic acid; b) Bioaccumulation: Cl⁻, Na, Zn, Pb, Cr, Cd, and possibly V, Ni. However, V, Ni and NO₃⁻ could also be tracers of the emissions from agricultural vehicles.
- 2>P2/P1>1: Ba, Ca, Mn, Sr, As, Co, SO₄²⁻, Mg, C₂₉ n-alkane, OC, C_{16:0} n-alkanoic acid, Rb, Sb, Cu, Sn, Li, NH₄⁺, C₃₀-OH n-alkanol, EC, C_{18:0} n-alkanoic acid, Fe, P, Ga, C₂₈-OH n-alkanol, Ti, Al₂O₃. These species showed no clear trend.
- P2/P1<1 (tracers of anthropogenic emissions other than biomass burning): C₁₈-OH n-alkanol, DHAA, C₁₉ n-alkane. The levels of these species showed no correlation with the tracers of rice straw burning. DHAA is a known tracer of softwood burning (mostly pine) and thus showed no increases in relation to the rice open fires. As described above, in the case of alkanes low and odd numbers of C-atoms (such as C₁₉) are linked to anthropogenic emissions (not related to biomass burning).

Table 2 also compares our results for the different organic fractions with the emission profile for rice straw burning of Hays et al. (2005). Note that the alkanol fraction was not reported in the Hays et al. study. Our organic fraction results show a similar pattern during the three different types of periods (P1, P2 and P3) but also remarkable similarities and differences with the rice straw burning profile (named REF from now on). A deeper discussion on each family of compounds is given below. The Carbon Preference Index (CPI) and the Carbon Number Maximum (C_{max}) of the homologous compound series in the PM10 extracts provide information on the relative importance of matter from biogenic origin (including biomass burning) to that from anthropogenic origin. The CPI for n-alkanes is expressed as a summation of the odd carbon number homologues over a range divided by a summation of the even carbon number homologues over the same range; for n-alkanoic acids and n-alkanols it is the same ratio only inverted to have even-to-odd homologues.

n-alkanes

The homologous series for n-alkanes in our samples seems to have a bi-modal distribution centred at C₁₉ and C₂₉₋₃₁ compared with the uni-modal distribution for the REF samples with a main peak at C₂₉₋₃₁ (Fig. 4a). The C₁₉ peak, which is only minor in REF, could point to lubricant oil residues (Simoneit, 1986) used in vehicles while the saw-tooth pattern (odd > even) at >C₂₅ is a typical signature of plant waxes. This part of the distribution also matches the REF profile and the CPIs>2 (2.2, 2.0, 2.0 and 2.3 for P1, P2, P3 and REF respectively) mark the biogenic origin of these compounds. Regarding the anthropogenic contribution (excluding biomass burning), the lubricant oil could be linked to the farm tractors used in the area and also to the traffic from the freeway at few kilometres from the sampling site. The biogenic emissions, on the other hand, are related to the release of rice plant waxes due to the mechanical abrasion during collection periods or due to the low temperature fires that essentially steam-distil the vascular plant waxes unaltered into the smoke, as observed after the first open fire

episodes. High correlations were then found between oxalate and levoglucosan, and C₂₆-C₃₄ n-alkanes.

n-alkanoic acids

The origin for the lighter fatty acids is not totally clear. While some authors (Schauer et al., 1999; He et al., 2004) have indicated that the <C₂₀ homologues of fatty acids are ubiquitous and that cooking is one of the important sources of these compounds, other authors (Simoneit, 1986) claimed that they could have a microbial origin or may even originate from anthropogenic vehicular emissions. A possible biomass burning origin has also been indicated in several articles (Oros and Simoneit, 2001a and 2001b; Hays et al. 2005). The C₁₆ and C₁₈ saturated acids were the two most prominent n-alkanoic acids in our samples (Fig. 4b) and they accounted for 37–46% of the total. The strong even carbon number predominance (CPI > 3.5, Table 2) suggests that the n-alkanoic acids were mainly biogenic. Comparing our distribution patterns with REF, we observe a much lower emission of homologues >C₂₀ but still a strong even carbon number predominance and high correlations of these compounds with levoglucosan after open burning episodes. Alkanoic acids are basic units of plant fats, oils and phospholipids. There are also noticeable contributions from unsaturated alkanoic acids which include C_{18:1} and C_{18:2} (Table 2) with a biogenic input as they were also detected in the pure rice straw burning pattern (Hays et al., 2005).

Resin acids

DHAA has been reported as a clear combustion marker of conifer resin (Simoneit et al. 1999; Oros and Simoneit 2001a). This compound is present in our aerosol samples in high average concentrations ranging from 0.95 to 1.74 mg/g OC (Table 2) and shows a significant correlation with levoglucosan. The concentrations of DHAA in REF are much lower, only around 0.067 mg/g OC. It is therefore quite likely that DHAA in our samples originates predominantly from another kind of biomass fires, such as pine wood combustion, than from rice straw burning.

n-alkanols

Homologous series of n-alkanols with even to odd C number predominance are present in our PM₁₀ samples (CPI = 7.9 – 8.8). The n-alkanols ranged from C₁₄ to C₃₄ with C_{max} at C₃₀ and a minor peak at C₁₈ (Table 2 and Fig 4c). Alkanols from vascular plant wax, homologues of >C₂₀ (Simoneit, 1986), accounted for about 74% of the total alkanols, and significant correlations were found with levoglucosan (except for C₂₈-OH, C₂₉-OH and C₃₃-OH). The homologues <C₂₀ may be derived from microbial sources, since they are not prevalent in fresh vascular plant waxes.

Sterols

Cholesterol, a major aerosol sterol compound, was present in our samples with an average concentration around 0.23 mg/g OC (Table 2). Main cholesterol sources are meat cooking and direct emissions from algae (Simoneit, 2002). Due to their location near the Mediterranean coast, the rice fields in our study area are generally watered with a mixture of freshwater and sea water (brackish waters). Sea water could be the origin for this algae biomarker and also could explain why the concentration of cholesterol was nearly constant in all our samples.

PAHs

The major sources of atmospheric PAHs are combustive processes using fossil fuels or biomass. The PAH distribution from rice straw smoke (Fig 4d) shows fluoranthene, pyrene, benz(a)anthracene and chrysene as major class compounds with minor contributions of phenanthrene and benzo(a)pyrene. Beside those PAHs also large amounts of benzo(b)fluoranthene, benzo(ghi)perylene and indene(1,2,3-cd)pyrene, which are usually linked with fossil fuel combustion sources as diesel engines, are

present in our PM10 samples. The relative proximity of a traffic motorway to our study area may explain the presence of these heavier PAHs.

Yang et al. (2006) observed characteristic ratios BaP/BghiP and IP/[IP+BghiP] of 2.0 and 0.64, respectively, during a rice straw burning period. Our ratios for these compounds (of 1.4-2.0 and 0.6-0.7, respectively) are close to the ratios in that study. On the other hand, the ratios in our non-burning samples are in good agreement with those of vehicular sources but they are not very conclusive. The IP/[IP+BghiP] ratio for the samples collected before and during the open fires are quite similar, which implies that the open fire period could have started before 19/09/2006 or that diesel vehicular emissions are also detected during the P2 periods. As was concluded by Yang et al. (2006), the IP/[IP+BghiP] ratio is not very useful for discriminating the two emission sources, because their characteristic values for diesel exhaust (0.3-0.7) and for rice straw burning emission (0.64) are too close.

Sugar derivatives

The major organic compound in the total extract of gramineae combustion is levoglucosan, which is derived from the thermal decomposition of cellulose (Simoneit, 2002). This was also the case in our samples with an average concentration of levoglucosan ranging from 20 to 27 mg/g OC (Table 3).

Finally, the ratios between certain tracer species have been shown to describe the characteristics of biomass burning emissions such as the type of fire or the fuel. Schkolnik et al. (2005) indicated that levoglucosan/K ratios are low for flaming combustion compared to smoldering combustion. In our study no significant difference was observed between P2 (levoglucosan/K = 292) and P1 (levoglucosan/K = 277). Our ratios are much higher than those reported by Ward et al. (2006) and Fine et al. (2001) for forest fires (levoglucosan/K = 9) and fireplace combustion (levoglucosan/K = 18), respectively. It is important to remember that in our study K levels refer to bulk K (as opposed to water-soluble K). Leithead et al. (2006) compiled levoglucosan/OC and DHAA/OC ratios from the literature for different types of biomass, ranging from loblolly pine to red maple or balsam fir, mostly forest species. The levoglucosan/OC ratio during our P2 periods (2.9%) was markedly lower than those literature ratios (4.0-16.8%), confirming that the emission profile from rice straw combustion is clearly distinguishable from that of forest fire emissions. As for the DHAA/OC ratio, a ratio of 0.1% was obtained as a mean for the P2 periods, with a maximum of 0.8% for the 17/10/2006 sample. The ratios reported by Leithead et al. (2006) ranged from <0.01 to 4.3%, with values close to 0.8% for a number of varieties of pine softwood (slash pine, 0.66%; E. white pine, 0.78%; loblolly pine, 1.2%).

The organic fraction results in Figure 4 do not show marked differences between the different study periods (P1, P2, P3). This is in contrast with the data for the inorganic fraction, for which significant differences were observed between the P1 and P2 periods (Table 1 and Figure 3). This suggests that the organic tracers are more sensitive to the influence of indirect biomass burning emissions than the inorganic species. Rice fields were burnt during the study period in the vicinity of the monitoring site (approx. 200 m to 4 km), but open fire burning of agricultural waste (rice straw residues) was carried out on a broader regional scale (approx. 50 km) for a longer period of time, before and after the study period. Consequently, it is probable that the influence of the long-range transport of biomass burning emissions was detected at our site during the study period, increasing the background levels of the organic markers and thus making a clear separation of study periods difficult.

Dependence on wind direction

The levels of specific trace species and elements were analysed as a function of wind direction, with the aim to characterise the spatial distribution of the PM sources. Pollution roses were plotted for PM₁₀, EC, OC, WSOC; Na, SO₄²⁻, oxalate, levoglucosan and DHAA, but significant relations with wind direction were only observed for EC, Na, SO₄²⁻, DHAA and levoglucosan (Figure 5). The remaining components (PM₁₀, OC, oxalate, WSOC) showed a mostly homogeneous distribution around the monitoring site, indicating that the emissions (mostly biomass burning) were produced in all directions around the site.

As for the species/elements with a marked spatial distribution, EC, Na and SO₄²⁻ showed higher levels towards the coast (60-120°) as a result of the higher sea-spray contributions as well as the impact of anthropogenic emissions (mainly traffic) from the urban agglomerations and the highway along the coast. The higher levels of SO₄²⁻ are probably related to regional-scale contributions travelling inland by means of sea-breeze circulations (Millán et al., 1997). The levels of DHAA peaked in the same direction (60-90° sector, Figure 5), probably coinciding with combustion emissions (pine-wood combustion, residential waste combustion, etc., as discussed below) at the coastal urban agglomerations. Finally, the levels of levoglucosan displayed a different pattern, with maximal levels in the 150-240° sector. This direction could reflect the contribution from rice straw residues, but it should be noted that even though this pattern was also observed for some tracers like C₃₁ n-alkane, it was not obtained for other main tracers such as WSOC, K or OC.

Wind speed did not show any significant relation with the levels of the PM components evaluated, and only a slight anti-correlation was observed with secondary species such as SO₄²⁻ or NO₃⁻. This could be due to the increased production of secondary species during atmospheric stagnation conditions. On the contrary, precipitation played a significant role regarding PM levels, as the levels of PM₁₀ and its components decreased with rainfall.

Contribution of open fires to PM₁₀ levels

The contribution of open fire emissions to PM levels in the study area is limited to the biomass burning periods, but it may account for a significant fraction of the PM during these times. In order to evaluate this contribution, PCA-MLRA receptor modelling techniques was applied, using the methodology of Thurston & Spengler (1985). It is essential to consider that only 38 samples were available, and consequently the results obtained can only be considered an approximation. The initial PCA allowed us to identify 5 main sources of PM₁₀ during the sampling period (Table 3):

Source 1: Mineral dust re-suspension. The main tracers of this source were mineral elements and compounds such as Al₂O₃, Ga, Rb, Fe, Sr, K, P, Cs and the Rare Earth Elements. A certain degree of mixture with biomass burning emissions is also detected by the correlation with OC, WSOC, C₂₉ or C₃₁ n-alkane (loadings >0.58 and <0.63), which had been previously identified as tracers of open fires. This correlation could be related to the re-suspension of soil dust during the open fires, by action of the wind or anthropogenic activities (e.g., road traffic).

Source 2: Anthropogenic emissions (excluding biomass burning). This source is interpreted as the combination of a variety of anthropogenic emissions including traffic (traced by EC, NO₃⁻, Sb) and industrial emissions/power generation/agricultural vehicles (V, Ni), mixed during regional-scale transport towards the study area. As a result, common tracers of regional and local pollution (SO₄²⁻, NO₃⁻) are also found in this source. Oxalate is also found to correlate with this source, coinciding with the secondary nature of this compound (linked to regional-scale transport).

Source 3: Combustion. This source reflects the combustion of an unknown fuel which could be either biomass combustion different to rice straw (e.g., pine softwood, traced by DHAA, and possibly from the nearby pine-tree forest where small fires occur occasionally) or to other fuels such as sporadic residential waste burning in a few rural sites in the study area (with possibly high levels of trace elements such as Ge, Zn, Co or Ti). The time evolution of the contributions of this source showed that only one major event was detected for this source, which coincided with the 17/10/2006 sample.

Source 4: Biomass burning (rice straw). Characterised by the contribution of C₃₀-OH n-alkanol, C₂₈-OH n-alkanol, C₂₉ n-alkane, C₃₁ n-alkane, WSOC, OC and levoglucosan, this component clearly represents the impact of open fire emissions from rice straw burning. The time evolution of these contributions also confirmed the nature of this source, with maxima coinciding with the P2 biomass burning periods. This source anti-correlated with tracers of other anthropogenic emissions (e.g., traffic, industry, etc.) such as C₁₈-OH n-alkanol or C₁₉ n-alkane.

Source 5: Sea-salt aerosol. The contribution of sea spray to PM10 levels is clearly detected by the correlation between Na, Cl⁻ and Mg.

The contributions of the identified sources to the PM10 mass were obtained by MLRA. The performance of the model was estimated as good, with an r^2 value of 0.92 for the regression line $y = 0.72x + 7.74$ with “y” representing the modelled and “x” the measured values, and $r^2 = 0.78$ for $y = 0.98x$. The large intercept obtained (7.74) indicated that the model significantly overestimated the PM10 mass, and thus implies that the quantification of the individual sources cannot be considered as fully reliable. The results of the source contribution analysis are shown in Figure 6. On average during the study period, the mineral fraction represented the highest contribution to the bulk PM10 mass (33%), followed by that of anthropogenic emissions (different to biomass burning, 24%) and rice straw burning (21%). The biomass burning source reached maximum contributions up to 40% of the PM10 mass during peak episode days in P2 periods. The results in Figure 6 confirm the relatively low significance of the combustion source with respect to the PM10 mass, as it represents only 2% of the mass. The results for the sea-salt contribution (20%, 5.4 $\mu\text{g}/\text{m}^3$) indicate that there is a marked overestimation for this component by the PCA-MLRA, given that the chemical analysis of the PM10 samples showed that there was only 1.4 $\mu\text{g}/\text{m}^3$ of sea salt (Na + Cl⁻, Table 1). Our PCA-MLRA sea-salt component may actually be a mixture of sea salt and biomass burning, given the enrichment of Na and Cl⁻ during P2 periods (Table 1). A similar situation is observed for the mineral source (8.8 $\mu\text{g}/\text{m}^3$ according to the model, 6.0 $\mu\text{g}/\text{m}^3$ according to the chemical analyses), and conversely the opposite was observed for the biomass burning fraction. According to the chemical analyses, the sum of OM+EC was 6.5 $\mu\text{g}/\text{m}^3$, but the contribution of the biomass burning source in the PCA-MLRA model (including OC but also K) is 5.6 $\mu\text{g}/\text{m}^3$. Furthermore, the time evolution of the anthropogenic source identified a number of peaks during open fire periods (P2), suggesting that the model was at times unable to clearly separate the contributions from these two sources. As a result, it may be concluded that the contribution from rice straw burning calculated by the model should be considered as a minimum value.

Conclusions

In this study we present a detailed chemical characterisation of ambient PM10 aerosols during rice straw burning episodes by means of open fires. Inorganic and organic tracer species were analysed. The following conclusions were extracted from our work:

- Open burning of rice field residues (rice straw) increased ambient PM10 levels on the regional-scale by 10-15 $\mu\text{g}/\text{m}^3$ on average, reaching 30 $\mu\text{g}/\text{m}^3$ during

- peak episodes. These emissions may represent up to 40% of the PM₁₀ mass during peak episodes.
- The biomass burning tracers, providing substantial contributions to the PM, were K and Cl⁻ (inorganic), and WSOC and oxalate (organic), with enrichment P₂/P₁>2. High enrichments were also obtained for NO₃⁻ and Na, which could be related to sea-salt contributions and/or anthropogenic emissions (in the case of NO₃⁻).
 - Furthermore, high enrichments were observed for Zn, Pb, Cr and Cd, probably due to bioaccumulation of these metals in rice straw.
 - The main trace-level organic markers of biomass burning were fluoranthene, C₃₁ n-alkane, levoglucosan and oleic acid. Long-chain PAHs such as indene(1,2,3-cd)pyrene showed unexpectedly high enrichments.
 - A different type of combustion (possibly softwood or residential waste) was detected by increased levels of DHAA, registered on one specific peak episode.
 - Anthropogenic contributions from lubricant oil residues (probably agricultural vehicles or nearby traffic emissions) were detected in the levels of n-alkanes (C₁₉).
 - The combined use of enrichments (P₂/P₁ ratios), pollution roses and principal component analysis allowed us to confirm the interpretations obtained by the three separate approaches:
 - Sea spray was detected as an ambient PM source but also as the source of Na enrichment during open fire episodes due to sea-salt deposition on the rice fields. The pollution rose analysis confirmed the predominantly coastal origin of these contributions.
 - Biomass burning (rice straw) was indicated by means of high P₂/P₁ ratios from organic and inorganic tracers (WSOC, K, Cl⁻), and a clear spatial distribution in the case of levoglucosan, but not for all tracers.
 - Anthropogenic emissions (local traffic, agricultural vehicles) were detected by means of low P₂/P₁ ratios and showed either a coastal origin (coinciding with the urban agglomerations, e.g., for EC) or a homogeneous distribution around the monitoring site (e.g., for OC or PM₁₀).
 - Regional-scale transport was evidenced by organic (oxalate) and inorganic (SO₄²⁻, NO₃⁻) tracers and a homogeneous spatial distribution around the monitoring site. High enrichments obtained for some of these compounds (especially oxalate) demonstrate the influence of indirect (regional scale or long-range transported) biomass burning emissions.

In sum, the influence of rice straw burning on PM₁₀ levels was clearly identified, and its impact constituted a major fraction of the PM₁₀ mass during peak episodes. Consequently, this PM source should be monitored in order to prevent adverse health effects on surrounding urban agglomerations. Our results show that, even though inorganic tracers are less specific to this particular source, they seem to be more sensitive than organic species to the influence of indirect (regional- or long-range) biomass burning emissions for the latter. Therefore, monitoring of biomass burning emissions should ideally combine the use of inorganic and organic tracer species.

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Figure captions

Figure 1. Location of the monitoring site, the forest, the rice fields and the nearby urban agglomerations of Valencia and Sueca.

Figure 2. Time evolution of PM₁₀ levels during the study period. P1 periods: no open fires in the vicinity of the monitoring site. P2 periods: open fires were detected near the monitoring site. P3 periods: no clear data were obtained regarding the presence of open fires near the monitoring site. The interpretation of the origin of the air masses by means of back-trajectories is also included: MED (Mediterranean), AW (Atlantic West), ASW (Atlantic South-West), REG (regional-scale re-circulation), AN (Atlantic North).

Figure 3. Enrichment ratio (P2/P1) during reported biomass burning episodes (P2) with respect to not identified biomass burning episodes (P1) for the different elements and compounds analysed.

Figure 4. Distribution diagrams of a) n-alkanes, b) n-alkanoic acids, c) n-alkanols and d) PAH average concentrations for the three episodes (P1, P2 and P3) compared with rice straw profile (REF, Hays et al. 2005). Cn: carbon number.

Figure 5. Wind rose analysis of the dependence of the concentrations ($\mu\text{g}/\text{m}^3$ and ng/m^3) of a number of selected PM₁₀ components (OC, Na, SO_4^{2-} , levoglucosan, DHAA) with wind direction, for the period 11/09/2006-19/10/2006.

Figure 6. Mean contribution (in %) of the 5 identified sources to the PM₁₀ mass, resulting from the PCA-MLRA analysis, for the period 11/09/2006-19/10/2006 (n=38 samples).

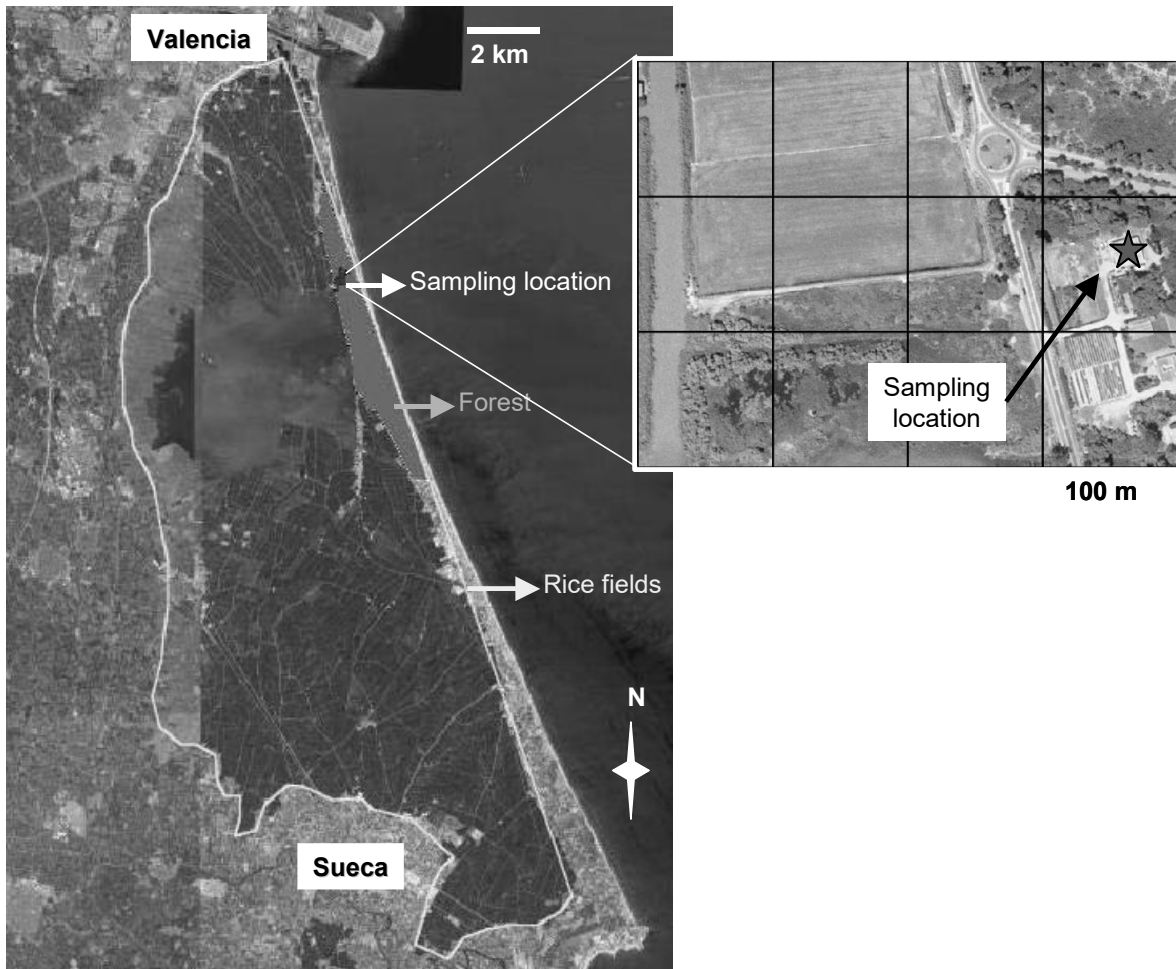


Figure 1

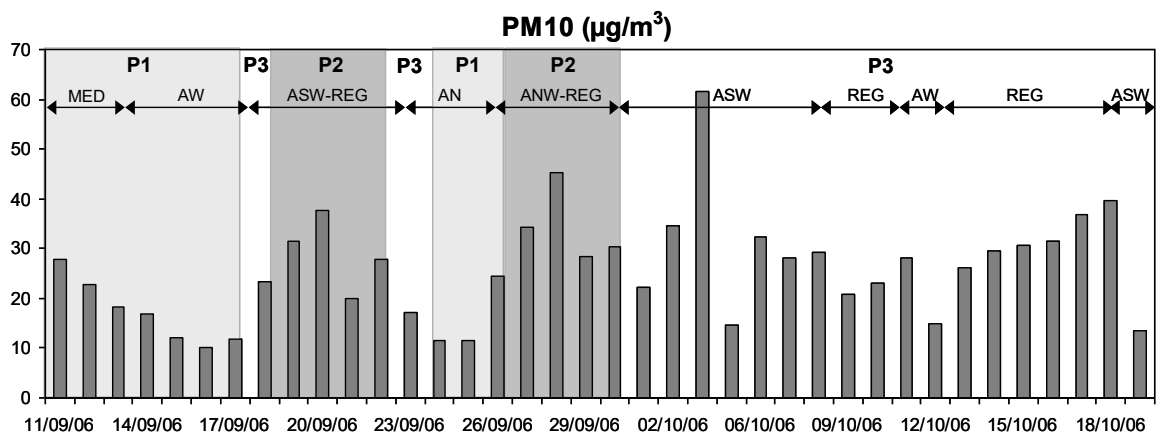


Figure 2.

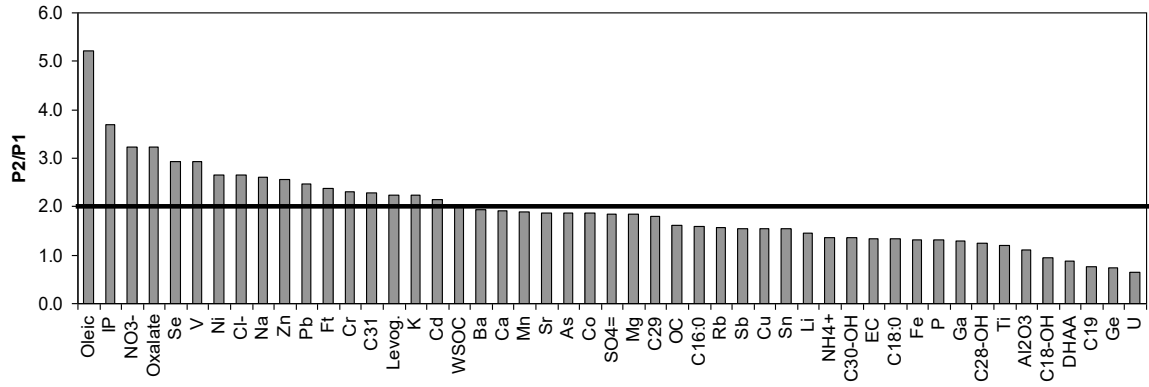


Figure 3

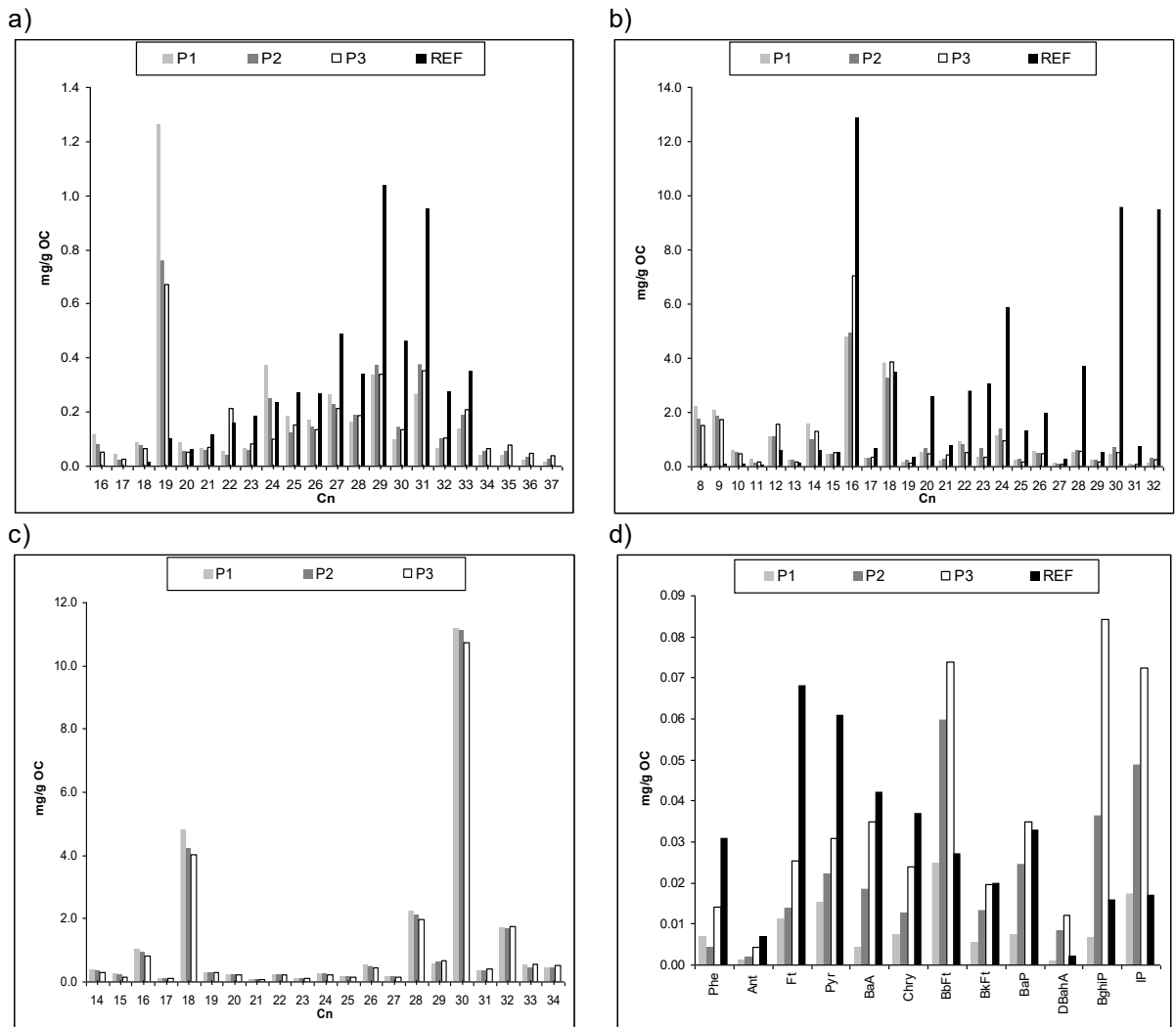


Figure 4

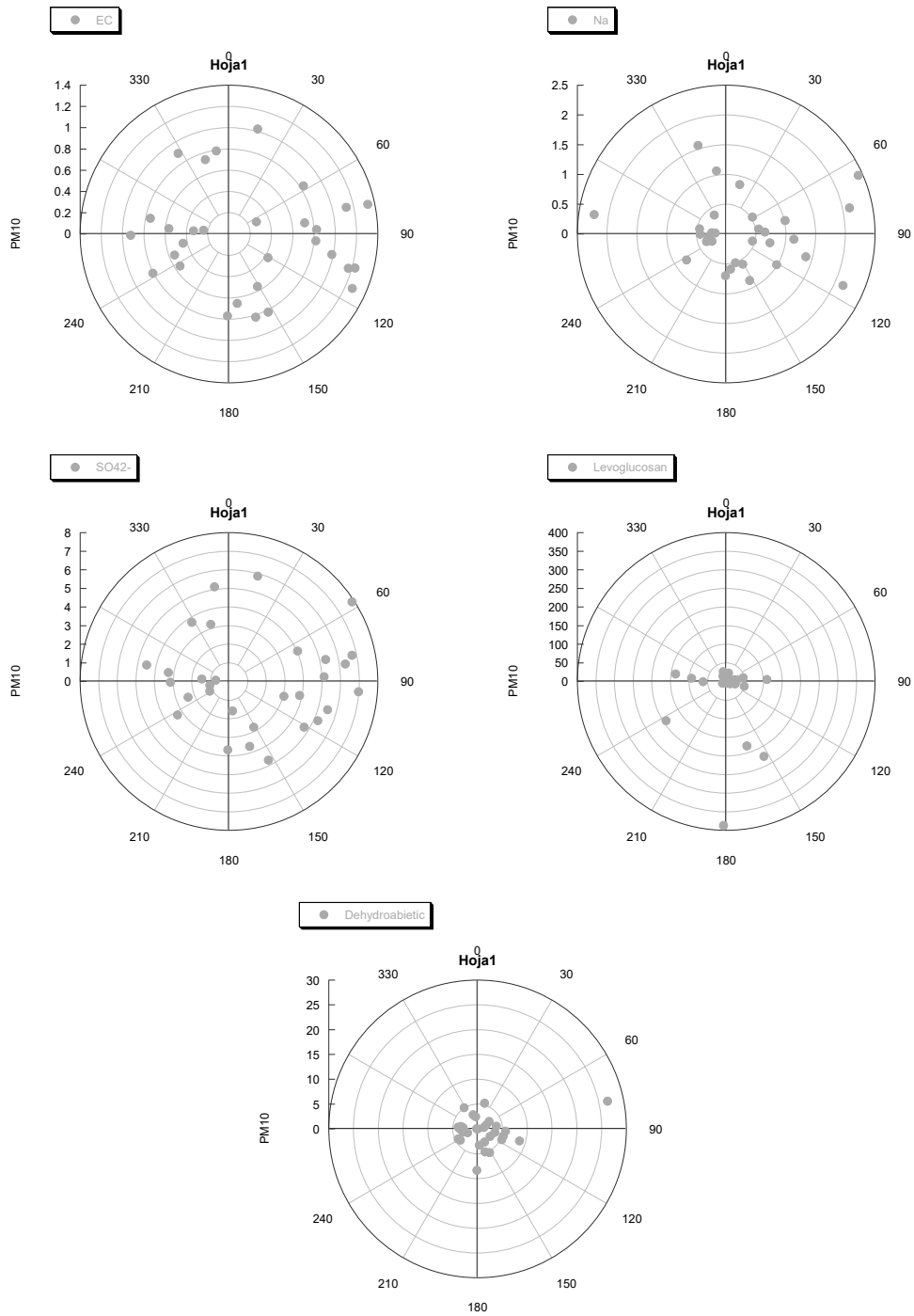


Figure 5

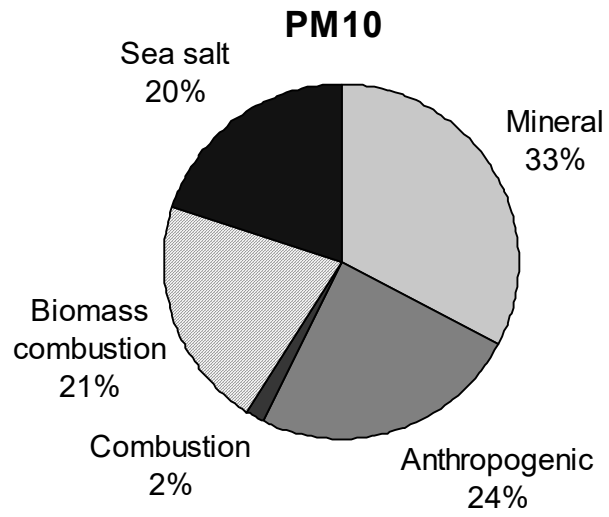


Figure 6

Table 1. Mean concentrations of major ($\mu\text{g}/\text{m}^3$) and trace (ng/m^3) elements and compounds in PM10 during open fire (P2) and non-open fire (P1) periods, their enrichment ratios (P2/P1), as well as mean values for the entire study period. Levog.: Levoglucosan. DHAA: dehydroabietic acid. OM+EC: organic matter + elemental carbon.

$\mu\text{g}/\text{m}^3$	Mean	P1	P2	P2/P1
PM10	26	17	32	1.9
OC	3.3	2.4	3.9	1.6
EC	0.8	0.6	0.8	1.3
WSOC	1.3	0.8	1.6	2.0
Al ₂ O ₃	0.5	0.4	0.4	1.1
Ca	1.3	0.9	1.7	1.9
K	0.3	0.2	0.4	2.2
Na	0.9	0.5	1.2	2.6
Mg	0.2	0.1	0.2	1.8
Fe	0.3	0.2	0.3	1.3
SO ₄ ²⁻	3.9	2.8	5.2	1.9
NO ₃ ⁻	1.7	0.8	2.6	3.2
Cl ⁻	0.5	0.3	0.7	2.7
NH ₄ ⁺	0.7	0.6	0.8	1.4
Oxalate	0.2	0.1	0.4	3.2
ng/m^3				
Levoglucosan	74	58	129	2.2
DHAA	4.4	3.7	3.2	0.9
C ₁₉	2.2	2.9	2.2	0.8
C ₂₉	1.2	0.8	1.5	1.8
C ₃₁	1.2	0.7	1.5	2.3
C ₁₈ -OH	10	11	10	0.9
C ₂₈ -OH	8	5	7	1.3
C ₃₀ -OH	29	26	35.1	1.4
C _{16:0}	18	11	18	1.6
C _{18:0}	11	9	12	1.3
Oleic acid (C _{18:1})	14	4.4	23	5.2
Li	0.3	0.2	0.3	1.5
P	31	28	37	1.3
Ti	26	21	25	1.2
V	9	5	16	2.9
Cr	3	1.7	4	2.3
Mn	7	5	9	1.9
Co	0.2	0.1	0.2	1.9
Ni	3.2	1.7	4.6	2.7
Cu	9	7	10	1.5
Zn	36	19	49	2.6
Ga	0.1	0.1	0.1	1.3
Ge	<0.1	<0.1	<0.1	0.7
As	0.9	0.6	1.1	1.9
Se	0.2	0.1	0.3	2.9
Rb	0.7	0.5	0.8	1.6
Sr	3.7	2.5	4.6	1.9
Zr	9	6	11	1.9
Mo	1.1	2.1	2.0	1.0
Cd	0.2	0.1	0.2	2.1
Sn	1.4	1.3	2.0	1.5
Sb	1.5	1.2	1.8	1.6

Cs	<0.1	<0.1	0.1	1.7
Ba	8	6	12	1.9
Pb	8	4	10	2.5
Bi	0.1	0.1	0.1	1.6
Th	<0.1	<0.1	<0.1	0.8
U	<0.1	<0.1	<0.1	0.6

Table 2. Summary of analytical results for organic compounds during the three episodes (P1, P2 and P3) compared with the rice straw burning profile (Hays et al. 2005). n.r.: no reference value available.

	P1	P2	P3	Hays et al. 2005
n-alkanes C₁₆-C₃₇				
Yield (mg/g OC)	0.015 – 1.26	0.024 – 0.757	0.025 – 0.672	0.015 – 1.037
<i>C_{max}</i>	<i>C₁₉, C₂₄, C₂₉, C₃₁</i>	<i>C₁₉, C₂₄, C₂₉, C₃₁</i>	<i>C₁₉, C₂₂, C₂₉, C₃₁</i>	<i>C₂₇, C₂₉, C₃₁</i>
CPI n>25	2.2	2.0	2.0	2.3
n-alkanoic acids C_{8:0}-C_{32:0}				
Yield (mg/g OC)	0.097 – 4.78	0.062 – 4.92	0.083 – 7.04	0.042 – 12.887
<i>C_{max}</i>	<i>C₁₆, C₁₈</i>	<i>C₁₆, C₁₈</i>	<i>C₁₆, C₁₈</i>	<i>C₁₆, C₂₄, C₃₀, C₃₂</i>
CPI	3.9	3.7	4.5	6.4
n-alkenoic acids				
C _{18:1} (mg/g OC)	1.90	4.84	5.07	10.772
C _{18:2} (mg/g OC)	0.578	0.339	0.332	6.943
Resin acids				
DHAA (mg/g OC)	1.53	0.950	1.74	0.067
n-alkanols C₁₄-OH-C₃₄-OH				
Yield (mg/g OC)	0.092 – 11.2	0.092 – 11.1	0.084 – 10.7	n.r.
<i>C_{max}</i>	<i>C₁₈, C₃₀</i>	<i>C₁₈, C₃₀</i>	<i>C₁₈, C₃₀</i>	n.r.
CPI	8.8	8.6	7.9	n.r.
Sterols				
Cholesterol (mg/g OC)	0.235	0.225	0.231	n.r.
PAH				
Yield (mg/g OC)	0.001 – 0.025	0.002 – 0.060	0.004 – 0.084	0.002 – 0.068
Max.	<i>BbFt, IP</i>	<i>BbFt, BghiP, IP</i>	<i>BbFt, BghiP, IP</i>	<i>Ft, Pyr, BaA</i>
Sugar derivatives				
Levoglucozan (mg/g OC)	20.7	27.5	20.1	126.5

Yield, average episode concentrations for the homologous series

C_{max}, The predominant homolog is italicized.

CPI, Carbon Preference Index, odd-to-even for n-alkanes, even-to-odd for n-fatty acids and n-fatty alcohols.

n.r., not reported.

PAH, Polycyclic Aromatic Hydrocarbons.

Table 3. Component loadings obtained after applying a Principal Component Analysis (PCA, Thurston and Spengler, 1985) with Varimax rotation to the PM10 data. The interpretation of the component loadings allowed us to identify 5 major PM sources. Loadings >0.65 are highlighted. Loadings <0.25 and >-0.25 are not shown. n=38 samples.

Mineral		Anthropogenic		Combustion*		Biomass		Sea salt	
Nd	0.93	Ni	0.83	DHAA.	0.89	C₃₀-OH	0.79	Na	0.89
Al₂O₃	0.92	NO₃⁻	0.82	Ge	0.75	C₂₈-OH	0.71	Cl⁻	0.87
Ce	0.90	V	0.79	Zn	0.73	C₂₉	0.69	Mg	0.82
Ga	0.89	Sn	0.78	C₁₈-OH	0.70	C₃₁	0.68	NO ₃ ⁻	0.38
La	0.86	Cu	0.75	Ti	0.68	WSOC	0.65	Ge	0.37
Rb	0.79	Oxalate	0.74	Co	0.68	OC	0.64	SO ₄ ²⁻	0.32
Fe	0.76	Pb	0.74	C _{18:0}	0.63	Levogluc.	0.61	Oxalate	0.31
Sr	0.71	SO₄²⁻	0.73	C _{16:0}	0.59	K	0.55	K	0.26
K	0.70	EC	0.67	Cd	0.47	C _{16:0}	0.53	Pb	0.24
P	0.68	Sb	0.65	Ba	0.44	C _{18:1}	0.41	Co	0.22
OC	0.63	Se	0.65	EC	0.43	Ca	0.40	Cd	0.21
Cs	0.62	As	0.64	Pb	0.43	Sr	0.36	Sb	-0.21
WSOC	0.60	Cs	0.63	Cr	0.38	Cr	0.35	Cu	-0.25
Ca	0.59	Cr	0.63	Sb	0.34	Oxalate	0.30	Sn	-0.26
As	0.59	Cd	0.62	Mn	0.34	P	0.29		
C ₂₉	0.59	NH ₄ ⁺	0.62	Oleic	0.29	V	0.28		
C ₃₁	0.58	Mn	0.61	Mg	0.25	C _{18:0}	0.25		
Ti	0.51	Co	0.53	Cl ⁻	0.23	Se	0.24		
Mn	0.43	Ba	0.51	C ₁₉	0.22	Rb	0.23		
Se	0.40	Oleic	0.49	Cu	0.22	Mn	0.20		
C ₃₀ -OH	0.39	Zn	0.49	Na	0.22	NH ₄ ⁺	-0.21		
C ₂₈ -OH	0.32	Fe	0.48			Ge	-0.23		
Mg	0.31	Rb	0.47			C ₁₈ -OH	-0.46		
SO ₄ ²⁻	0.29	P	0.47			C ₁₉	-0.63		
Oxalate	0.27	C _{18:0}	0.45						
Co	0.26	Sr	0.36						
V	0.24	La	0.35						
Sn	0.23	Ca	0.33						
EC	0.22	Ga	0.31						
Pb	0.22	Ti	0.28						
Cd	0.22	C _{16:0}	0.20						
Cu	0.21	Mg	0.20						
C _{18:0}	-0.22	WSOC	0.20						
Na	-0.23								
%Var	40	%Var	15	%Var	8	%Var	7	%Var	6

*Combustion = combustion different from rice straw burning, such as pine softwood combustion or combustion of other fuels (e.g., sporadic residential waste burning).