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7 **Particle sized-resolved source apportionment of primary and**

8 **secondary organic tracer compounds at urban and rural**

9 **locations in Spain**

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Abstract

Atmospheric particulate matter (PM) was fractionated in six aerodynamic sizes, >7.2, 7.2-3, 3-1.5, 1.5-1, 1-0.5, <0.5 μm , using a cascade impactor. These fractions were collected at urban and rural sites during warm and cold seasons. Analysis of the organic tracer compounds by gas-chromatography coupled to mass-spectrometry showed that the composition in the smallest size fractions (<0.5 μm) was more uniform than in the larger sizes (7.2>PM>0.5 μm). Thus, markers of photochemically synthesized organic compounds or combustion sources, either biomass burning or traffic emissions, were predominantly observed in the fraction <0.5 μm whereas the larger particles were composed of mixed sources from combustion processes, vegetation emissions, soil re-suspension, road dust, urban life-style activities and photochemically synthesized organic compounds.

Important seasonal differences were observed at the rural site. In the <0.5 μm fraction these were related to strong predominance of biomass burning in the cold period and photochemically transformed biogenic organic compounds in the warm period. In the 7.2>PM>0.5 μm fractions the differences involved predominant soil-sourced compounds in the warm period and mixed combustion sources, photochemical products and vegetation emissions in the cold.

Multivariate Curve Resolution Alternating Least Squares showed that these organic aerosols essentially originated from six source components. Four of them reflected primary emissions related with either natural products, e.g. vegetation emissions and up whirled soil dust, or anthropogenic contributions, e.g. combustion products and compounds related with urban life-style activities, mainly vehicular exhausts and tobacco smoking. Two secondary organic aerosol components were identified. They accumulated in the smallest (<0.5 μm) or in the larger fractions (>0.5 μm) and involved strong or mild photochemical transformations of vegetation precursor molecules, respectively.

Toxicologically relevant information was also disclosed with the present approach. Thus, the strong predominance of biomass burning residues at the rural site during the cold period involved atmospheric concentrations of polycyclic aromatic hydrocarbons that were three times higher than at the urban sites and benzo[a]pyrene concentrations above legal recommendations.

1 Introduction

Atmospheric aerosols are constituted by particles with diameters between a few nanometers to tens of micrometers (Seinfeld and Pandis, 2006) and a high diversity of chemical compounds. These complex mixtures have influence on atmospheric visibility (Watson, 2002), climate forcing (Forster et al., 2007) and human health (Pope et al., 2002; Brunekreef et al., 2005). A significant but variable aerosol fraction is constituted of organic material, e.g. between 20-90% of the particulate matter (PM) (Kanakidou et al., 2005). This organic aerosol (OA) originates from primary and secondary sources (Donahue et al., 2009). At urban locations the primary organic aerosols (POA) are emitted from combustion sources, including heavy and light duty vehicles, wood smoke, cooking activities, industries, soil, and road dust. At rural areas, biomass burning, including wood burning, is an important primary aerosol source (Fine et al. 2004, Puxbaum et al. 2007) together with soil dust particles (Simoneit et al., 2004). Saccharides, as constituents of soil dust and vegetation detritus, and also present in residues generated after biomass combustion, can make up an important part of the POA fraction (Simoneit et al., 2004; Medieros and Simoneit, 2007).

In the absence of these saccharides, most of the water-soluble fraction is thought to derive from secondary organic aerosols (SOA) that are composed of oxygenated compounds, such as dicarboxylic acids (Hallquist et al. 2009). Although these acids are emitted in small quantities from traffic and vegetation, they are mostly formed in the atmosphere after photochemical transformation of volatile and semi-volatile organic compounds from non-fossil, e.g. vegetation, and fossil origins, e.g. fossil fuel combustion residues (Heald et al. 2010; Kleindienst et al. 2012; Paulot et al. 2011). The importance of oxidized organic compounds is emphasized by their strong contribution (40–90%) to the total organic fraction in the fine PM (Jimenez et al. 2009).

Important information on sources, fate and mutual interaction of gas phase and aerosol organics has been obtained from filtration of large volumes of ambient air and analysis (Schauer et al., 2007; Goldstein and Galbally, 2007; Bi et al., 2008). The constituents of the organic

primary and secondary aerosols are distributed among the wide aerodynamic size range of the constituent particles (Aceves and Grimalt, 1993a; Kavouras and Stephanou, 2002). Collection and analysis of particles in different size ranges provides insight into the sources and fate of the OA which is useful for characterizing the different types of aerosols that may be found in diverse environments, either urban or rural. The combination of particle size filter techniques with gas chromatography-mass spectrometry (GC-MS) allows in-deep speciation that is useful to reconstruct the emissions from different sources (Schauer et al., 2007; Alier et al., 2013).

This approach is used in the present manuscript to characterize the size distribution of organic aerosol from an urban background site in Barcelona and a rural site in the Pyrenees during warm and cold periods (2012 and 2013), and to identify the similarities and differences of the OA generated in these sites. The urban study area of Barcelona is characterized by one of the highest vehicle densities in Europe as well as a densely populated city center. Moreover, its geographical position (western Mediterranean basin) favors photo-chemical reactions and accumulation of secondary aerosols (Querol et al., 2009; Pey et al., 2009; Perez et al., 2010; [Pandolfi et al. 2014](#)).

The rural site, in a forested area of the Pyrenees, is exposed to biomass burning in the cold period for domestic heating. In other seasons, such as fall, biomass particles could be generated from biogenic waste combustion in fields and gardens (van Drooge and Perez-Ballesta, 2009). Air quality in this rural site is not influenced by industrial activities and traffic intensity in the area is very low. Due to its geographical situation (surrounded by mountains), the site is prone to thermal inversion episodes, especially in the cold periods.

The study of the main sources contributing to the GC amenable organic compounds of the atmospheric aerosol size fractions generated in cold and warm weather in these sites affords a combined physical-chemical description of the changes in organic constituents from the two most typical areas inhabited by humans. Multivariate Curve Resolution Alternating Least Squares (MCR-ALS) (Tauler et al., 1995a and 1995b) has been used for source apportionment in the present study. This method, previously used for source apportionment of aquatic pollutants (Terrado et al., 2009) and urban OA (Alier et al., 2013), is based on an alternating linear least

squares optimization under non-negativity constraints which generates source components with better physical sense than principal component analysis (PCA; Tauler et al., 2009). The database of the analyzed organic tracer compounds has been used as input for these calculations affording to identify similarities and differences between locations. The results will be useful for gaining insight into the processes of aerosol formation and into the pervasiveness of different compounds in the human respiratory tract.

2. Methods and Materials

2.1. Organic molecular tracer compounds

Filters were analyzed by solvent extraction subsequent gas chromatography coupled to mass spectrometry. This method allows detection and quantification of a wide range of semi-volatile organic compounds with different polarities. Seventy-two compounds have been detected in ambient air and emission sources, and therefore, many of them have been used as molecular tracers of these sources and atmospheric processes (Alier et al. 2013).

2.2. Sampling and analytical procedure

A six stage (including back-up filter) Anderson cascade impactor was used to collect atmospheric particles in different sizes (>7.2 ; $7.2-3$; $3-1.5$; $1.5-1$; $1-0.5$; <0.5 μm) with a sampling efficiency of 50%, using a HiVol-sampler (MCV) at a sampling rate of $20 \text{ m}^3 \text{ h}^{-1}$. The particles were collected on custo-made glass-fiber filters (Whatman). Each sample encompassed 72 hours pumping. The sampling campaigns were conducted under prolonged calm weather conditions in an urban background site of Barcelona ($41^\circ 23.232' \text{N}$; $2^\circ 6.943' \text{E}$; 77 m asl.) and in a rural site of La Pobla de Lillet in the Pyrenees ($42^\circ 14.731' \text{N}$; $1^\circ 58.488' \text{E}$; 870 m asl.) during different periods (Figure 1).

The meteorological conditions were determined from local meteorological stations. The samples were divided into those belonging to “warm” and “cold periods” (see table S1 Supplementary Information). Temperature was the meteorological parameter involving highest

132 difference between the urban and rural sites. In the former, they involved average values of 20°C
133 and 4°C in the warm and cold periods whereas in the latter these values were 22°C and 10°C,
134 respectively (Table S1). Other meteorological parameters such as relative humidity, wind speed,
135 wind direction and atmospheric pressure ranged among nearly the same intervals in both sites
136 (Table S1).

137 Before sampling, all filters were baked at 450°C overnight. After sampling, they were split
138 in two sections one half was analyzed for organic compounds and the other was stored for
139 toxicity testing. The filter section for chemical analysis was Soxhlet extracted with (2:1, v/v)
140 dichloromethane:methanol (60 mL; Merck, Germany) for 8 hours. Before extraction 25 µL of the
141 surrogate standards d₇-levoglucosan, d₅₀-n-C₂₄ (Cambridge Isotopic Laboratories, UK), d₄-
142 succinic acid (Sigma Aldrich), d₁₀-anthracene, d₁₂-benz[a]anthracene, d₁₂-benzo[k]fluoranthene
143 and d₁₂-benzo[ghi]perylene (Dr. Ehrenstorfer) were added. The extracts were filtered through
144 glass fiber filters using a glass syringe to remove insoluble particles. Then, they were
145 concentrated to 1 mL under a gentle nitrogen stream.

146 Anhydro saccharides, acids, polyols and nicotine were analyzed following procedures that
147 was similar to those described elsewhere (Medeiros and Simoneit, 2007; van Drooge et al.,
148 2012). Briefly, an aliquot of the extract (25 µl) was evaporated under a gentle nitrogen stream
149 until dryness. Then, 25 µL of bis(trimethylsilyl)trifluoroacetamide (BSFTA)+trimethylchlorosilane
150 (99:1) (Supelco) and 10 µL of pyridine (Merck) were added and heated at 70°C during 1 h for
151 derivatization of the saccharides, acids and polyols to their trimethylsilyl esters. Before
152 instrumental analysis, 25 µL of the internal standard, 1-phenyldodecane was added to the vial.

153 PAHs, hopanes, n-alkanes and quinones were analyzed in the remaining extract that was
154 evaporated to almost dryness under a gentle nitrogen stream and re-dissolved in 0.5 mL (9:1 v/v)
155 hexane:dichloromethane (Merck, Germany). This solution was cleaned-up by adsorption column
156 chromatography packed with 1 g of aluminum oxide (Merck, Germany) that was activated
157 overnight at 120°C. The analytes were eluted with 4 mL of (9:1 v/v) hexane:dichloromethane and
158 4 mL of (1:2 v/v) hexane:dichloromethane, respectively (Merck, Germany). The fractions were

collected together and concentrated under a gentle nitrogen stream to 50 μ L. The internal standard, 1-phenyldodecane, was added before injection into GC-MS.

The sample extracts were injected into a Thermo GC-MS (Thermo Trace GC Ultra – DSG II) equipped with a 60 m fused capillary column (HP-5MS 0.25-mm x 25- μ m film thickness). The oven temperature program started at 60°C (holding time 1 min) and then was heated to 120°C at 12°C/min and to 310°C at 4°C/min where it was held for 10 min. The injector, ion source, quadrupole and transfer line temperatures were 280°C, 200°C, 150°C and 280°C, respectively. Helium was used as carrier gas at 0.9 mL/min⁻¹. The MS detector was operated in full scan (m/z 50 – 650) and electron impact (70 eV) ionization mode.

Table S2, in the supplementary information, contains the list of quantified molecular organic tracer compounds. Besides retention time comparison, levoglucosan, mannosan, α - and β -glucose were identified with ion m/z 204, galactosan and xylitol with ion m/z 217, mannitol with m/z 319, sucrose and myose with m/z 361, and nicotine with ion m/z 84. Acids and polyols were identified with the following ions: succinic acid (m/z 247), glutaric acid (m/z 261), adipic acid (m/z 275) pimelic acid (m/z 289), suberic acid (m/z 303), azelaic acid (m/z 317), glyceric acid (m/z 292), malic acid (m/z 233), , phthalic acid and terephthalic acid (m/z 295), cis-pinonic acid and pinic acid (m/z 171), dehydroabiatic acid (m/z 239), 3-hydroxyglutaric acid (m/z 349), 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA) (m/z 405), 2-methylglyceric acid (m/z 219), C₅-alkene triols (m/z 231), 2-methylthreitol and 2-methylerythritol (m/z 219). No standards for 3-hydroxyglutaric acid, MBTCA, C₅ alkene triols, 2-methylthreitol and 2-methylerythritol were available and their chromatographic peaks were identified by comparison of their mass spectra with literature and library data (Claeys et al., 2007; Kourtchev et al., 2005; Cleemans et al., 2007). Straight chain carboxylic acids were identified in the m/z 117 mass fragmentogram and the corresponding retention times. Quantification was performed with the external standard calibration curves. The concentrations were corrected by the recoveries of the surrogate standard d₄-succinic acid (m/z 251) and d₇-levoglucosan (m/z 206).

PAH were identified by retention time comparison of the peaks generated with the following ions: phenanthrene (m/z 178), anthracene (m/z 178), fluoranthene (m/z 202), pyrene

(*m/z* 202), benz[a]anthracene (*m/z* 228), chrysene+triphenylene (*m/z* 228), benzo[b]fluoranthene (*m/z* 252), benzo[k]fluoranthene (*m/z* 252), benzo[e]pyrene (*m/z* 252), benzo[a]pyrene (*m/z* 252), indeno[1,2,3-cd]pyrene (*m/z* 276), benzo[ghi]perylene (*m/z* 276) and coronene (*m/z* 300). Quinones were identified by comparison to authentic standards using the following ions: fluorenone (*m/z* 180), phenanthrenequinone (*m/z* 208), anthracenequinone (*m/z* 208), benzo[a]fluorenone (*m/z* 230), benzo[b]fluorenone (*m/z* 230), benzanthrenone (*m/z* 230). 17(H) α -21(H) β -29-Norhopane and 17(H) α -21(H) β -hopane were identified in the *m/z* 191 mass fragmentogram and the corresponding retention times. The n-alkanes were identified in the *m/z* 71 mass fragmentogram and the corresponding retention times. Quantification was also performed by the external standard method and the calculated concentrations were corrected by the recoveries of the above mentioned surrogates: d₁₀-anthracene (*m/z* 188), d₁₂-benz[a]anthracene (*m/z* 240), d₁₂-benzo[k]fluoranthene (*m/z* 264), d₁₂-benzo[ghi]perylene (*m/z* 288) and d₅₀-n-C24 (*m/z* 66).

In all cases the recoveries of the surrogate standards were higher than 70%. Field blanks were between 1% and 30% of the sample concentrations. Reported data were corrected for blank levels. The limits of quantification (LOQ) were calculated by dividing the lowest measured levels in the standard calibration curves by the volumes of the analyzed sample fraction. These were 0.02 ng m⁻³ for the saccharides, 0.01 ng m⁻³ for the acids and 0.002 ng m⁻³ for PAHs, quinones, hopanes and n-alkanes.

2.3. Data analysis

In order to observe the similarities and differences between the studied locations, the experimental data were merged for evaluation with Multivariate Curve Resolution Alternating Least Squares (MCR-ALS). The joint dataset was imported into MATLAB 7.4 (The Mathworks, Natick, USA) for subsequent calculations using MATLAB PLS 5.8 Toolbox (Eigenvector Research Inc, Masson WA, USA). The MCR-ALS method had been applied successfully in a previous study on urban organic aerosol. A detailed description of these results can be found in Alier et al. (2013). Briefly, The MCR-ALS method decomposes the data matrix using an

Alternating Least Squares algorithm under a set of constraints such as non-negativity, unimodality, closure, trilinearity or selectivity (Tauler et al., 1995a and 1995b). The explained variance by the different components is similar to a PCA, however, it is not orthogonal as in PCA (Jolliffe, 2002). Since the natural sources in the environment are rarely orthogonal, the MCR-ALS method provides more realistic descriptions of the components than the orthogonal database decomposition methods.

3 Results

3.1 Particle size distribution of the organic tracer compounds present in the aerosols

Mean and standard deviation ($\pm 1\sigma$) concentration values of the compounds analyzed are reported in Table S32.

3.1.1. Polycyclic aromatic hydrocarbons (PAH)

PAH are toxic components of fossil fuels and primary products of incomplete combustion of organic materials (Linuma et al., 2007; Rogge et al., 1993; Schauer et al., 2007) and they were found in all samples. Significant concentration differences were observed among particle size fractions and sampling periods. Overall, more than 70% of the sum of all quantified PAH were present in the fraction $<0.5 \mu\text{m}$, while around 10% was present in particles $>3 \mu\text{m}$. The urban samples collected in the warm period constituted an exception since around 20% of the sum of PAH were in the coarse fraction and only 50% of these hydrocarbons were found in the $< 0.5 \mu\text{m}$ fraction. The dominance of PAH in the smallest fraction is in agreement with former studies (Aceves and Grimalt, 1993b) and consistent with combustion processes as a major source of these particles.

At the urban site, the average ΣPAH concentrations were 6.4 ng/m^3 in the cold period and two times lower in the warm period ($3.3 \pm 1.0 \text{ ng/m}^3$). The ΣPAH concentrations (summed PAH from the six size fractions) observed in this site were in agreement with those observed in year-round (2008-2009) PAH analyses from Mediterranean cities (Reche et al., 2012a; Mesquita et al.,

2014). The lowest average Σ PAH concentration was observed in the warm period at the rural site ($1.2 \pm 0.5 \text{ ng/m}^3$). In the cold period, this site exhibited twenty times higher average Σ PAH concentrations ($22 \pm 8 \text{ ng/m}^3$) and toxic PAHs, such as benzo[a]pyrene, had levels around 1 ng/m^3 , which is the annual limit value (EC, 2004). Accordingly, in the cold periods rural populations are exposed to elevated PAH concentrations. The high PAH concentration observed in the cold period is similar to others observed in European rural areas (Puxbaum et al. 2007; van Drooge and Perez-Ballesta, 2009), and are often attributed to biomass burning emissions in combination with stable atmospheric conditions. In fact, in winter they are much higher at the rural than at the urban sites.

The assignment to wood burning is consistent with the high concentrations of retene at the rural site of the present study in the cold period ($3.2 \pm 2.4 \text{ ng/m}^3$). Conversely, in the warm period the concentrations of this hydrocarbon were very low, around LOQ (0.003 ng/m^3). Retene is a marker for pine wood combustion (Ramdahl, 1983b) and can also be found in small quantities in smoke from other wood types, such as oak or even synthetic log (Rogge et al., 1998). At the urban site, retene is also found in lower concentrations in the warm ($0.016 \pm 0.002 \text{ ng/m}^3$, <2% of Σ PAH) than the cold period (0.12 ng/m^3 , 20%-6% of Σ PAH) (Fig. 2).

The relative composition of PAH is useful to discriminate between the combustion processes at the rural and urban site. The isomeric ratios fluoranthene vs. pyrene (fla/(fla+pyr)), benz[a]anthracene vs. chrysene (baa/(baa+chr)), benzo[a]pyrene vs. benzo[e]pyrene (bap/(bap+bep)), and indeno[123cd]pyrene vs. benzo[ghi]perylene (ip/(ip+bgp)) reflect combustion inputs from different fuels but they may also be modified by photochemical transformations in the atmosphere in the presence of O_3 , OH, and NO_2 (Galarneau, 2008; [Siere Simó et al., 1991](#); Simo et al., 1997). The baa/(baa+chry), bap/(bap+bep) and ip/(ip+bgp) ratios at the rural site, 0.43, 0.53 and 0.50, match those observed for wood combustion in several studies (Galarneau, 2008; [Simó et al., 1991](#); Khalili et al., 1995; van Drooge et al., 2012). The ratio ip/(ip+bgp) has the highest diagnostic potential for source contributions. Values in the order of 0.2 and 0.3 correspond to vehicular diesel and gasoline emissions, respectively (Galarneau, 2008; [Simó et al., 1991](#)). Ip/(ip+bgp) ratios of 0.3 are observed in the average

summer aerosol of both sites (Fig. 3). At the urban site in the cold period this ratio is a bit higher, 0.35, which may reflect some minor contribution of wood combustion to the atmospheric aerosol besides the dominant vehicular inputs. The lower baa/(baa+chry) and bap/(bap+bep) ratios in the warm than in the cold periods are consistent with lower wood combustion inputs in these seasons. However, baa and bap are more labile to photodegradation than their respective isomers, chry and bep (Galarneau, 2008; Simo et al., 1997). Thus, these ratio differences could also reflect higher photooxidation in the warm periods.

3.1.2. Oxygenated PAH (quinones).

Quinones, with toxic potential, are released into the atmosphere along with PAH during incomplete combustion (Ramdahl, 1983a; Iinuma et al., 2007; Valavanidis et al., 2006). Atmospheric transformation of PAHs can also generate quinones by reaction with atmospheric oxidants (Alam et al. 2014; Atkinson and Arey, 2007). Quinones were found in all sample fractions but more than 68% of the sum of quinones were observed in the finest <0.5 μm fraction (Table S32). These compounds, like the PAH, are emitted to the atmosphere by incomplete combustion of fossil fuels or biomass although they may also be generated in the atmosphere by PAH oxidation. The lowest Σ quinone concentrations were observed in the samples collected at the rural site during the warm period (0.11 ng/m^3), followed by the urban site during the warm period (0.42 ng/m^3). Much higher concentrations were found in the cold periods (4.9 ng/m^3 and 1.1 ng/m^3 at the rural and urban site, respectively). The concentrations of these compounds, e.g. phenanthraquinone (pheno) and anthraquinone (anto), are similar to those observed in other studies at rural and urban sites (Alam et al., 2014). In the warm periods, the average relative composition of the quinones is dominated by anthraquinone (37%) at the rural site but they only encompassed 19% at the urban site (Fig. 3). In this period, the average anto/pheno ratio is 6 and 2 at the rural and urban sites, respectively.

In the cold period, the Σ quinone concentration increases and anthraquinone loses predominance (Table S32). At the urban site, this is reflected with a proportion of this quinone of 6% and an anto/pheno ratio of 1.1 (Fig. 3). Other compounds, such as benzofluorenone and

benzoanthrenone range among the most abundant in this period. At the rural site, phenanthraquinone is one of the most abundant compounds, resulting in a low anto/pheno ratio (0.3). Anthraquinone has been proposed as indicator of extent of photochemical formation, while the other quinones may be more influenced by primary emissions (Alam et al. 2014; Ramdahl, 1983a), which is in agreement with the results of the present study.

3.1.3. Hopanes

These hydrocarbons are molecular markers of mineral oils, whose occurrence in atmospheric samples can be related to unburned lubricating oil residues from primary vehicles emissions (Rogge et al., 1993; Schauer et al., 2007). The compounds selected for quantification were $17\alpha(\text{H}),21\beta(\text{H})$ -29-norhopane and $17\alpha(\text{H}),21\beta(\text{H})$ -hopane, and they were found in all samples. At the urban site Σ hopane average concentrations of 2-2.2 ng/m³ were observed in both warm and cold periods whereas at the rural site the observed Σ hopane average concentrations were 0.9 ng/m³ and 0.5 ng/m³ in the warm and cold periods, respectively. Important differences between the size distribution of these compounds at the rural and urban site were observed (Table S32). In the former, they were highest in the fraction <0.5 μm , and in the latter 40% of the compounds were present in the fraction <0.5 μm whereas another 30 – 40% were present in the coarse fraction between 3 μm and >7.2 μm . The presence of hopanes in the larger particles of the urban site could be related to road dust, since hopanes, as constituents of lubricant oils (Rogge et al., 1993; Schauer et al., 2007), may be deposited on the street pavement.

3.1.4. n-Alkanes.

C_{21} - C_{34} n-alkanes are present in ambient air PM as consequence of biogenic and anthropogenic emissions, such as plant waxes or fossil fuel residues (Mazurek et al, 1989; ~~Simoneit et al. 1991~~; Schauer et al., 2002), and in the present study, C_{21} - C_{34} n-alkanes were found in all samples. The widest concentration range was found in the warm period with lowest Σ n-alkane average concentration at the rural site (12 ng/m³) and highest at the urban site (43

ng/m³; Table S32). In the cold period the mean concentrations were 35 ng/m³ and 29 ng/m³ at the rural and urban sites, respectively. These concentrations are in the range of those found in other studies in forested and urban areas (Kavouras and Stephanou, 2002). However, they are much lower than those observed in one site with heavy traffic in Barcelona 20 years ago (165-830 ng/m³; Aceves and Grimalt, 1993b) probably as a consequence of the introduction of cleaner cars and natural gas for domestic heating in the urban site over the past decades.

At the rural site, during the warm period the n-alkanes were evenly distributed among all particle sizes (Table S32), with predominance of n-C₂₉, followed by n-C₃₁ and n-C₂₇ (Fig. 4), while in the cold period they were predominantly in the fraction <0.5 µm (54%±13%). In this period, the relative composition of n-alkanes was dominated by n-C₂₂ to n-C₂₅, although n-C₂₉ and n-C₃₁ were also present (Fig.4). In general, the presence of n-C₂₇, n-C₂₉ and n-C₃₁ reflects contributions from waxes from terrestrial higher plants, while the n-alkanes in the range between n-C₂₂ to n-C₂₅ are more related to combustion sources (Mazurek et al., 1989; ~~Simoneit, 1991~~).

The odd-to-even n-alkane carbon preference index (CPI) is another indicator of biogenic or combustion contributions, where CPI>1 is related to biogenic (vegetation) origin, while CPI≈1 indicates combustion processes as primary emission sources (Mazurek et al., 1989; Simoneit, 1991). Here, the CPI was calculated by dividing the odd carbon numbered $\sum(C_{21}-C_{33})$ by even carbon numbered $\sum(C_{22}-C_{34})$. At the rural site the average values were 3.0±1.3 in the warm period and 1.7±0.3 in the cold period. The higher CPI in the warm period indicates a larger influence of vegetation material (detritus) in the aerosol, which is in agreement with the presence of these compounds in the larger particle sizes. In the cold period, combustion processes are more important, resulting in lower CPI and the dominant presence of these compounds in the smaller particles. The distributions at the urban site are similar but higher proportion of n-alkanes (47%±3%) were found in the larger particles (>3 µm) during the warm period than at the rural site which is consistent with higher influence of biogenic inputs, as also reflected in the high CPI, 3.5±0.6, and the predominance of n-C₂₉ and n-C₃₁ in the distribution of isomers. In the cold period of the urban area, the n-alkanes were mostly present in the finest particle fraction, and n-C₂₂ to n-C₂₅ were more abundant, resulting in lower CPI, 1.9±0.3. This agreement in the n-alkane

distributions of the cold seasons in both sites indicates a predominance of combustion over biogenic inputs in this period.

3.1.5. Nicotine.

This alkaloid is present in high concentrations in tobacco smoke. It is mainly present in the gas-phase due to its high volatility but it can also be detected at trace levels on PM filter samples (Rogge et al., 1994; Bi et al., 2005). In the area of Barcelona, this compound has recently been found in PM representing anthropogenic contributions (Alier et al. 2013). In the present study, nicotine was mostly found in the fraction $< 0.5 \mu\text{m}$. At the urban site 80% and 90% of total nicotine were found in this size fraction in the warm and cold periods, respectively, and at the rural site it was only present in these fine particles (Table S32). At the rural site, the average concentrations were 0.6 ng/m^3 and 1.7 ng/m^3 in the warm and cold periods, respectively, and at the urban site they were about one order of magnitude higher, 13 ng/m^3 and 15 ng/m^3 in the warm and cold periods, respectively. These last concentrations were similar to those found in one urban background site previously studied but lower than those in the city center (Alier et al. 2013). The higher concentrations of nicotine at the urban areas are consistent with the higher intensities of human activities in these sites which include cigarette smoking (Rogge et al., 1994; Bi et al., 2005; Sureda et al., 2012).

3.1.6. Anhydrosaccharides (levoglucosan, galactosan and mannosan)

These monosaccharide anhydrides are generated by thermal alteration of cellulose and hemi-cellulose that are emitted in large quantities during biomass burning (Simoneit et al., 2002; Fine et al., 2004). Levoglucosan and its isomers, galactosan and mannosan, were found in all samples. Major differences were found between sites and sampling periods (Table S32). These compounds predominated in the fraction $< 0.5 \mu\text{m}$ and their concentrations were significantly correlated ($r^2 > 0.90$). Those of levoglucosan were three times higher than the sum of galactosan+mannosan at the rural site, and five times higher at the urban site, while galactosan and mannosan showed similar concentrations. Lowest and highest levoglucosan concentrations

(8 ng/m³ vs. 1600 ng/m³) were observed the rural site, in the warm and cold periods, respectively. These high levels at the rural site in the cold period can directly be related to the presence of local biomass burning for domestic heating or biomass waste removal as consequence of the high abundance of cellulose in vegetation (Puxbaum et al. 2007). At the urban site, the higher concentrations of these compounds were also observed in the cold period (155 ng/m³). The mean levoglucosan concentration in the warm period was about one order of magnitude lower (18 ng/m³). These urban concentrations were very similar to those previously observed in Barcelona (van Drooge et al. 2014). The presence of levoglucosan in this urban area has been related to regional biomass burning instead of local emissions (van Drooge et al. 2014; Reche et al. 2012b).

3.1.7. Primary saccharides and polyols

α - and β -glucose, sucrose and mycose are an important constituents of soil organic matter and related to plant tissue and micro-organisms. Xylitol and mannitol are reduced saccharides that are generally associated to organic matter in soils. Mannitol is related to funghi (Simoneit et al. 2004). These compounds can enter into the atmosphere by wind erosion and up whirling of soil dust (Simoneit et al. 2004).

α - and β -glucose, sucrose, mycose, xylitol and mannitol were found in all samples but their relative composition changed between sites and seasonal periods (Table S32). Higher concentrations were observed in the warm period (Σ saccharides = 1150 ng/m³ and 810 ng/m³, at the rural and urban sites, respectively), which is coincident with higher biological activities in soils and plant growth. At the rural site, glucose, mycose, xylitol and mannitol were present in similar concentrations and sucrose was a minor compound. These compounds were predominantly present in the particle fractions between 1.5 and 7.2 μ m, which indicates an occurrence related to soil dust contributions. Mannitol and mycose are related to fungi and their occurrence is linked to soil contributions.

At the urban site, sucrose was the most abundant saccharide (>50% of Σ saccharides) and predominated in the coarse fractions between 1.5 and >7.2 μ m. Its concentration in the warm period, 411 ng/m³, was about one order of magnitude higher than at the rural site, 46 ng/m³,

whereas the concentration of the other saccharides were about two times lower at the urban site, indicating the influence of different soil dust particles in the two studied sites.

In the cold period, the concentrations of saccharides and polyols in the different fractions decreased by one order of magnitude, which is consistent with the seasonal decrease of biological activities. An exception was observed for the fraction $<0.5\ \mu\text{m}$ in which glucose, xylitol and sucrose increased. This different behavior could reflect the incorporation of these compounds into the atmosphere by thermal stripping during biomass burning (Medeiros and Simoneit, 2007). In contrast, the fungal-sourced mannitol and mycose did not increase in the fraction $<0.5\ \mu\text{m}$.

3.1.8. Carboxylic acids.

$\text{C}_{16}\text{-C}_{21}$ fatty acids are constituents of vegetable oils, animal fats and lubricants, among others. They may also originate from vegetation and soil organic matter (Mazurek et al. 1989; Schauer et al., 2007). Seven straight chain saturated and unsaturated fatty acids are considered for study. Dehydroabietic acid, also included in the study, is related to the combustion of pine wood (Linuma et al., 2007; Medeiros and Simoneit, 2007⁸)

The $\text{C}_{16}\text{-C}_{21}$ straight chain carboxylic acids were found in all samples (Table S3²), with similar concentrations in the two sites and between periods. Palmitic acid ($\text{C}_{16:0}$) was the most abundant followed by stearic acid ($\text{C}_{18:0}$). Over 50% of the carboxylic acids were present in the coarse fractions between $1.5\ \mu\text{m}$ and $>7.2\ \mu\text{m}$, except in the cold period at the rural site, when about 70% were present in the fraction $<0.5\ \mu\text{m}$. In this period the carboxylic acids could have been emitted into the atmosphere by biomass burning and submitted to thermal stripping for incorporation into the atmosphere while in the warm season soil dust may have contributed to these compounds (Mazurek et al. 1989⁷). The presence of high proportions of unsaturated fatty acids, such as oleic acid ($\text{C}_{18:1}$), is consistent with contributions from food cooking, e.g. in $\text{C}_{18:1}/\text{C}_{18:0} > 1$ (Robinson et al., 2006), but other biological emissions sources may also contribute to the occurrence of these compounds (Fang et al., 2002; Schauer et al., 2002). In the present study, concentrations of $\text{C}_{18:1}$ higher than $\text{C}_{18:0}$ were only observed in one filter sample in the

fraction > 7.2 μm collected in the cold period at the rural site ($C_{18:1}/C_{18:0} = 3.2$). In all other samples a rather constant ratio of 0.6 (± 0.2) was observed, indicating that food cooking was not a significant source for PM in the studied sites.

Dehydroabietic acid, a resin acid, was found in all samples. The highest average concentrations, 470 ng/m^3 , were found at the rural site during the cold period (Table S32). As observed for the other biomass burning tracers, the concentrations were more than one order of magnitude lower in the warm period. Accordingly, at the urban site, higher average levels were observed in the cold than in the warm periods, 23 ng/m^3 and 5 ng/m^3 , respectively. More than 75% of this compound were predominantly found in the <0.5 μm fraction which is consistent with the size-distribution of levoglucosan corresponding to pine wood combustion (Linuma et al., 2007; Medeiros and Simoneit, 2007).

3.1.10. Dicarboxylic acids, hydroxydicarboxylic acids and aromatic-dicarboxylic acids.

These compounds are emitted from various primary sources (mobile emission, meat cooking, etc.) although atmospheric photochemical formation is probably their main source in the studied samples (Jang et al., 1997; Kerminen et al., 2000; Heald et al., 2010; Sheesley et al., 2010; Paulot et al., 2011).

Dicarboxylic acids were found in all samples (Table S32) with predominance in the finest <0.5 μm fraction in all cases, except for terephthalic acid, that is evenly distributed among the different particle sizes. Malic acid, succinic acid, azelaic acid and terephthalic acid were the most abundant, which is in agreement with previous studies at urban sites (van Drooge et al. 2012; Alier et al. 2013). At the rural site, succinic and malic acid encompassed >70% of the dicarboxylic acids in the <0.5 μm fraction during the warm period, while this proportion was >30 % in the cold period. The higher concentrations of malic acid in the warm period at the rural site, 99 ng/m^3 , are consistent with an origin of this compound related to oxidation instead of primary emission or biomass burning as was observed for other compounds the cold period. For example, azelaic acid (33% of total dicarboxylic acids - ΣDCAs -) and terephthalic acid (15%) were more abundant in the cold period. In all cases, except terephthalic acid, the dicarboxylic acids predominated in

the fraction $<0.5 \mu\text{m}$ which is consistent with the above mentioned origin related to photooxidation. In one of the samples collected in fall (cold period) at the rural site terephthalic acid concentrations around 60 ng/m^3 were observed in the fractions between $1 \mu\text{m}$ and $7.2 \mu\text{m}$. These concentrations were one order of magnitude higher than in the other rural samples, which indicated a primary emission contribution in that sampling period.

3.1.11. Tracers of α -pinene oxidation

Cis-pinonic acid, pinic acid, 3-hydroxyglutaric acid and 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA) are related to the photo-chemical oxidation of biogenic volatile α -pinene (Claeys et al., 2007; Szmigielski et al., 2007), which is the most abundant mono-terpene in the study area (Seco et al., 2011). 3-MBTCA is formed by OH-initiated oxidation of *cis*-pinonic acid (Szmigielski et al., 2007) and was first detected in aerosol samples from Amazonia and Belgium (Kubatova et al., 2000).

The further generation oxidation products, 3-hydroxyglutaric acid and MBTCA, were only found in the fraction $<0.5 \mu\text{m}$ showing high average concentrations in the warm period at the rural site, $\sim 45 \text{ ng/m}^3$. In the cold period and at the urban site, the concentrations of these compounds were about 6 ng/m^3 . Significant correlation between the concentrations of these two acids have been observed, $r^2 > 0.82$, which is consistent with their common source at the rural and urban samples and also with the results from previous studies in urban atmospheres (Alier et al., 2013; 2014).

Oxidation of α -pinene also forms pinic and *cis*-pinonic acid. These acids also showed the highest concentrations at the rural site in the warm period, 135 ng/m^3 and 230 ng/m^3 , respectively. The lower concentrations in the cold period suggest that primary emissions from biomass burning were not important contributors. Pinic acid also shows a significant correlation with 3-hydroxyglutamic acid and MBTCA, suggesting that α -pinene is probably its major precursor and is consistent with previous studies (Claeys et al., 2007; Szmigielski et al., 2007). On the other hand, the concentrations of *cis*-pinonic acid showed a weak correlation with those of pinic acid, or with those of the other oxidation products ($r^2 < 0.4$). The ratio of *cis*-pinonic+pinic acid to MBTCA

has been used to estimate the degree of aging of α -pinene SOA (Ding et al., 2011). The observed ratios in the fractions $<0.5 \mu\text{m}$ of the rural site were 4 and 6, in the warm and cold periods, respectively. At the urban site, these ratios were 3 and 6, respectively, indicating that in the present study the α -pinene SOA tracers were relatively fresh.

3.1.12. Tracers of isoprene oxidation.

C_5 -alkene triols, 2-methylglyceric acid, 2-methylthreitol and 2-methylerythritol are generated by isoprene oxidation. (Claeys et al., 2004; Hallquist et al., 2009), a major volatile organic compound emitted from land vegetation. This unsaturated hydrocarbon usually occurs in the atmosphere as consequence of vegetation emissions (Guenther et al., 1995) but tailpipe sources may also contribute to non-negligible amounts of this hydrocarbon at urban areas (Borbon et al., 2001; Park et al., 2011). The isoprene oxidation products were found in all samples (Table S32) and the highest concentrations occurred in the fraction $< 0.5 \mu\text{m}$. The highest concentrations were found in the warm period in the particles $< 0.5 \mu\text{m}$ collected at the rural site, with mean values of 41, 123, 60 and 221 ng/m^3 for 2-methylglyceric acid, C_5 -alkene triols, 2-methylthreitol and 2-methylerythritol, respectively. These concentrations are in the range of those observed in previous studies in European urban areas (Kourtchev et al., 2005; El Haddad et al., 2011; Alier et al., 2013) and southeastern USA (Edney et al., 2005; Lin et al., 2013).

These concentrations in the warm period were much higher than those observed in the cold period at the rural and urban sites, where the compound of highest concentration, 2-methylerythritol, ranged between 5 ng/m^3 and 10 ng/m^3 , respectively. The concentration of this compound in the warm period at the urban site was 22 ng/m^3 . The 2-methylerythritol concentrations were about three times higher than those of 2-methylthreitol. The concentrations of the two compounds were highly correlated at both sites ($r^2 = 0.9$; $P < 0.05$), as previously observed in other studies (Edney et al., 2005; Ion et al., 2005; El Haddad et al., 2011; Alier et al., 2013).

3.2 Source apportionment of organic aerosol

MCR-ALS allowed to identifying similarities and differences of the OA constituents in the sampled sites and periods. Six components were identified from the use of this multivariate method. These components covered 93% of the total variance of the concentrations of these compounds and the score-values (see loadings in Fig. 5a-f) provided a description of the contributions of the different potential OA sources (Fig. 6).

3.2.1. Organic aerosol from combustion sources (Combustion POA)

This was the most dominant component and explains 40% of the total variance. It was composed by primary biomass burning tracers, such as anhydrosaccharides, dehydroabietic acid, PAHs, quinones, C₂₀-C₂₄ n-alkanes with low CPI index, carboxylic acids, and dicarboxylic acids (Fig. 5a). This component was very abundant in the finest <0.5 µm fraction of the fall-winter samples in both sites (Fig. 6). However, the rural site showed three to six times higher score values than the urban site, which indicates that direct combustion sources were much more significant at the rural site during the cold season than at the urban site.

The presence of levoglucosan and its isomers, galactosan and mannosan, in this component is consistent with these contributions from biomass burning, including biomass waste from fields and gardens, as well as wood. On the other hand, the presence of dehydroabietic acid and retene indicate contributions of pine wood combustion. At the rural site considered for study, pine wood from the Scots pine (*Pinus sylvestris*) is the major fuel for domestic heating, although it can be combined with European Beech (*Fagus sylvatica*). Combustion of biomass waste is common in fall, while it hardly occurs in winter. Therefore, wood combustion for domestic heating is expected to dominate in winter, which would lead to lower levoglucosan/dehydroabietic acid and levoglucosan/retene ratios. In fact, the former ratio lower in winter (2.7) than fall (5.4), and also the later ratio was a lower ratio in winter (370) than fall (1560), indicating higher contributions of wood burning over biomass waste combustion in winter.

Although the difference between biomass waste burning and wood combustion could not be resolved in the augmented data set (joint urban and rural data set), a separate MCR-ALS analysis of the rural data set did identify them in a six component resolution (Fig. S1). Levoglucosan and its isomers were present in the loadings of both components (Fig.S1.1), while in one of the components (red) dehydroabietic acid was less dominant and retene was missing. Retene was entirely present in the other (red) component. The score values of these two components (Fig.S1.2) show that both components are represented in the fall samples (R_COLD_1.x), while only one (blue) is represented in the winter sample (R_COLD_2.x). These findings suggests that about 50% of the biomass burning in fall could be contributed by wood burning, probably from domestic heating, while another source, probably biomass waste burning, could contribute to the other 50%. In agreement with the previous statements, in winter the biomass burning component was dominated by (pine) wood combustion.

At the urban area, the presence of levoglucosan in the samples from the cold period, with a moderate average value of 160 ng/m³ (Table S32), points to a contribution from the regional biomass burning.

3.2.2. Vegetation-derived organic aerosol (Vegetation POA)

Carboxylic acids, high molecular weight n-alkanes with high CPI and sucrose are the constituents of the component that represents biogenic primary sources, e.g. plant tissue particles, at the urban area (20% of the total variance; Fig. 5b). This component is mainly present in the coarse fractions between >7.2 and >1 µm (Fig. 6). These fractions usually contain a portion of dust particles. However, other typical tracers of soil micro-organisms, such as mannitol and mycose, are absent. In any case, the presence of hopanes in this component suggest that some contributions from road dust may also be present, as hopanes are constituents of lubricant oils from vehicle engines that are found in road dust.

3.2.3. Urban organic aerosol (Urban POA)

Hopanes, nicotine, carboxylic acids, low molecular weight PAHs and small contributions of dicarboxylic acids constitute a third component involving 12% of the variance (Fig.5c). This component is essentially found in the fraction $<0.5\ \mu\text{m}$ in all samples of the urban area (Fig.6). At the rural site, it is not relevant, showing that it is very much related to anthropogenic activities in urban environments. These activities are related to urban life-style, e.g. smoking and traffic. Thus, nicotine and hopanes and low molecular weight PAH, i.e. phenanthrene and anthracene, are significant compound related to these activities. The contribution of dicarboxylic acids in a small proportion may reflect that this traffic component is not free from secondary inputs as consequence of oxidation processes.

3.2.4. Aged secondary organic aerosol (Aged SOA)

Another component is grouping several secondary organic compounds of biogenic origin such as malic acid, 3-hydroxyglutaric acid, MBTCA, pinic acid, C_5 -triols, 2-methylglyceric acid, 2-methylthreitol, and 2-methylerythritol, representing 11% of the variance (Fig. 5d). This constituent mostly occurs in the fraction $<0.5\ \mu\text{m}$ of the warm period at the rural site and, to a smaller extend, at the urban samples (Fig.6). The presence of further generation oxidation products from isoprene and α -pinene as well as a substantial contribution of malic acid and succinic acid suggests that this component is representing aged SOA, rather than fresh SOA. This is also consistent with the lower contributions of cis-pinonic acid in the component.

3.2.5. Soil-derived organic aerosol (Soil POA)

α - and β -glucose, the hydroxysaccharides and mycose constitute another primary organic matter aerosol constituent (9% of variance; Fig. 5e). This constituent is essentially found in the coarse particle fraction between 7.2 and $1\ \mu\text{m}$ at the rural site during the warm period, and, to a smaller extend, in the warm period of the urban site (Fig.6). These compounds are structural molecules of biological systems, such as plant tissue or micro-organisms (fungi and bacteria), and form part of the soil dust. These systems are more active in summer that is much drier than the winter period, leading to larger contributions at the rural than at the urban sites. The presence of these

compounds in the coarse fraction of the aerosols is consistent with wind erosion and up whirling of soil dust for their mobilization into the atmosphere.

3.2.6. Fresh secondary organic aerosol (Fresh SOA)

Adipic, cis-pinonic, phthalic and terephthalic acids, and, to smaller extend, high molecular weight n-alkanes group together in another component of chemically-modified organic aerosol products (9 % of variance; Fig. 5f). The presence of the dicarboxylic acids and also phthalic acid suggests an origin related with secondary aerosol formation. cis-Pinonic acid is also a first generation product of α -pinene-oxidation. Among the n-alkanes, the dominance of even carbon numbered homologues is also indicative of reworked n-alkane distributions.

This constituent essentially occurs in the size fractions between 0.5 μm and 1.5 μm , and sometimes up to > 7 μm (Fig.6). This size distribution is very different from the other secondary aerosol constituents that essentially occurred in the < 0.5 μm fraction. The main difference concerns the degree of transformation of the organic precursors. In the present component the observed organic compounds are early transformation products of biogenic precursors and they could therefore still be found in the size fraction in which the precursors are located. The previous Aged SOA component (see 3.2.4) was formed by molecules representing more extensive structural transformations and the component was essentially found in the smallest size fraction available with the sampling method.

The score values are highest at the urban site, with exception of the rural sample collected in fall, when biomass waste burning was substantially contributing to the overall biomass combustion. In this period all PM fractions showed high score values, and high concentrations of phthalic and terephthalic acid. The origin of these compounds during that event is not clear, but could be related to thermal stripping during combustion. In previous studies, terephthalic acid was related to combustion of plastic in the presence of 1,3,5-triphenylbenzene, a typical organic tracer for plastic combustion (Fu et al. 2010; Simoneit et al. 2005). However, this compound has not been found in the aerosols of the present study.

4. Implications and conclusions

The analysis of the concentrations of 72 organic compounds present in six size fractions of urban and rural aerosols from Mediterranean areas has allowed the identification of the main organic aerosol source constituents and the description of their particle size distribution. The six main components identified exhibit strong particle size, seasonal and geographical dependences (Figure 6 and 7).

The main component identified in the present study is related to combustion sources. It involves 40 % of the total variance and is essentially represented in the aerosols collected in the cold period, with a dominating presence in the smaller $PM_{<0.5}$ fraction (84 % of all OA components) at the rural site (Combustion POA; Fig.7). The higher significance of this component in the cold period at the rural site reflects the higher concentrations of biomass burning tracers in this environment in comparison with the urban location. This biomass burning concentrations also involved enhanced PAH concentrations, 22 ng/m^3 , at the rural site. That is nearly three times higher than at the urban site, 6.4 ng/m^3 . In this respect, the benzo[a]pyrene winter concentrations at the rural site exceeded the limit value of 1 ng/m^3 , indicating that rural communities undergo higher exposures due to this carcinogenic compound as consequence of biomass burning. These results are consistent with the previously reported occurrence of higher biomass burning tracer compounds in rural Europe during winter (Puxbaum et al., 2007) and the relationship between, high PAH concentrations in these zones and this source (van Drooge, Perez-Ballesta, 2009). The biomass burning contributions found in the present study at the urban background location are similar to those found at the same site in a previous study (Reche et al. 2012b; van Drooge et al. 2014) and suggest that regional biomass burning influences the urban background air quality in winter.

In contrast, biomass burning is only a minor contributor to the organic aerosol in the warm period. Then, the $PM_{<0.5}$ fraction at the rural location is dominated (90 % of OA) by organic compounds resulting from the transformation of biogenic volatile organic compounds such as α -pinene and isoprene (Aged SOA; Fig.7) The formation of these secondary organic constituents is enhanced in the summer samples when the oxidation processes and precursor concentrations

are high. In the urban location these contributions are smaller (14 % of OA). The occurrence of this component is in agreement with the results of a previous study of one month in the same location involving 18% of total variance (Alier et al. 2013). Nevertheless, in this previous study another component of aged SOA products from isoprene oxidation contributing to another 18% of the OA could also be identified. In any case, it is not clear whether the identified SOA tracers for isoprene, i.e. 2-methylglyceric, C5-alkene triols and methyltetrols encompass all secondary isoprene SOA, since it is possible that these reaction compounds combine further with other (less volatile) organic compounds (Nguyen et al. 2014; Lin et al. 2013) or other oxidants (Surrat et al., 2010), including NO_x (Hoyle et al., 2011) leading to compounds, such as organosulfates, that were not analyzed in this study.

In the present study, the third component (12% of the variance) was constituted by nicotine, hopanes and low molecular weight PAH, corresponding to tobacco smoke and vehicular traffic emissions. This component was essentially found at the urban particles in the smallest PM_{<0.5} fraction and was dominating the OA in the warm (49 % of OA) and cold periods (47 % of OA). This component has not been previously described in urban areas but shows the ubiquitous occurrence of tobacco and traffic emissions in the outdoor atmosphere of the cities (Urban POA; Fig.7).

According to these results, the organic composition of the smallest size fraction (< 0.5 μm) was much simpler than that of the larger sizes (Fig.7). At the rural environment the winter particles < 0.5 μm were dominated by compounds from biomass burning (84% of OA) and in summer from secondary molecules originating from the transformation of biogenic precursors such as α-pinene and isoprene (90% of OA). At the urban environment this size fraction reflected more constituents but still the composition was simple involving molecules from combustion processes, compounds of urban life-style and secondary transformation compounds both in the cold (96% of OA) and the warm (94% of OA) periods.

The particles >0.5 μm showed a higher diversity of constituents. At the rural environment they involved soil-sourced organic matter and transformed compounds (92% of OA) in the warm period and transformed compounds, biomass burning molecules and vegetation-sourced

compounds in the cold period (90% of OA). At the urban environment, vegetation and soil sourced compounds, primary compounds of urban life, and transformed compounds were the main components in the warm period (97% of OA) and vegetation-sourced compounds, primary compounds of urban life, and transformed compounds were the dominant components in the cold (97%).

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Figure 1. Location of the urban background sampling site in Barcelona and the rural sampling site in La Pobla de Lillet in the Pyrenees.

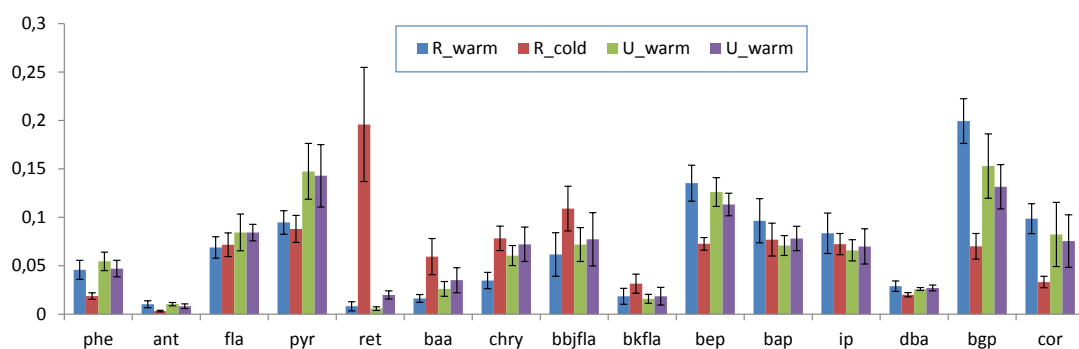


Fig.2. Relative composition of PAHs to Σ PAH for the different period (warm vs. cold) in the rural (R) and urban (U) sites.

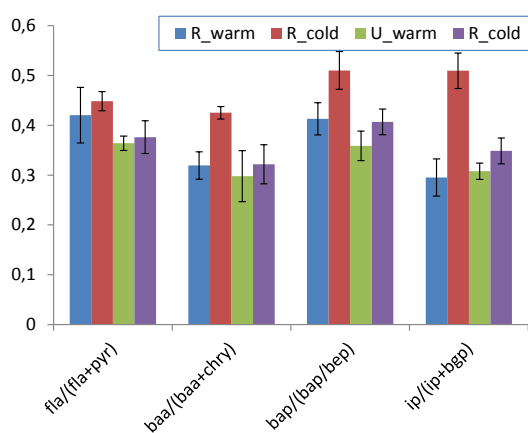
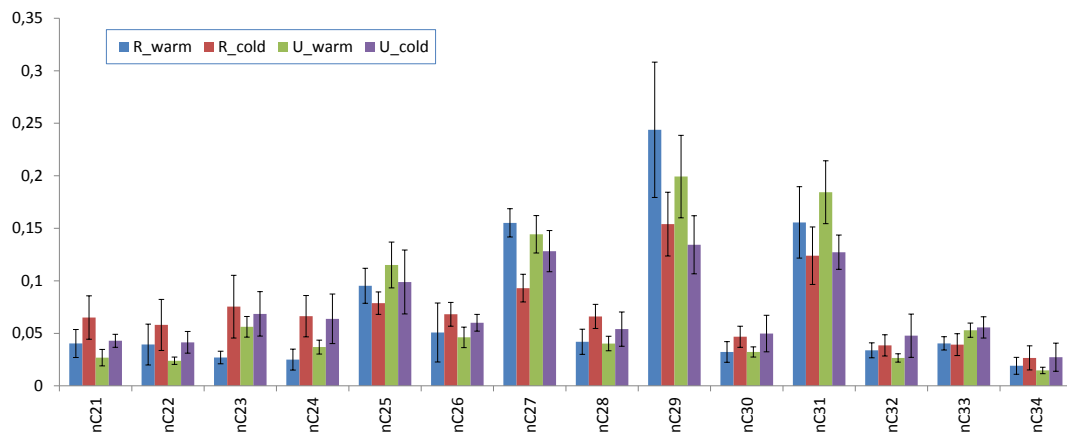


Fig.3. Isomeric PAH ratios for the different period (warm vs. cold) in the rural (R) and urban (U) sites. fla = fluoranthene; pyr = pyrene; baa = benz[a]anthracene; chry = chrysene; bap = benzo[a]pyrene; bep = benzo[e]pyrene; ip = indeno[123cd]pyrene; benzo[ghi]perylene.

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991 Fig.4. Relative composition of n-alkanes to Σ n-alkanes for the different period (warm vs. cold) in
 992 the rural (R) and urban (U) sites
 993

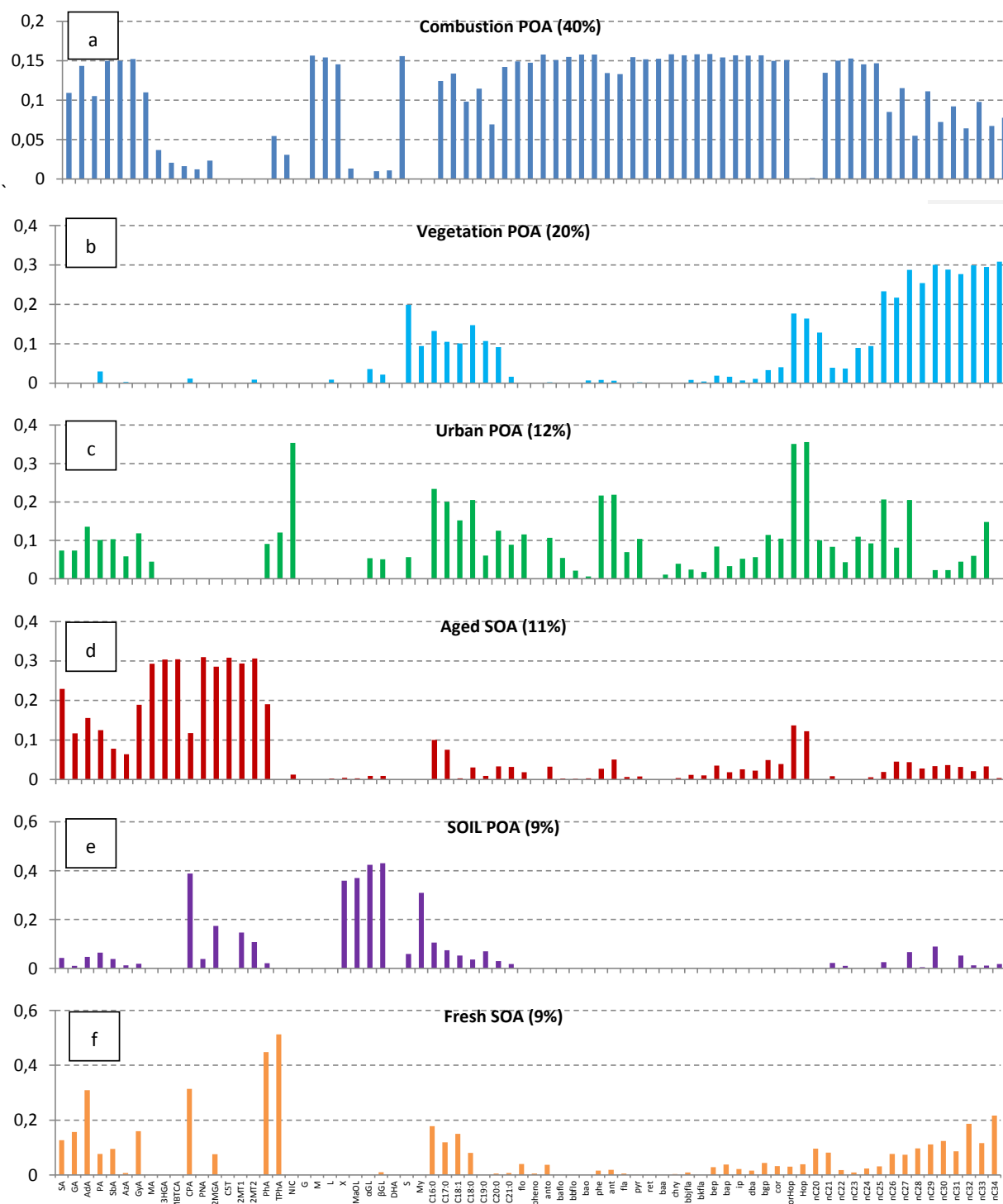
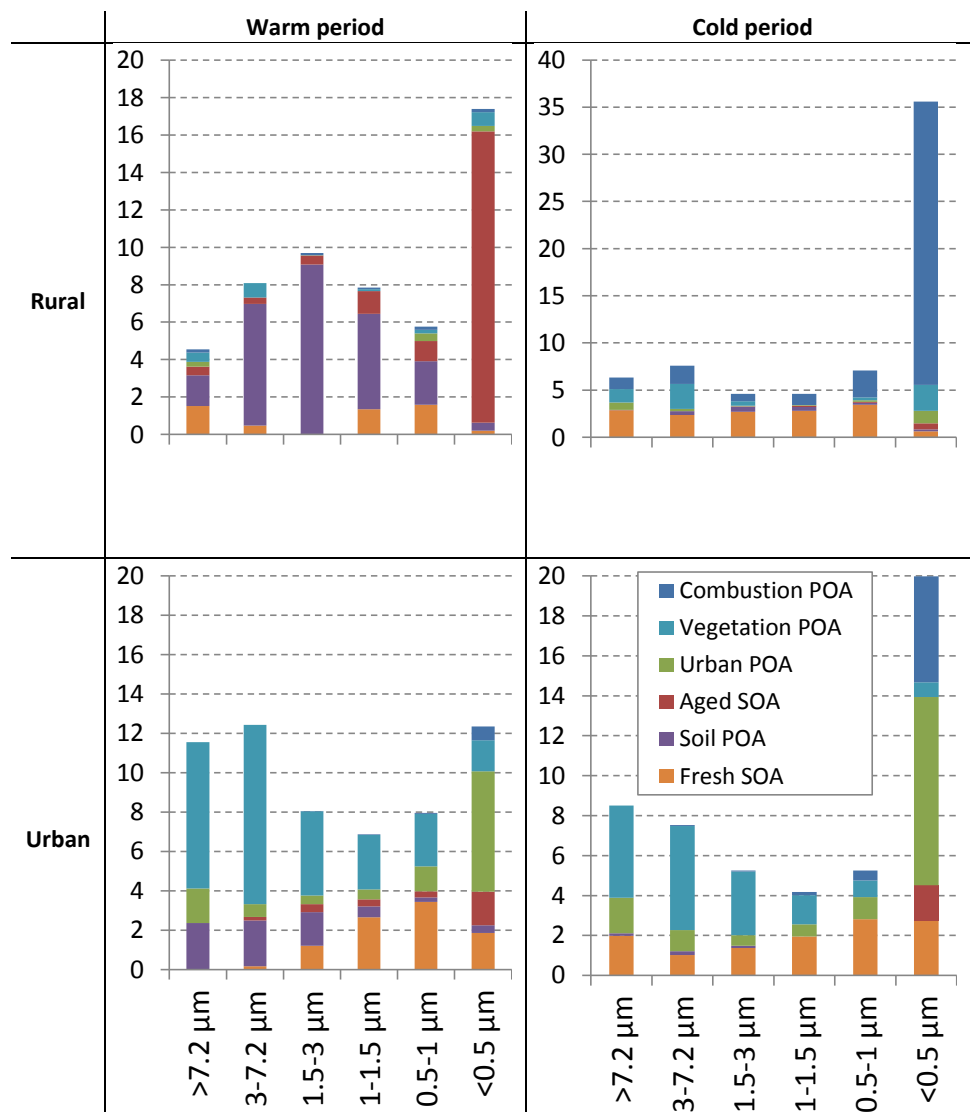


Fig.5 a-f. Loading of the six components from MCR-ALS resolved profiles for the organic compound composition

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999 Fig.6. The average Σ score-values of the six components for the different size fractions in the
000 warm and cold period for the rural and urban site, obtained from the MCR-ALS resolved profiles
001 for the organic compound composition.

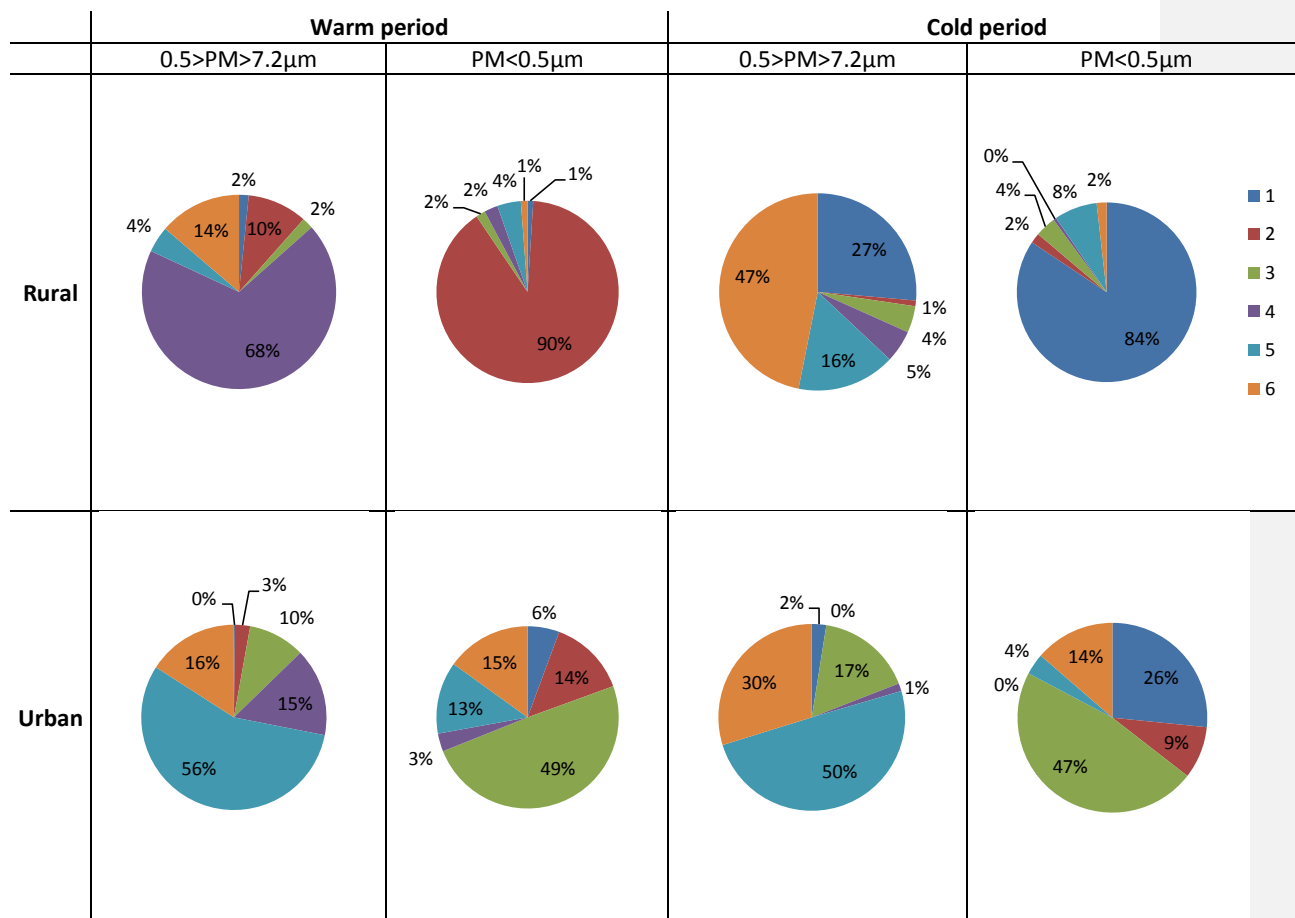


Fig.7. Relative scores of the components (%) in rural and urban site in relation to the warm and cold period. with 1) Combustion POA; 2) Vegetation POA; 3) Urban POA; 4) Aged SOA; 5) Soil POA; 6) Fresh SOA.