Characterization of organic aerosol at a rural site influenced by olive waste biomass burning

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HIGHLIGHTS

- Air pollution exceeds PM10 & PM2.5 limit values in Spanish rural areas in winter.
- GC/MS characterization of 77 polar and apolar organic compounds.
- Daily concentrations up to 26 ng m^{-3} of Benzo(a)pyrene were reached.
- Biomass burning was identified as the main source of many organic compounds.
- Other sources were biogenic emissions, SOA, soil dust and lubricating oil.

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ABSTRACT

Biomass burning is a major air pollution problem all around the world. However, the identification and quantification of its contribution to ambient aerosol levels is a difficult task due to the generalized lack of observations of molecular markers. This paper presents the results of a yearlong study of organic constituents of the atmospheric aerosol at a rural site in southern Spain (Villanueva del Arzobispo, Jaén). Sampling was performed for PM$_{10}$ and PM$_{2.5}$, and a total of 116 and 115 samples, respectively, were collected and analyzed by GC/MS, quantifying 77 organic compounds.

Higher levels of organic pollutants were recorded from November to March, coinciding with the cold season when domestic combustion is a common practice in rural areas. This jointly with adverse meteorological conditions, e.g. strong atmospheric stability, produced severe pollution episodes with high PM$_x$ ambient levels. High daily concentrations of tracers were reached, up to 26 ng m^{-3} for B(a)P and 6065 ng m^{-3} for levoglucosan in PM$_{2.5}$, supporting that biomass burning is a major source of pollution at rural areas.

A multivariate statistical study based on factor and cluster analysis, was applied to the data set with the aim to distinguish sources of organic compounds. The main resulting sources were related with biomass combustion, secondary organic aerosol (SOA), biogenic emissions, lubricating oil and soil organic components.

A preliminary organic source profile for olive wastes burning was evaluated, based on cluster results, showing anhydrosacharides and xylitol are the main emitted compounds, accounting for more than 85% of the quantified compounds. Other source compounds were fatty acids, diacids, aliphatics, sugars, sugar alcohols, PAHs and quinones.

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1. Introduction

Atmospheric particulate matter (PM) has recognized effects on climate, air quality and human health (IPPC, 2013; WHO, 2014).

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These effects depend on their physico-chemical properties. Among them chemical composition and size distribution are of special relevance. PM, either from natural or anthropogenic origin, can be primarily emitted by diverse sources or formed as secondary pollutants from precursors. Thus, their composition varies according to the characteristics of the emission sources as well as of the formation processes in the atmosphere. Nowadays aerosol organic composition is a major focus on atmospheric pollution research, since organic compounds represent a significant fraction of the PM mass (Jimenez et al., 2009; Hoyle et al., 2011, among others).

The EU Directive 2008/50/EC established daily and annual average limits in the ambient air for a number of atmospheric pollutants. Regarding organic compounds, a target value of 1 ng m^{-3} (annual average) for Benzo(a)Pyrene, B(a)P, measured as content in PM$_{10}$ (PM of aerodynamic diameter lower than 10 μm) is presently in force for the protection of health. This air quality standard has been frequently surpassed in air quality monitoring sites of different European countries, especially in urban and suburban locations in the last years (EEA, 2018). It has been estimated that 20−24% of the European urban population was exposed to B(a)P annual mean concentrations above the European target value between 2014 and 2016 (EEA, 2018). Emissions from the domestic combustion of coal and wood have been the main cause that produced relatively high ambient air concentrations of B(a)P. Moreover, the contribution of agricultural waste burning can be also relevant for some countries in Europe (EEA, 2014; EEA, 2015; EEA, 2018; Salvador et al., 2016; Sánchez de la Campa et al., 2018).

It is known that emissions from biomass burning are one of the main sources of primary and secondary organic PM (WHO, 2015; Denier van der Gon et al., 2015; Gao et al., 2108; Vicente and Alves, 2018). This type of PM is mainly made up of ultrafine particles (UFP, <100 nm) with a high content of organic compounds (80%) and a lower one of black-carbon BC (5−10%) and inorganic salts (10−15%) such as potassium, sulphate, chloride and nitrate (Sánchez de la Campa et al., 2018 and references therein). Bougiatioti et al. (2014) concluded that biomass burning can contribute almost half of the organic aerosol mass during periods with significant fire influence.

Several studies have been conducted in recent years to establish the contribution of biomass burning sources to pollution in different European regions. The AIRUSE-LIFE-AXA project has the main aim of improving air quality in Southern Europe by implementing source receptor techniques to PM levels and chemical composition data and suggesting air quality measures based on this information (http://www.cleanaircities.net/, last access September 2019). In the framework of this project, biomass burning contributions were estimated in five European cities based on measurements of tracers such as levoglucosan and K (Amato et al., 2016). Within the European project TRANSPHORM (Transport related Air Pollution and Health impacts- Integrated Methodologies for Assessing Particulate Matter), source apportionment results were obtained for 20 urban areas in Europe (Querol, 2016). These studies pointed out the different patterns of northern and southern regions across Europe, and showed that in rural areas and small towns, due to the widespread use of wood fuels, emissions of biomass burning in wintertime contribute to exceedances of the B(a)P target value of 1 ng m^{-3}.

So far, few studies have analyzed the health impact of PM produced by biomass combustion. However most of them provided evidences that biomass combustion processes may be a significant contributor to adverse health outcomes (WHO, 2013 and references therein). Linares et al. (2018) have recently analyzed the impact on daily mortality of PM$_{10}$ produced by biomass combustion from wildfires in the different geographical regions of Spain. The results indicated that in those regions where wildfires were most frequent, namely the northwestern, central and southwestern areas of the Iberian Peninsula, PM$_{10}$ was associated with higher daily mortality on days with biomass contributions than on other days across the period 2004−2009. Naeher et al. (2007) stated that most of the evidence on the health effects of residential wood combustion was indirect, because most of the studies analyzed had been conducted in areas affected by this source, but no specific indicators of wood combustion were available. More recently it has been confirmed that the toxicity of the emitted PM from biomass combustion can vary significantly but it seems to be clearly contingent on the organic fraction (Cassee et al., 2013). For this reason, it is urgent to perform comprehensive experimental studies devoted to obtain data on organic constituents of PM, in regions that could be under the influence of different sources of them, and especially where intensive biomass burning is carried out.

Spain has olive groves scattered over almost all the south of the country, where they made up 85% of the total area of Andalusia, Castilla-La Mancha and Extremadura today. Andalusian olive groves are the country's biggest producers and the world's leading olive tree grower, with over 1.5 million hectares, 900,000 tonnes of olive oil and 380,000 tonnes of table olives (AgroES, 2019). On average, Andalusian production accounts for 80% of national production and 30% of global production CAPDR, 2015. The main olive groves areas in Andalusia are Jaén (0.57 MHa), Córdoba (0.34 MHa) and Sevilla (0.22 MHa). Olive oil manufacture generates large amounts of agricultural wastes and of solid wastes with high humidity (water content up to 80%), which is treated and transformed in olive oil refineries. The oil extraction process also produces large quantities of wastewater. Current production techniques have adopted a two-phase system, which generates oil, waste water and a mixed solid-liquid waste called "alperujo" (a portmanteau from "orujo", essentially pulp, and "alpechin", the liquid waste). The alperujo is treated in secondary extraction plants to produce olive pomace oil (Sánchez de la Campa et al., 2018). The dry residues resulting from this process ("orujillo") together with the agricultural wastes are currently used as biofuel for residential heating and in the biomass boilers and energy production plants of <25 MW. It has been considered for years as an efficient and economical way for reducing olive wastes in this region. The processes related to the olive oil production last usually from November to March (Salvador et al., 2016; Sánchez de la Campa et al., 2018).

In recent years, several rural monitoring stations located close to olive groves in Southern Spain have registered a poor air quality, specifically due to high PM levels. It is especially noticeable the case of Villanueva del Arzobispo, a village (8400 inhabitants) located in one of the most relevant olive oil producing regions of Jaen. The annual reports on air quality in Spain by the Spanish Ministry for Ecological Transition (MITECO, 2016; 2017; 2018) showed that the PM$_{10}$ daily limit value - DLV (50 μg m^{-3} not to be exceeded more than 35 days/year according the 2008/50/EC European Directive) was exceeded in Villanueva del Arzobispo in 2015, 2016 and 2017. Furthermore, the annual PM$_{2.5}$ (PM of aerodynamic diameter lower than 2.5 μm) limit value (25 μg m^{-3}, according the above Directive) was exceeded in 2015 (the only excedence recorded in Spain).

Becerril-Valle et al. (2017) documented BC temporal patterns associated to the use of biomass burning after a source apportionment study based on an annual BC time series of aeathalometer measurements at Villanueva del Arzobispo. That study confirmed the dominance of this source in the BC aerosol component.

This paper presents a comprehensive chemical characterization of PM$_{10}$ and PM$_{2.5}$ samples obtained at Villanueva del Arzobispo, focusing on their organic composition. The most probable origin of

the organic compounds registered in the ambient aerosol in this area was determined by means of the analysis of their seasonal variations and by the application of different multivariate statistical techniques.

The main objective of this work was to relate organic compounds with their possible sources in this area, in order to establish key compounds to simplify the analytical procedure in future studies, reducing the expensive and time consuming analytical methods and also the number of samples in field campaigns.

The results obtained in this work can thus contribute to assess further policies for the control of emissions in this area.

2. Sampling and analysis

2.1. Sampling site

Sampling of PM_{10} and $PM_{2.5}$ was simultaneously performed from July 1st, 2014 to June 29th, 2015 at an air quality station in Villanueva del Arzobispo (38°10′28″N, 3°00′17″W, 692 m. a.s.l.), which belongs to the Andalucía Regional Air Quality Network (Fig. 1a). Meteorological parameters (wind speed and direction, precipitation temperature and relative humidity) and levels of gaseous pollutants (CO, NO, NO_2 and O_3) were also obtained during the period of study. Data were registered for 10 min periods.

Sampling site is located inside the town. It is surrounded by buildings where olive residues are widely used as biofuel for residential heating.

Industrial activities in the area are mainly related to olive oil production. At a distance of 3.8 km from the urban center, in a Northeast direction, there is an industrial complex which includes an olive oil extraction plant and a power plant partially fueled with olive waste biomass.

It is important to stress that the urban area of Villanueva is located inside the deep valley formed among the Guadalimar and Guadalquivir rivers. Therefore, it frequently experiences high stability and stagnant atmospheric conditions that give rise to the accumulation of local air pollutants.

2.2. PM sampling

Sequential high volume samplers Digitel, DHA-80 (30 m^3 h^{-1}) were used for collecting PM_{10} and $PM_{2.5}$ particles during the period of study. Those equipment are considered as reference samplers for PM_{10} and $PM_{2.5}$ particles according Annex B of EN 12341, 2014 standard (EN EN 12341, 2014 standard) in Europe (Commission Directive (EU), 2015/1480 of 28 2015). Samples were taken each 3 days. Quartz fiber filter (diameter 150 mm) previously baked at 450 °C for 3 h were used. Filters were conditioned and weighted in a conditioned room for gravimetric analysis according EN 12341, 2014. Finally, 116 and 115 samples of PM_{10} and $PM_{2.5}$, respectively, were collected. After sampling, filters were equilibrated, weighted and stored at −18 °C until analysis. Field blank filters were collected periodically and analyzed with each batch of samples in order to establish the artifacts due to adsorption of constituents into quartz filter during and after sampling.

2.3. Analytical characterization of organic compounds

A portion of 1/8 of each filter was extracted and derivatized based on methods previously described (Alier et al., 2013; Mirante et al., 2013).

Briefly, filter was spiked with 50 μL of surrogate standards (sedoheptulosan, n-C_{24}-d_{50}, succinic acid-d_4, anthracene-d_{10}, benzo(a)anthracene-d_{12}, benzo(k)fluoranthene-d_{12} and benzo(g,h,i)

a)

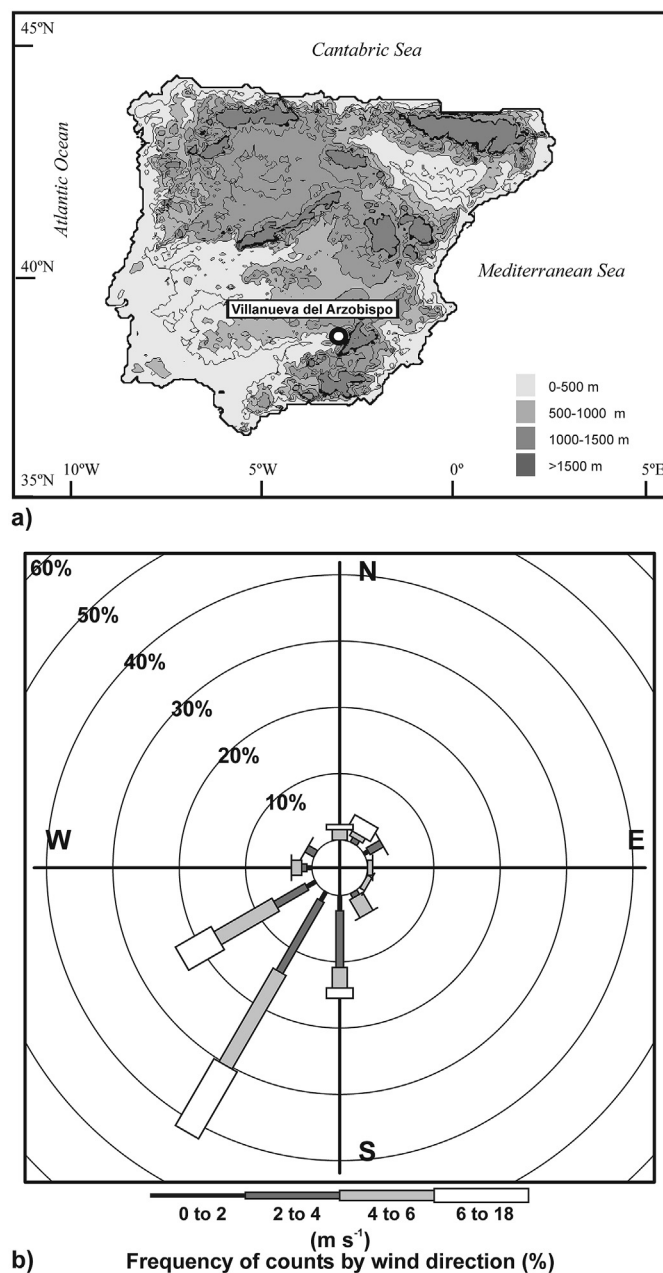**b) Frequency of counts by wind direction (%)**

Fig. 1. Location of Villanueva del Arzobispo in the Iberian Peninsula (a) and wind rose plot obtained from the wind speed and direction measurements registered at its air quality monitoring station during the sampling period (b).

perilene-d_{12}), and then sonicated in a closed culture tube with 5 mL of a mixture of dichloromethane:methanol 2:1 v/v during 15 min, by triplicate.

Result extract was filtered over a 0.45 μm PTFE membrane, and then concentrated to 1 mL blowing down with a nitrogen stream.

Polar compounds were derivatized to their trimethylsilyl esters as follows:

25 μL of the extract were evaporated until dryness under nitrogen, then 25 μL of BSTFA/TMCS, 25 μL of isooctane, 10 μL of pyridine and 5 μL of internal standard, palmitic acid-d_{31} were added, and then kept at 70 °C during 1 h.

2 μL of this solution were splitless injected into a GC/MS Agilent 7890/5977 A, equipped with a DB5MS column (60 m, 0.25 mm × 0.25 μm). Oven temperature started at 60 °C, hold

1 min, heated to 120 °C (rate 12 °C min^{-1}), then to 310 °C (4 °C min^{-1}), kept 10 min, for a total run time of 53 min. Injector temperature was 250 °C. Ion source was maintained at 230 °C, and the quadrupole at 150 °C. Helium was used as carrier gas at 1 mL min^{-1}. MS detector operated in electronic impact ionization mode at 70eV and SIM. Table 1 shows selected ions and polar analyzed compounds.

Peak identification was done by comparison of retention times with those of authentic standards when available, comparison of mass spectra with literature and library data.

Calibration curves (internal standard method) were constructed by analyzing aliquots of a stock solution of authentic standards in methanol, evaporated and derivatized in the way shown above. Results were corrected by the recovery of surrogate standards succinic acid-D$_4$ and sedoheptulosan.

No standards were available for 2-methyl glyceric, MBTCA, xylitol, mannitol, dehydrabietic acid, C5 alkene triols, 2-methylthreitol, 2-methylerytritol, sucrose and trehalose that were tentatively identified by their mass spectra and comparison with literature data.

For those compounds whose standards were not available, succinic or a-glucose curves were applied for semi-quantification.

The remaining extract (975 μL) was concentrated under nitrogen and re-dissolved in 0.5 mL of hexane:dichloromethane (9:1 v/v) for aliphatics, quinones and PAHs analysis.

A clean-up procedure on 1 g of activated alumina was applied. Apolar compounds were eluted with 4 mL of hexane:dichloromethane (9:1 v/v), then 4 mL of hexane:dichloromethane (1:2 v/v).

Obtained fraction was concentrated to 50 μL, internal standard (pyrene-d$_{10}$) was added and submitted to analysis by GC/MS:

2 μL of this solution were splitless injected into a GC/MS Agilent 6890/5975 B, equipped with a DB5MS column (30 m, 0.25 mm × 0.25 μm). Oven temperature started at 100 °C, hold 5 min, heated to 300 °C (rate 5 °C min^{-1}), keep 10 min, for a total run time of 50 min. Injector temperature was 280 °C. Ion source was maintained at 230 °C, and the quadrupole at 150 °C. Helium was used as carrier gas at 1 mL min^{-1}. MS detector operated in SIM mode and the electronic impact ionization mode at 70eV.

Compounds analyzed in this fraction, as far as selected ions for quantification are compiled in Table 2.

Table 1
Analytical parameters of identified polar compounds, and selected ions in MS detection.

	Compound	Ions (m/z)	Linear range (ng mL^{-1})	r^2	LOD (ng m^{-3})	RSD (%)
Diacids	Succinic-D$_4$ (Surrogate standard)	251				
	Succinic acid C4	247	0.02−2	0.9988	0.70	6
	Glutaric acid C5	261	0.02−2	0,9997	0.31	14
	Adipic acid C6	275	0.01−1	0.9999	1.3	11
	Pimelic acid C7	289	0.05−5	0.9999	0.48	8
	Suberic acid C8	303	0.02−2	0.9972	0.50	14
	Azelaic acid C9	295	0.02−2	0.9929	0.42	16
	Pthalic acid	295	0.02−2	0.9956	0.48	7
	Terepthalic acid	295	0.01−1	0.9974	0.15	11
Hydroxy/polyacids	Malic acid	245	0.02−2	0.9930	0.48	14
	Glyceric acid	292	0.02−2	0.9995	0.31	13
SOA tracers (α-pinene)	Cis-pinonic acid	171	0.02−2	0.9988	0.35	14
	Pinic acid	171	0.02−2	0.9999	0.18	13
	3-hydroxyglutaric acid	349	0.02−2	0.9996	0.84	14
	(MBTCA)[a]	405			0.50	16
SOA tracers (isoprene)	C5-alkene triol (1) [b]	231			0.26	13
	C5-alkene triol (2)	231			0.13	24
	C5-alkene triol (3)	231			0.82	13
	2-methylglyceric acid	219			0.33	13
	2-methylerythritol	219			0.52	13
	2-methylthreitol	219			0.55	3
Biomass burning tracers	Levoglucosan	204	0.02−2	0.9996	0.27	13
	Mannosan	204	0.02−2	0.9999	0.05	9
	Galactosan	217	0.02−2	0.9997	0.01	8
	Dehydroabietic acid	239			0.04	14
	Sedoheptulosan (surrogate standard)	217				
Fatty acids	n-C14	285	0.01−1	0.9954	0.81	14
	n-C15	299	0.02−2	0.9994	0.51	5
	Palmitic acid n-C16	313	0.02−2	0.9950	5.3	5
	n-C17	327	0.01−1	0.9981	0.91	17
	Estearic acid n-C18	341	0.01−1	0.9908	2.6	16
	n-C19	355	0.02−2	0.9996	0.50	18
	n-C20	369	0.02−2	0.9990	0.94	9
	n-C21	383	0.01−1	0.9988	0.17	18
	Palmitic acid-D$_{10}$ (Internal Standard)	344				
Alkenoic acids	Oleic acid	339	0.05−5	0.9990	1.5	3
	Linoleic acid	337	0.03−3	0.9997	0.15	8
Sugars	α-glucose	204	0.02−2	0.9960	0.42	17
	β-Glucose	204	0.02−2	0.9960	0.64	14
	sucrose	361			0.42	12
	trehalose	361			0.42	12
sugar alcohols	xylitol	217			0.02	11
	mannitol	319			0.06	14

[a] MBTCA: 3-methyl-1,2,3-butanetricarboxylic acid.
[b] C5-alkene triols: *cis*-2-methyl.1,3,4-trihydroxy-1-butene (1), *trans*-2-methyl.1,3,4-trihydroxy-1-butene (2) and 3-methyl-2,3,4-trihydroxy-1-butene (3).

Table 2
Analytical parameters of identified apolar compounds, and selected ions in MS detection.

	Compound	Ions (m/z)	Linear range (ng mL^{-1})	r^2	LOD (ng m^{-3})	RSD (%)
Aliphatics	n-C20	85	0.1−10	0,9999	0.023	16
	n-C21	85	0.1−10	0,9999	0.029	22
	n-C22	85	0.1−10	0,9998	0.045	12
	n-C23	85	0.1−10	0,9995	0.041	8
	n-C24	85	0.1−10	0,9994	0.046	10
	n-C25	85	0.1−10	0,9993	0.051	9
	n-C26	85	0.1−10	0,9994	0.050	8
	n-C27	85	0.1−10	0,9994	0.053	8
	n-C28	85	0.1−10	0,9994	0.045	10
	n-C29	85	0.1−10	0,9995	0.050	11
	n-C30	85	0.1−10	0,9995	0.054	12
	n-C31	85	0.1−10	0,9998	0.054	9
	n-C32	85	0.1−10	0,9994	0.067	22
	n-C33	85	0.1−10	0,9996	0.031	22
	n-C34	85	0.1−10	0,9992	0.050	22
	n-C24-d$_{50}$ (surrogate standard)	66				
PAHs	Phenanthrene	178	0.01−1	0,9880	0.002	5
	Anthracene	178	0.01−1	0,9930	0.005	7
	Fluoranthene	202	0.01−1	0,9993	0.002	8
	Pyrene	202	0.01−1	0,9996	0.002	9
	Benzo(a)Anthracene	228	0.01−1	0,9990	0.003	3
	Crysene	228	0.01−1	0,9996	0.003	6
	Benzo(b+j)Fluoranthenes	252	0.01−1	0,9988	0.004	2
	Benzo(k)Fluoranthene	252	0.01−1	0,9992	0.004	6
	Benzo(e)Pyrene	252	0.01−1	0,9917	0.002	4
	Benzo(a)Pyrene	252	0.01−1	0,9990	0.008	2
	Indene(1,2,3-cd)pyrene	276	0.01−1	0,9993	0.004	3
	Dibenzo(a,h)anthracene	278	0.01−1	0,9996	0.003	13
	Benzo(g,h,i)perylene	276	0.01−1	0,9997	0.003	4
	Coronene	300	0.01−1	0,9952	0.007	17
	Retene	219	0.01−1	0.9996	0.002	20
	Anthracene-d$_{10}$ (surrogate standard)	188				
	Pyrene-d$_{10}$ (internal standard)	212				
	Benzo(a)Anthracene-d$_{12}$(surrogate standard)	240				
	Benzo(k)Fluoranthene-d$_{12}$(surrogate standard)	264				
	Benzo(g,h,i)perylene-d$_{12}$ (surrogate standard)	288				
Quinones	9-fluorenone	180	0.01−1	0.9990	0.010	8
	Anthraquinone	208	0.01−1	0.9996	0.010	14
	Benzo(a)Fluorenone	230	0.01−1	0.9971	0.002	11
	Benzo(b)Fluorenone	230				10
	Benzanthrone	230				7
Hopanes	17(H)α-21(H)β-29-norhopane	191				7
	17(H) α −21(H)β-hopane	191				11

Internal standard method was used for quantification. Results were corrected by the recovery of surrogate standards: n-C24-d$_{50}$ for n-alkanes, Anthracene-d$_{10}$, Benzo(a)Anthracene-d$_{12}$, Benzo(k) Fluoranthene-d$_{12}$ and Benzo(g,h,i)perylene-d$_{12}$ for quinones and PAHs.

No standards were available for benzo(b)fluorenone, benzanthrone and hopanes. Calibration curves of benzo(a)fluorenone and benzo(a)pyrene were used for semi-cuantification of quinones and hopanes respectively.

Accuracy of method was checked by analyzing SRM1649b with each batch of samples, including control of those compounds, such as anhydrossacharides not certified but discussed in the literature (Larsen et al., 2006; Louchouarn et al., 2009; Gao et al., 2018).

Blank filters were also analyzed with each batch of samples. Small amounts of some analytes were encountered, typically some n-alkanes and fatty acids, which were less than 2% of compounds in real samples, or corrected to final results.

MDL were calculated as three times the standard deviation of results from analysis of six blank filters, and were estimated from 0.001 ng μL^{-1} for benzo(a)fluorenone to 0.17 ng μL^{-1} for hexadecanoic acid, which correspond to 0.01−5 ng m^{-3}, assuming a sample volume of 740 m^3.

Replicate analyses of six fractions of a filter sample showed that the precision of the method, expressed as RSD was below 20% for most analytes.

Analytical parameters of the method are summarized in Tables 1 and 2

2.4. Statistical data treatment

Wind rose and polar plot diagrams were performed using the OPENAIR package for R (Carslaw and Ropkins, 2012) using meteorological data, as well as PM$_{10}$ and PM$_{2.5}$ concentrations registered during the period of study. This software was specifically designed for processing air pollution and meteorological data (Carslaw, 2015).

Otherwise, when biomass combustion takes place, large amounts of numerous organic compounds are generated, mainly anhydrosugars, PAHs, methoxyphenols and resin acids (Vicente and Alves, 2018). In order to distinguish the different apportionments of organic compounds, different multivariate statistical methods, cluster and factor analysis (CA and FA, respectively), were used for data treatment. These analyses were done using Statgraphics Centurion XVII.

First, CA divided the set of samples into a given number of homogeneous groups, using Ward's method and Euclidean distance.

In this way, groups of similar samples in terms of seasonality and/or the levels of specific groups of organic compounds can be identified. Then, a varimax rotated FA was performed to identify the main sources or processes affecting the organic aerosol composition at the sampling site. With this statistical method a set of multiple intercorrelated variables (the chemical compounds analyzed) is replaced by a smaller number of independent variables (factors) by orthogonal transformations (rotations). Each factor is a linear combination of the original variables that explain a maximum of the total variability of the data set, and is uncorrelated with the rest. The coefficients of the linear combinations (loadings) represent the degree of correlation between the variables and the factor. Thus, the chemical compounds with higher loadings in each factor are interpreted as fingerprints of the emission source or the formation process that it represents. Finally, the factor scores were calculated for all the samples. The scores are the result of inserting the daily values of each organic compound in the factor equations. Thus, box and whiskers plots were obtained for each time series of factor scores corresponding to the samples grouped in the clusters. These plots were analyzed and interpreted with the aim to relate the factors with specific groups of homogeneous samples.

3. Results and discussion

During the period of study, mean PM_{10} and $PM_{2.5}$ concentrations recorded from gravimetric measurements reached 37 and 26 μg m^{-3}, respectively. Both levels fall in the usual 2000−2010 range of mean concentrations for urban background air quality monitoring stations in Spain (Querol et al., 2012), but these can be considered as very high when compared with the current concentrations (MITECO, 2018; EEA, 2018).

Strong seasonal variations were registered for PM mean concentrations with a drastic increase registered in the cold months from November 2014 to March 2015 (Fig. 2). At this time of the year the production of oil and the use of olive wood waste as biofuel increase in this region. The highest PM levels were reached in December 2014 and January 2015 when mean monthly PM_{10} and $PM_{2.5}$ concentrations exceeded 70 and 60 μg m^{-3}, respectively, coinciding with several periods of high atmospheric stability induced by the presence of stationary high pressure systems over the Iberian Peninsula (Fig. 3). During most of the spring, summer and autumn months mean monthly PM_{10} and $PM_{2.5}$ levels remained below 30 and 20 μg m^{-3}, respectively (Fig. 2).

The 90.4 percentile value of daily PM_{10} concentrations (equivalent to the 50 μg m^{-3} PM_{10} DLV not to be exceeded in more than 35 days/year, when the number of daily samples do not cover 365 days according the 2008/50/EC European Directive) reached 75.4 μg m^{-3}, thus exceeding the 50 μg m^{-3} PM_{10} DLV. In 21 out of the 116 PM_{10} daily samples, this DLV was exceeded, with 100 μgPM_{10} m^{-3} being exceeded during 6 days in December 2014−January 2015. Most of the PM_{10} DLV exceedances (20 out of 21) occurred from November 2014 to March 2015 (Fig. 2).

The wind rose for the whole sampling period indicates that the prevailing regional air flows over Villanueva del Arzobispo came from the S-WSW sector for any wind speed (Fig. 1b). However, the polar plot showed that the highest PM_{10}, $PM_{2.5}$, NO and CO levels were registered during low wind speeds and without any given prevailing direction (Fig. 4). Hence, it can be interpreted that high pollution is caused by the accumulation of the emissions from local combustion sources during the above mentioned periods of strong high stability. Due to the fact that the industrial complex is located downwind of the village, its emissions plume will be probably advected toward the Northeast direction across the valley. These results, thus discard a significant impact of the power plant emissions on the levels of atmospheric pollutants registered in Villanueva del Arzobispo during the period of study.

3.1. Chemical characterization

A summary of the results of the chemical characterization of the PM_{10} and $PM_{2.5}$ organic content in Villanueva del Arzobispo is included in Table 3, according to the season, for thirteen compounds classes based on functional groups and sources.

Results show a clear difference between spring and summer samples, when combustion related to olive processing was no significant, showing values of pollutants similar to other rural sites (Pindado et al., 2009), and autumn and winter samples.

Most organic compounds occurred in the fine PM fraction, as detailed below, increasing $PM_{2.5}$ levels during colder seasons (Fig. 5). It suggests the existence of a link between the emission and/or secondary production of most organic compounds and the olive processing and biomass combustion processes in the study area.

Only monosaccharides, related to soil dust contribution (Simoneit et al., 2004), and short-chain diacids, with diverse sources are predominately in the coarse fraction. So, unless indicated, described data would correspond to $PM_{2.5}$ results.

Sum of quantified organic compounds on average corresponds to a 2% of the total measured mass in $PM_{2.5}$ summer samples, increasing to 4 and 5% in spring and autumn respectively, and
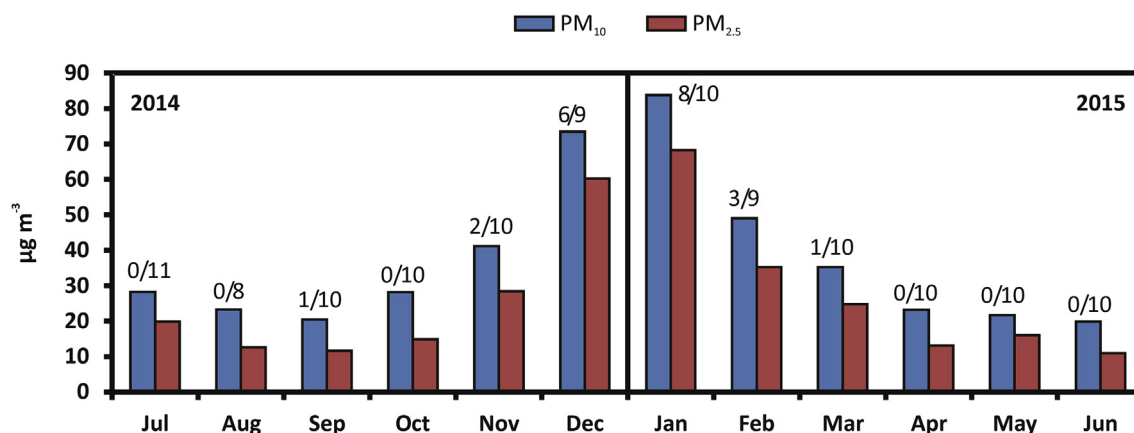

Fig. 2. Monthly mean PM_{10} and $PM_{2.5}$ levels registered at Villanueva del Arzobispo during the period of study, derived from the samples. The ratio between the number of exceedances of the PM_{10} daily limit value (50 μg m^{-3}) and the total number of PM_{10} samples is also highlighted for each month.
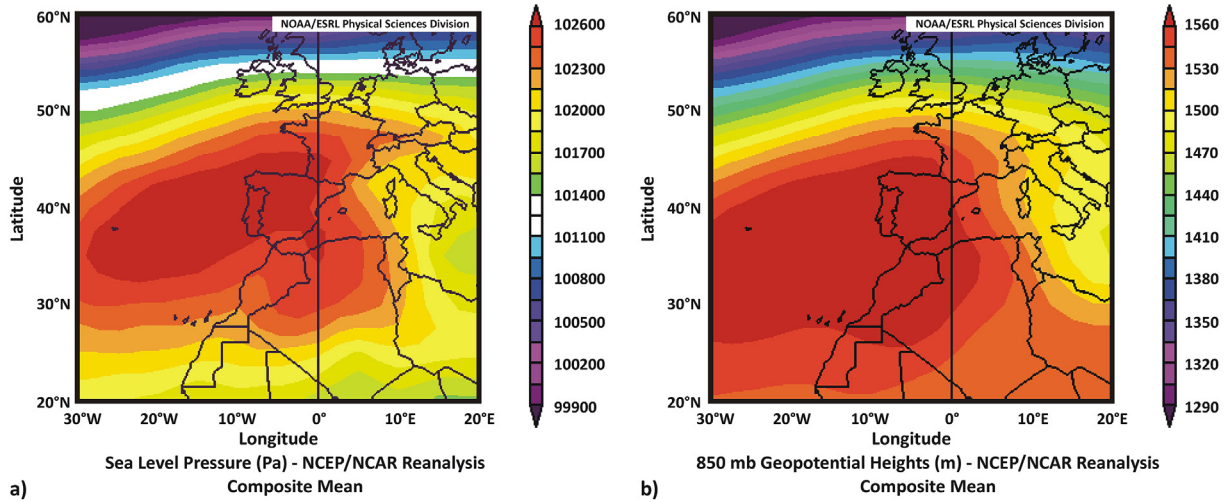
Fig. 3. Composite synoptic maps of Sea Level pressure (a) and Geopotential Height at the 850 mb level (b) for days in which the PM_{10} daily limit value was exceeded at Villanueva del Arzobispo in 2014. Those exceedances registered during African dust outbreaks were excluded. The meteorological variables used were obtained from the NCEP/NCAR Reanalysis datasets files (Kalnay et al., 1996), provided by the NOAA/ESRL Physical Sciences Division.
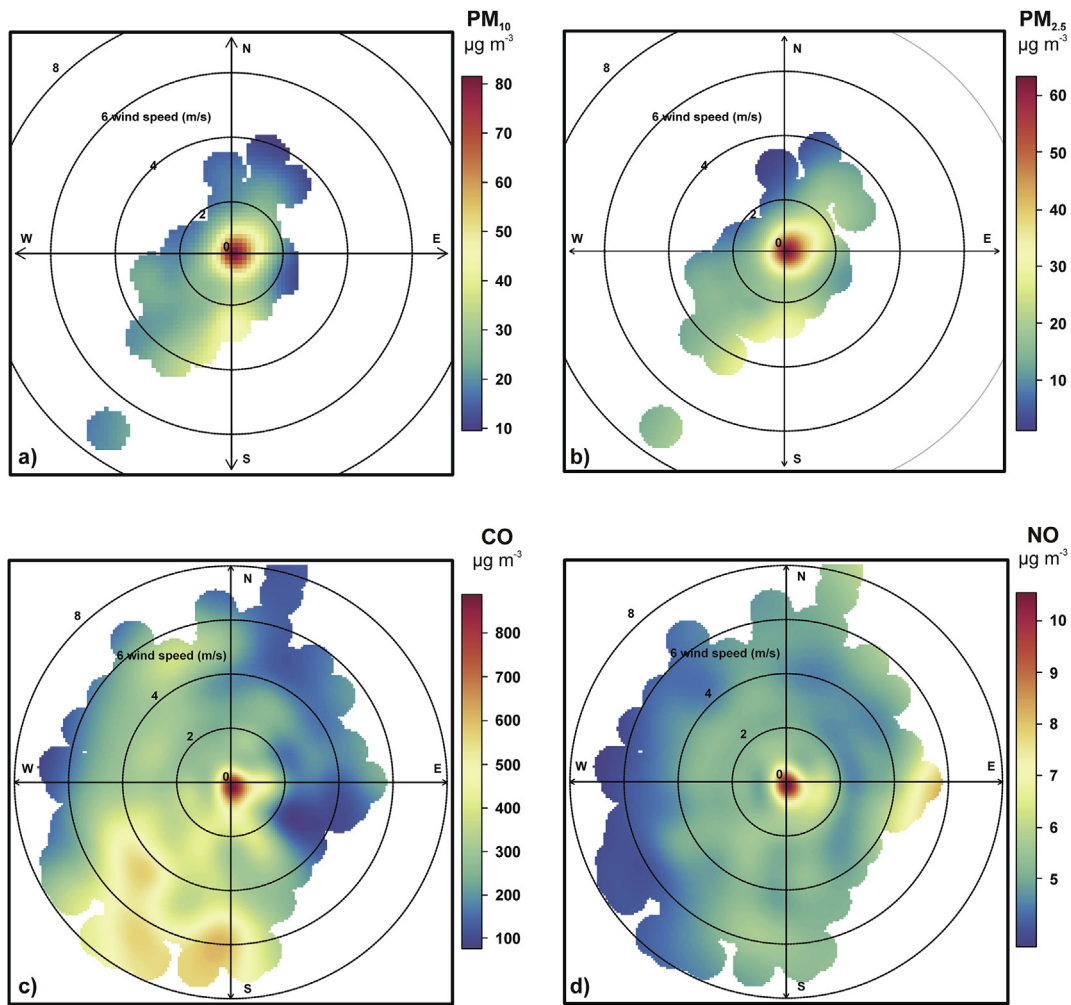

Fig. 4. Polar plots of daily PM_{10} (a) and $PM_{2.5}$ (b) levels and 10 min CO (c) and NO (d) levels as a function of the wind speed during the period of study.

Table 3
Mean concentrations (ng m^{-3}), according to season and families of analyzed compounds in PM$_{10}$ and PM$_{2.5}$ aerosols collected in Villanueva del Arzobispo from July 2014 to June 2015.

ng m^{-3}	PM$_{10}$					PM$_{2.5}$				
	Spring (n = 30)	Summer (n = 29)	Autumn (n = 28)	Winter (n = 29)	Annual (n = 116)	Spring (n = 29)	Summer (n = 30)	Autumn (n = 27)	Winter (n = 29)	Annual (n = 115)
$\sum$ n-alkanes	18.1	17.7	36.3	79.4	35.8	14.7	14.2	30.4	64.9	29.6
$\sum$PAHs	1.70	0.59	21.0	93.6	26.2	1.6	0.56	20.2	80.2	23.0
$\sum$ quinones	0.33	0.11	2.84	18.2	4.82	0.33	0.10	2.80	14.8	4.07
$\sum$ hopanes	0.24	0.07	0.20	0.56	0.25	0.24	0.07	0.18	0.53	0.24
$\sum$Diacids	41.8	52.6	108	186	95.7	37.1	48.6	85.1	172	84.1
$\sum$Hydroxy/polyacids	8.30	11.0	12.5	27.8	14.4	7.80	10.2	11.9	28.4	13.9
SOA tr (α-pinene)	11.4	29.1	17.1	23.0	20.4	12.1	29.7	16.3	21.6	20.1
SOA tr (isoprene)	22.5	35.5	6.70	8.70	19.4	10.4	18.6	3.00	5.40	10.3
Biomass burning tracers	73.1	20.1	1074	1220	530	70.3	15.6	1035	1316	534
Fatty acids	50.8	132	131	189	116	49.8	118	134	193	115
Alkenoic acids	6.40	8.70	26.5	36.8	18.0	9.50	7.70	25.7	32.0	17.1
Sugars	35.9	46.2	247	32.0	83.1	40.4	34.1	94.0	26.5	47.2
Sugar alcohols	61.9	33.5	204	197	114	27.7	13.8	158	182	84.0

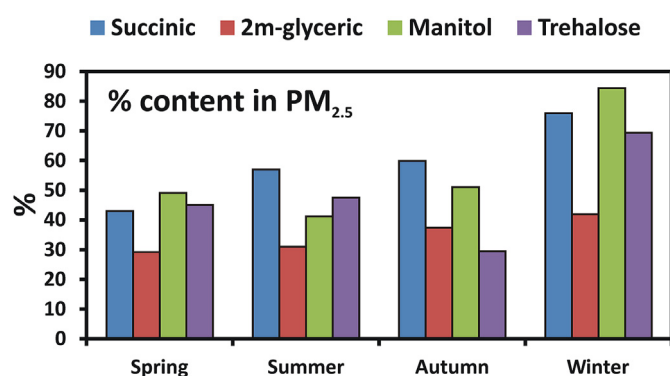**Fig. 5.** Percentage of selected compounds in the PM$_{2.5}$ fraction.

reaching up to 6% of the total measured mass in winter samples. It reflects the high contribution of biomass burning to the content of organic compounds, in accordance with Bougiatioti et al. (2014).

A preliminary cross-correlation analysis of the whole data set (PM$_{10}$ and PM$_{2.5}$) showed a strong correlation among PAHs, quinones, n-alkanes, anhydrosacharides, diacids and fatty acids ($r^2 = 0.7-0.9$). These compounds have been related with combustion sources such as biomass burning (Decesari et al., 2006; Alves, 2008 and references therein).

A good correlation among isoprene and α-pinene derivatives, tracers of biogenic secondary organic aerosol (BSOA), was also observed ($r^2 = 0.6-0.9$). Monosaccharides also showed good correlations among them ($r^2 = 0.6-0.9$). Hopanes only correlated with each other ($r^2 = 0.8$).

According to the families of analyzed organic compounds, the results obtained are discussed in the next sections.

3.1.1. Organic compounds related to biomass burning

PAHs, quinones, n-alkanes, anhydrosacharides, diacids and fatty acids showed the same pattern. These families were mainly contained in the PM$_{2.5}$ fraction and their levels increased several orders of magnitude during winter with respect to spring and summer seasons.

Aliphatic hydrocarbons are known to be emitted by two main sources: biogenic processes such as activity from higher plant waxes, wood-burning fires and oceanic aerosols, and anthropogenic emission related to fossil fuel combustion and vehicle exhausts (Simoneit and Mazurek, 1982; Mazurek et al., 1989).

Concentration levels of particulate n-alkanes were similar to those observed in other rural areas (around 14 ng m^{-3}) during summer and spring (Pindado et al., 2009), but increasing up to 65 ng m^{-3} in winter (Table 3).

PAHs are recognized as primary products of incomplete combustion of fossil fuels and are emitted in large amounts during biomass combustion (Rooge et al., 1998; Alier et al., 2013).

Spring and summer results were similar to those obtained at other European rural areas (total PAHs 1.6 and 0.56 ng m^{-3} respectively) (Pindado et al., 2009; van Drooge and Grimalt, 2015). But in the cold seasons, especially during winter, their concentrations increased up to very high levels (autumn and winter total PAHs were 20 and 80 ng m^{-3}, respectively). These results point to biomass combustion as one of the main sources of PAHs in the study area, and evidence the exposure risk of population to these elevated levels. The high levels of PAHs in rural areas during winter has been previously discussed in the literature (Van Drooge and Grimalt, 2015), and are mainly attributed to biomass burning in combination with highly stable atmospheric conditions.

B(a)P annual concentrations reached 2.1 ng m^{-3}, quite higher than the annual target value (ATV, 2008/50/CE, 1 ng m^{-3}) showing a maximum daily mean value of 26 ng m^{-3}, and a seasonal mean value during winter of 7.3 ng m^{-3}.

These levels can be comparable to results from polluted urban areas in China (Wang et al., 2009) where B(a)P reached average concentrations of 33 and 11 ng m^{-3} in spring and winter respectively.

Quinones are toxic compounds emitted during incomplete combustion or through reaction of PAHs with atmospheric oxidants (Van Drooge and Grimalt, 2015).

The highest concentrations were found during winter (14.8 ng m^{-3}), and the lowest values were registered during summer (0.1 ng m^{-3}).

The most frequently quantified products associated to biomass burning **are levoglucosan** and its isomers, galactosan and mannosan. They are generated by thermal decomposition of cellulose and hemicellulose (Simoneit et al., 1999; Simoneit, 2002, Vicente and Alves, 2018).

In the study area, only summer samples presented values typical for zones with low influence of biomass burning (Puxbaum et al., 2007), whereas daily mean concentrations up to 6066 ng m^{-3} were reached for levoglucosan in PM$_{2.5}$ samples during winter. Marked seasonal variations in concentrations have also been documented by other authors (Jedynska et al., 2014, Van Drooge and Grimalt, 2015).

Dehydroabietic acid, a more specific biomass-burning tracer of conifer resin (Rooge et al., 1998; Medeiros and Simoneit, 2007) was

also measured. As it was observed for the other biomass burning tracers, the concentrations increased during the cold periods (from 4.0 ng m^{-3} in spring to 55 ng m^{-3} in winter).

Dicarboxylic acids have been identified as ubiquitous organic aerosol constituents, which may derive from photo oxidation of organic precursors of both anthropogenic and biogenic origin, as well as direct emission from fossil fuel or biomass combustion (Rooge et at. 1993; Kawamura and Ikushima, 1993).

The relative importance of primary emissions and secondary production of dicarboxylic acids in the atmosphere is still poorly understood, in spite of their strong contribution to the total organic fraction in the aerosol. It can range from 40% to 90% (Ho et al., 2007; Van Drooge and Grimalt, 2015).

The average total concentration of aliphatic dicarboxylic acids in winter was 172 ng m^{-3} (Table 3). High concentrations of dicarboxylic acids have been found in plumes from biomass burning (Rooge et al., 1991). Photooxidation is a likely source of these compounds in the aerosol (Graham et al., 2002). Results obtained in this work (37 ng m^{-3} in spring, 49 ng m^{-3} in summer) suggest that secondary formation of these compounds was more important in summer, but the general trend suggests that other sources, such as biomass combustion, could be dominant. When it comes to the quantified diacids, succinic was the most abundant. Oxalic acid is usually the most abundant species, followed by malonic and succinic acids, but the two formers were not analyzed.

Pthalic acid is considered a secondary organic tracer for fossil fuel combustion. This compound is emitted from combustion sources and/or has been considered to generate in the atmosphere by the photochemical oxidation of PAHs such as naphthalene (Kawamura and Ikushima, 1993). Seasonal trends point to biomass burning as a major source of this compound, due to the fact that during the warmer seasons its values remained very low (1.6 ng m^{-3}) but increased during the autumn and winter up to 10 ng m^{-3}.

The same trend was observed for terepthalic acid. That is, low mean spring value (2 ng m^{-3}) and much higher mean winter values (50 ng m^{-3}). These results also suggest a strong influence of the combustion processes.

Terepthalic acid is a tracer for plastic waste burning. It has been found in high concentrations in smoke plumes from open burning of plastic bags and landfill trash (Simoneit et al., 2005).

Azelaic acid (C9) is considered a specific photochemical oxidation product of biogenic unsaturated fatty acids (Kawamura and Sakaguchi, 1999). The mean seasonal concentrations of azelaic acid (9 ng m^{-3} in summer and 46 ng m^{-3} in winter) showed the same pattern of other dicarboxylic acids.

Fatty acids are emitted to the atmosphere from different sources. They can be biogenic or anthropogenic in origin. Sources of lower homologues (<C20) can be microbial, cooking and food preparation, but have also been found in emissions from petroleum based sources (Pio et al., 2001).

Palmitic acid (C16) and in a lower proportion stearic acid (C18) were the most abundant fatty acids in all the samples. The highest mean seasonal values of the sum of the concentrations of the C14 to C34 acids were found during winter (193 ng m^{-3}) probably due to the influence of the biomass burning processes (Table 3). Significantly lower mean values were obtained in spring (50 ng m^{-3}) and summer (118 ng m^{-3}).

Two alkenoic acids, oleic and linoleic acids, were also quantified. Mean seasonal variations of the sum of both compounds (Table 3) were similar to those obtained for other compounds (minimum values in summer and maximum in winter, 7.7 ng m^{-3} and 32 ng m^{-3}, respectively). The main source of these compounds is usually cooking, but they can also be generated by traffic and emitted by biogenic sources (Rooge et al., 1991).

The temporal pattern found for the values of these compounds at the sampling site indicates that they may be released during the burning of olive branches.

3.1.2. BSOA tracers

Cis-pinonic acid, pinic acid, 3-hydroxyglutaric acid and MBTCA are considered BSOA **tracers for α-pinene oxidation** (Ding et al., 2014; Fu et al., 2010).

Maximum concentrations of the sum of the four compounds were found in summer (30 ng m^{-3}).

MBTCA was registered in the PM$_{2.5}$ fraction, and the higher concentrations (8.9 ng m^{-3} in summer, 1.4 ng m^3 in winter) found in the summer period were similar to those found in other studies (Alier et al., 2013).

Cis-pinonic, 3-hydroxyglutaric and pinonic acids showed higher concentrations during summer and winter (*cis*-pinonic 6.4 ng m^{-3} in summer, 8.4 mg m^{-3} in winter; pinonic 9.0 ng m^{-3} in summer, 7.7 ng m^{-3} in winter; 3-hydroxyglutaric 4.9 ng m^{-3} in summer, 5.6 ng m^{-3} in winter), indicating either photodegradation in summer and biomass burning during winter.

Oxidation of isoprene generates C5-alkene triols, 2-methylglyceric acid, 2-methylthreitol and 2-methylerythritol (Claeys et al., 2004; Ding et al., 2014). High correlations (r^2>0.7) were found among six compounds.

The highest mean concentrations of the sum of the six compounds were found in summer (19 ng m^{-3}). The lower mean winter concentrations (5.4 ng m^{-3}) indicated that isoprene was emitted from vegetation and was not related to biomass burning, which is in agreement with previous studies (Alier et al., 2013).

3.1.3. Hopanes

17(H)α-21(H)β-29-norhopane and 17(H)α-21(H)β-hopane are molecular markers for mineral oils, and their presence can be related to unburned lubricating oil residues from vehicles emissions (Rooge et al., 1993; Alier et al., 2013).

Mean seasonal values of the sum of both hopanes (0.07 in summer and 0.53 ng m^{-3} in winter) were similar to those found in other rural sites (Wang et al., 2009; Harrison and Yin, 2010).

Finally, hopanes were not correlated with other measured organic compounds in this area of study. They were only well correlation between them (r^2 > 0.8).

3.1.4. Sugars and sugar alcohols

Alpha, beta-glucosa, sucrose and trehalose are constituents of soil dust and related to plant tissue and microorganisms. They are also present in residues generated after biomass combustion (Simoneit et al., 2004; Van Drooge and Grimalt, 2015).

Xylitol and mannitol are reduced sacharides associated with organic matter in soils. Mannitol is a tracer for airborne fungal spores (Simoneit et al., 2004; Fu et al., 2016).

These compounds were found mainly in the coarse fraction of

Table 4
Seasonal diagnostic ratios.

	ratio	Spring	Summer	Autumn	Winter	mean
ANT	Ant(Phe + Ant)	0.13	0.01	0.08	0.16	0.13
FA	FA(FA + Pyr)	0.43	0.60	0.46	0.43	0.43
BAA	B(a)A/(B(a)A + Pyr)	0.43	0.60	0.46	0.43	0.43
BAP	B(a)P/(B(a)P + B(e)P)	0.49	0.46	0.54	0.59	0.57
IP	ip/(ip + bgp)	0.72	0.20	0.50	0.51	0.51
RET	retene/(retene + crysene)	0.03	0.49	0.29	0.53	0.14
	malic/(malic + succinic)	0.59	0.63	0.38	0.33	0.43
L/M	levoglucosan/mannosan	12	6.2	11	10	14
	oleic/stearic	0.3	0.1	0.2	0.6	0.3

aerosol in Villanueva del Arzobispo, which is related to the prevalent soil dust contribution. Mean seasonal values of the sugars and sugar alcohols in PM_{10} were higher during autumn (247 ng m^{-3} and 204 ng m^{-3}, respectively).

Sugar alcohols in the $PM_{2.5}$ fraction presented higher mean values in winter (182 ng m^{-3}) than in summer (14 ng m^{-3}). Xilitol has been previously correlated with levoglucosan and its isomers, indicating that it was also emitted during biomass burning (Urban et al., 2014).

3.2. Diagnostic ratios

PAHs diagnostic ratios according to season can be found in Table 4. These indices have been widely used to distinguish sources of combustion but, unfortunately, there are not definitive values for a given source. They can be similar for many sources and can change during the environmental fate of these compounds (Tobiszewski and Namiesnik, 2012).

Winter ANT, FA, BAA, and IP ratios (0.16, 0.43, 0.43 and 0.51, respectively) obtained from the Villanueva del Arzobispo samples are typical of vegetation and wood combustion, and can be related to burning of olive waste (Pies et al., 2008; Galarneau, 2008).

Lower values of ANT, BAP and IP ratios during summer indicate the photodegradation of these compounds (Ladji et al., 2007).

B(a)P is photodegraded more rapidly than its isomer B(e)P. Their ratio, BAP, is considered to be a marker of atmospheric particle ageing and the photodegradation of PAHs. The lower mean value of the BAP ratio obtained for the summer period (Table 4) can be explained by the enhanced photodegradation of B(a)P and the lower biomass combustion emissions produced in this season. This ratio is increasing with lower temperatures according to seasons.

Retene is considered a marker of pine wood combustion, but it can also be found in smoke for other wood types, such as oak (Rooge et al., 1998; Alves et al., 2012). Retene concentrations were very low during spring, summer and autumn (0.01−0.1 ng m^{-3}), and increased up to 1.8 ng m^{-3} during winter.

Values of the ratio Ret/Ret + Cry in the range 0.8−1.0 indicates softwood burning (Beizhan et al., 2005; Tobiszewski and Namiesnik, 2012), whereas hardwood burning can consistently reduce this index. In this work, this ratio was about 0.5 either in summer and winter, decreasing the rest of the seasons, which could indicate hardwood combustion (Beizhan et al., 2005).

Malic acid is a product of the OH oxidation of succinic acid (Kawamura and Ikushima, 1993; Van Drooge and Grimalt, 2015) as a consequence of photochemical aging.

The ratio malic/(malic + succinic) was around 0.6 in the summer and spring periods and 0.3 during winter and autumn (Table 4). These values indicate that malic acid was likely formed by photochemical reactions rather than combustion processes. Similar results have been observed elsewhere (Van Drooge and Grimalt, 2015).

Regarding **anhydrosugars,** the relative contributions of the isomers depend on the type of biofuel, and can be used to differentiate hardwood and softwood burning or allow differentiate combustion conditions (Simoneit, 2002; Fu et al., 2016; Vicente and Alves, 2018). Thus, the ratio levoglucosan/mannosan (L/M) in smoke from softwood has been reported to be around 5, whereas this ratio for hardwood burning is usually in the range 10−20.

High levoglucosan concentrations with respect to mannosan and galactosan (88% sum of 3 compounds), can indicate the great influence of hardwood combustion in the area of study. The ratio L/M presented values close to 10 during the cold periods (Table 4), which is consistent with this suggestion. Lower values in summer, as retene proportions showed above, could be associated with different sources. Due to the fact that olive is considered hardwood, this could indicate the impact of combustion of rests of the olive pruning in residential workplaces.

Becerril-Valle et al. (2017) showed a good correlation of levoglucosan with estimated equivalent black carbon (eBC), proving olive wood was the main biomass burning organic aerosol source in this site.

When the ratio **oleic acid/stearic** acid is higher than 1 it is interpreted as there have been significant contributions from food cooking (Abdullahi et al., 2013). In this study a mean value of 0.6 was obtained for the ratio in winter, which decreased to values in the range 0.1−0.3 in summer (Table 4). It indicated that food
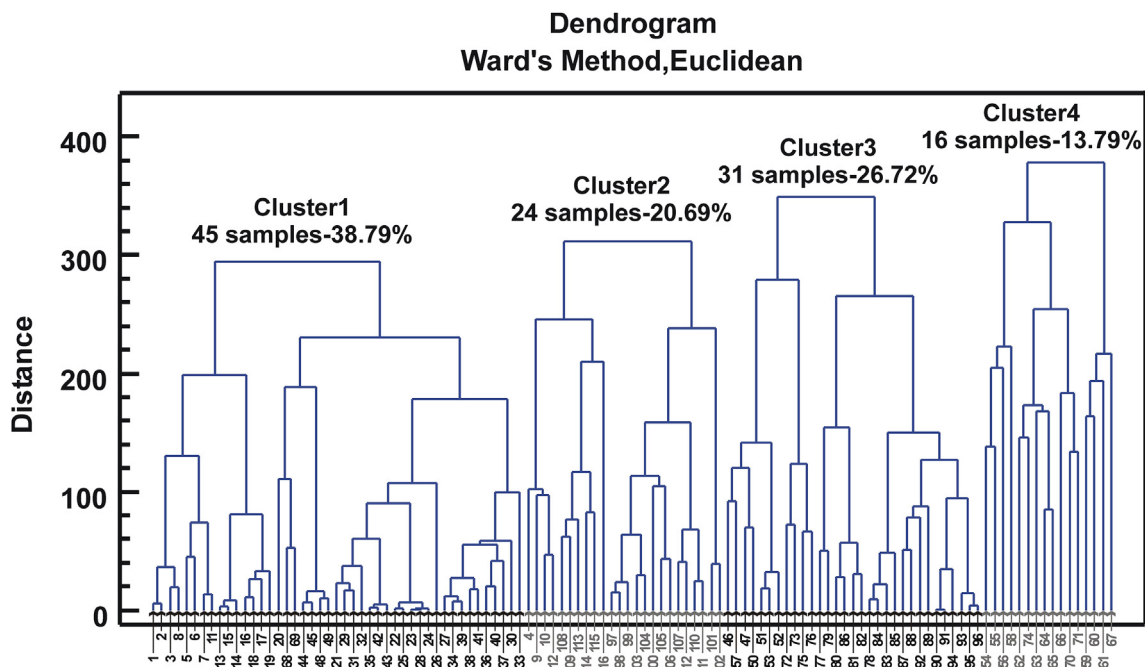

Fig. 6. Dendrogram and membership of cluster analysis.

Table 5
Eigenvalues and accumulated variance of factors.

Factor Analysis			
Factor *Number*	*Eigenvalue*	Percent of *Variance*	Cumulative *Percentage*
1	41.4936	57.630	57.630
2	7.6418	10.614	68.244
3	5.093	7.074	75.317
4	3.58544	4.980	80.297
5	3.31118	4.599	84.896
6	1.46263	2.031	86.927
7	1.07173	1.489	88.416

cooking was not an important source in this case.

3.3. Multivariate analysis

Cluster analysis allowed sharing the set of samples into four homogeneous groups. Fig. 6 shows the dendrogram obtained as far as the member number of each group.

Cluster 1 (45 samples) includes summer samples (July–August) as well as low pollution samples obtained in other months (November and January).

Cluster 2 (24 samples) includes spring and summer samples (May–August), characterized by low pollution and higher BSOA levels.

Cluster 3 (31 samples) includes those samples collected from November to April, showing intermediate pollution levels.

Cluster 4 (16 samples) corresponds to samples collected during December, January and February, being the most polluted ones.

The varimax rotated FA for the PM$_{2.5}$ fraction showed 7 main factors explaining 88.4% of the variance (Table 5). Factor loading matrix, after varimax rotation, is given in Table S1.

Box and whisker plots of clusters against factor scores are shown in Fig. 7.

Factor 1 was associated with biomass combustion processes. This factor explains 58% of the variance. It is formed by primary biomass burning compounds, mainly PAHs, quinones and aliphatic
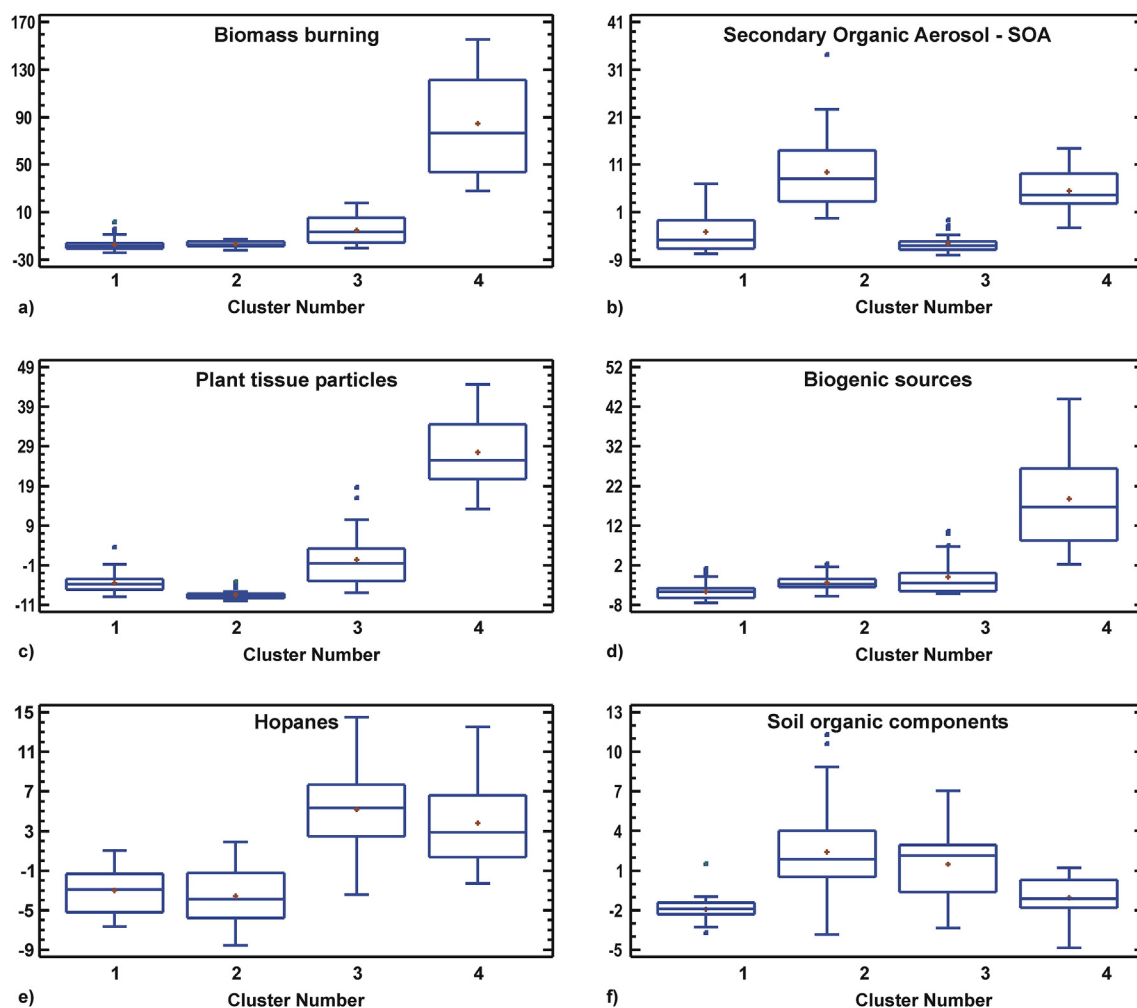

Fig. 7. Box and whisker plots of clusters against main factors.

hydrocarbons (score 0.98−0.84). The presence of dicarboxylic and fatty acids (scores 0.80−0.77), levoglucosan (score 0.97) and its isomers (score 0.77) could be related to burning of biomass resulting from olive oil industry (olive tree branches and orujillo). Dehydrabietic acid and retene showed also positive but lower scores for this factor (around 0.7), suggesting that the contribution from pine wood was not predominant in the area of study. The main contributions to this factor were obtained from the winter samples included in Cluster 4, from 19 December to 20 February, when high pollution episodes occurred and the highest levels of B(a)P were reached (Fig. 7).

Factor 2 could be related with the generation of SOA. This factor included high loadings for 2-methylgliceric acid, C5-alkenetriols, malic acid, 2methyleritrol and treithol, 3-hydroxyglutaric acid and MBCTA (scores 0.86−0.78), and to less extent by pinic (0.72) and cis-pinonic (0.38) acids. These compounds were mainly registered in the fine fraction and showed higher values in the spring and summer than in the other seasons. The lower loadings obtained for cis-pinonic acid suggested that this factor represented aged aerosol. Cluster 2 presented the highest scores for this factor (Fig. 7). It included samples from May, June, July and one of August.

Factor 3 included higher molecular weight n-alkanes (score 0.88−0.67) that can be attributed to biogenic primary sources, such as plant tissue particles. These compounds showed a similar seasonal trend of factor 1 (Fig. 7) as they were also emitted in high concentrations during biomass combustion processes.

Factor 4 could be allocated to biogenic sources. This factor included positive loadings for succinic, glutaric, pthalic and azelaic acids, C14 acid and glucose (scores 0.87−0.45). It showed a similar trend than factors 1 and 3 (Fig. 7) and included compounds that could be both emitted by biogenic sources or during combustion.

Factor 5 only showed contribution from hopanes (scores 0.82−0.65). Clusters 3 and 4 showed the highest scores for this factor (Fig. 7). These clusters gathered samples corresponding to the period November−April, when traffic emissions usually reach their highest values in urban and suburban sites. Hopanes concentrations were very low along the sampling period. These are constituents of lubricating oils from vehicles, and this factor may represent punctual traffic close to the sampling site.

α, β-glucose and sucrose showed high loadings for **factor 6** (scores 0.82−0.51). These are structural molecules of biological systems, such as plant tissue and microorganisms (fungi and bacteria) and form part of the soil dust. They were contained predominately in the coarse fraction, suggesting that their origin could be associated with wind erosion and incoming of soil particles into the atmosphere by resuspension processes. For this reason factor 6 was related with soil organic components. Low scores for this factor were found during the pollution episodes (cluster 4) being the samples contained in cluster 2 and 3 (summer and winter low polluted samples) those that contributed the most to this factor.

Factor 7 did not show clear contributions, so it was finally assigned to mixed sources.

According to these results, an approximation of organic species profile of olive waste biomass burning on the quantified compounds has been determined (Sun et al., 2019). For this purpose, the mean % mass of each organic compound to the total mass of aerosol was calculated for the set of samples included in cluster 4, which corresponds to the most polluted samples, and related to olive waste burning. As many of the studied compounds have shown to be related to different sources, a subtraction was made for the same calculation for samples included in Cluster 2, which were spring and summer samples characterized by low pollution, and taken as a blank. Results are shown in Table 6.

Table 6
Organic profile in $PM_{2.5}$ from olive wastes burning.

COMPOUND	% mass	% organics
succinic	003	068
glyceric	001	025
galactosan	024	51
mannosan	027	58
pthalic	002	034
levoglucosan	32	68
xilitol	031	67
terepthalic	009	19
azelaic	007	14
a-glucose	006	13
manitol	005	11
b-glucose	002	037
linoleic	002	036
oleic	004	082
dehydrabie	003	0,60
0:C20	003	0,65
0:C21	001	027
C23	001	012
C25	001	019
C27	001	018
phenanthrene	0001	001
antracene	0000	000
fluorantene	0011	023
pyrene	0015	031
retene	0002	004
b(a)a	0010	021
chrysene	0014	030
B(b+k)FA	0024	051
B(e)P	0009	020
B(a)P	0014	030
inde(cd)pyr	0.014	0.31
dib(a,h)A	0.002	0.05
B(ghi)per	0.013	0.29
coronene	0.012	0.26
90fluorenone	0.001	0.03
antraquinone	0.008	0.17
B(a)fone	0.007	0.15
B(b)fone	0.005	0.11
bzantrone	0.006	0.12
∑PAHs	0.142	3.0
∑anhydrosugars	3.71	79
∑sugars/sugar alcohols	0.44	9.4

Levoglucosan accounted for a 68% of total quantified organic compounds, followed by xilitol (6,7%), galactosan and mannosan (5−6%), while sum of PAHs represents a 3% of the profile.

4. Conclusions

The identification of sources contributing to levels of specific organic compounds in the atmospheric aerosol is crucial to assess policies on the control of emissions in areas where the exceedances of PM_x air quality standards are frequent. Biomass burning is presently a major global air quality concern. Moreover, many recently published studies have shown that it is a major contributor to the atmospheric PM levels, especially at rural areas. In Villanueva del Arzobispo (Jaen, Southern Spain), due to the widespread use of olive waste as biofuel for domestic heating during winter, emissions of biomass burning have been found to contribute to exceedances of the PM_{10} and $PM_{2.5}$ standards.

The analysis of 77 organic species in PM_{10} and $PM_{2.5}$ samples along a year in this site allowed us to identify the main sources contributing to increased levels of the organic aerosols according to their particle size after multivariate analysis. The factors identified showed the main sources and seasonal variation of these compounds.

The main contribution is related to biomass combustion. This

factor explained 58% of the variance, corresponding to aerosols collected in winter. It was identified as the main source of PAHs, quinones, aliphatic hydrocarbons, dicarboxylic and fatty acids, levoglocosan and its isomers. The combination of the geographical and meteorological conditions of the study area, with widespread use of olive wastes as a fuel for domestic heating, produced severe pollution episodes, with B(a)P reaching a daily maximum of 27 ng m^{-3} in PM$_{10}$ (26 in PM$_{2.5}$), well above the annual mean target value of 1 ng m^{-3}.

Profile of organic species related to olive waste burning is dominated by levoglucosan (68% of total contributing organic compounds), xylitol, galactosan and mannosan. Other source compounds included fatty acids, diacids, aliphatic hydrocarbons, sugars, sugar alcohols, PAHs and quinones.

These results highlight, as other published studies did (Van Drooge and Grimalt, 2015), the high impact of biomass burning on air quality at specific areas of Spain.

In these regions urgent measures to abate emissions from domestic biomass burning should be urgently implemented. In this sense, the replacement of old inefficient wood-burning appliances by cleaner systems has been suggested as one of the most positive measures that can be accomplished (AIRUSE-LIFE-AXA, 2017).

Other identified sources of organic compounds have been primary vegetation emissions, BSOA, soil dust and lubricating oil, mainly in other periods of the year.

These results can be considered as a previous step to perform further source apportionment studies involving organic and inorganic species and meteorological parameters, and can be useful to reduce the number of organic compounds to be analyzed.

CRediT authorship contribution statement

Rosa Pérez Pastor: Formal analysis, Resources, Investigation, Validation, Writing - original draft. **Pedro Salvador:** Formal analysis, Data curation, Resources, Visualization, Writing - review & editing. **Susana García Alonso:** Methodology, Formal analysis, Validation, Writing - review & editing. **Andrés Alastuey:** Resources, Writing - review & editing. **Saúl García dos Santos:** Resources, Investigation, Writing - review & editing. **Xavier Querol:** Funding acquisition, Project administration, Supervision, Writing - review & editing. **Begoña Artíñano:** Conceptualization, Supervision, Writing - review & editing.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2020.125896.

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