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Particle size-resolved source apportionment of primary and secondary organic tracer compounds at urban and rural 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 and $< 0.5\,\mu m$, using a cascade impactor. These fractions were collected at urban and rural sites during warm and cold seasons. Organic tracer compounds, such as levoglucosan, isoprene, pinene oxidation products, polycyclic aromatic hydrocarbons and quinones, were analyzed by gas chromatography coupled with mass spectrometry. These analyses showed that the composition in the smallest size fractions ($< 0.5\,\mu m$) was more uniform than in the larger sizes ($7.2 > \mathrm{PM} > 0.5\,\mu m$). Thus, markers of photochemically synthesized organic compounds or combustion sources, either biomass burning or traffic emissions, were predominantly observed in the fraction $< 0.5\,\mu m$, whereas the larger particles were composed of mixed sources from combustion processes, vegetation emissions, soil resuspension, road dust, urban lifestyle activities and photochemically synthesized organic compounds.

Important seasonal differences were observed at the rural site. In the $< 0.5\,\mu m$ fraction these were related to a strong predominance of biomass burning in the cold period and photochemically transformed biogenic organic compounds in the warm period. In the $7.2 > \mathrm{PM} > 0.5\,\mu m$ fractions the differences involved predominantly 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 to either natural products, e.g., vegetation emissions and upwhirled soil dust, or anthropogenic contributions, e.g., combustion products and compounds related to urban lifestyle activities like vehicular exhaust and tobacco smoking. Two secondary organic aerosol components were identified. They accumulated in the smallest ($< 0.5\,\mu m$) or in the larger fractions ($> 0.5\,\mu m$) 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 3 times higher than at the urban sites and benzo[a]pyrene concentrations above legal recommendations.

1 Introduction

Atmospheric aerosols are comprised of particles with diameters between a few nanometers and tens of micrometers (Seinfeld and Pandis, 2006) and a high diversity of chemical compounds. These complex mixtures have an influence on atmospheric visibility (Watson, 2002), climate forcing (Forster et al., 2007) and human health (Pope III et al., 2002; Brunekreef and Forsberg, 2005). A significant but variable aerosol fraction is comprised of organic material, e.g., between 20 and 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 ve-

hicles, 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 that are present in residues generated after biomass combustion, can make up an important part of the POA fraction (Simoneit et al., 2004; Medeiros 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 semivolatile organic compounds from non-fossil, e.g., vegetation, and fossil, e.g., fossil fuel combustion residues, origins (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; Fu et al., 2010). 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). The 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-depth speciation that is useful for reconstructing 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 photochemical reactions and accumulation of secondary aerosols (Querol et al., 2009; Pey et al., 2009; Pérez 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 Pérez-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 at 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., 1995; Tauler, 1995) 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 that 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, allowing the identification of 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 and subsequent gas chromatography coupled to mass spectrometry. This method allows detection and quantification of a wide range of semivolatile 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; $7.2–3$; $3–1.5$; $1.5–1$; $1–0.5$; $< 0.5 \,\mu m$) with a sampling efficiency of 50 %, using a HiVol sampler (MCV) at a sampling rate of $20 \,m^3 \,h^{-1}$. The particles were collected on custom-made glass-fiber filters (Whatman, Maidstone, UK). Each sample encompassed 72 h pumping. The sampling campaigns were conducted under prolonged calm weather conditions in an urban background site, Barcelona ($41°23.232'$ N, $2°6.943'$ E; 77 m a.s.l.), and in a rural site, La Pobla de Lillet, in the Pyrenees ($42°14.731'$ N, $1°58.488'$ E; 870 m a.s.l.) during different periods (Fig. 1).

The meteorological conditions were determined from local meteorological stations. The samples were divided into
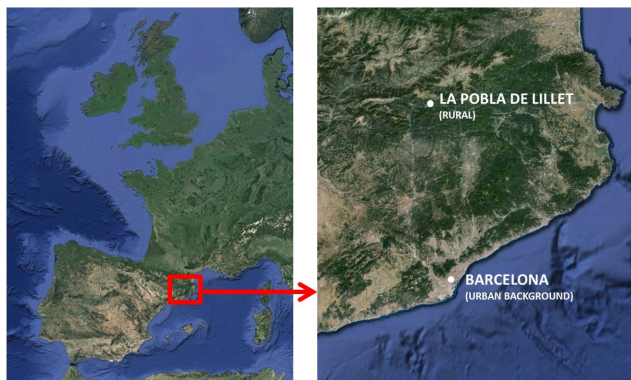
Figure 1. Location of the urban background sampling site in Barcelona and the rural sampling site in La Pobla de Lillet in the Pyrenees.

those belonging to "warm" and "cold" periods (see Table S1 in the Supplement). Temperature was the meteorological parameter with the largest difference between the urban and rural sites. In the former, the average temperatures were 20 and 4 °C in the warm and cold periods, respectively, whereas in the latter these values were 22 and 10 °C (Table S1). Other meteorological parameters such as relative humidity, wind speed, wind direction and atmospheric pressure ranged within similar intervals at both sites (Table S1).

Before sampling, all filters were baked at 450 °C overnight. After sampling, they were split in two sections: half was analyzed for organic compounds and half was stored for toxicity testing. The filter section for chemical analysis was a Soxhlet extraction of $(2:1, v/v)$ dichloromethane : methanol (60 mL; Merck, Darmstadt, Germany) for 8 h. Before extraction, 25 µL of the surrogate standards d_7-levoglucosan, d_{50}-n-C_{24} (Cambridge Isotopic Laboratories, UK), d_4-succinic acid (Sigma Aldrich, Steinheim, USA), d_{10}-anthracene, d_{12}-benz[a]anthracene, d_{12}-benzo[k]fluoranthene and d_{12}-benzo[ghi]perylene (Dr. Ehrenstorfer, Ausburg, Germany) was added. The extracts were filtered through glass-fiber filters using a glass syringe to remove insoluble particles. Then they were concentrated to 1 mL under a gentle nitrogen stream.

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

Polycyclic aromatic hydrocarbons (PAHs), hopanes, n-alkanes and quinones were analyzed in the remaining extract, which was evaporated to almost dryness under a gentle nitrogen stream and redissolved in 0.5 mL (9 : 1 v/v) hexane : dichloromethane (Merck, Darmstadt, Germany). This solution was cleaned up by adsorption column chromatography packed with 1 g of aluminum oxide (Merck, Darmstadt, Germany) that was activated overnight at 120 °C. The analytes were eluted with 4 mL of (9 : 1 v/v) hexane : dichloromethane and 4 mL of (1 : 2 v/v) hexane : dichloromethane (Merck, Darmstadt, Germany). The fractions were collected together and concentrated under a gentle nitrogen stream to 50 µL. 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 – DSQ II) equipped with a 60 m fused capillary column (HP-5MS, 0.25 mm × 25 µm film thickness). The oven temperature program started at 60 °C (holding time 1 min) and then heated to 120 °C at 12 °C min^{-1} and to 310 °C at 4 °C min^{-1}, at which point it was held for 10 min. The injector, ion source, quadrupole and transfer line temperatures were 280, 200, 150 and 280 °C, respectively. Helium was used as a 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 Supplement, contains a 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 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), dehydroabietic 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), C_5-alkene triols (m/z 231), 2-methylthreitol and 2-methylerythritol (m/z 219). No standards for 3-hydroxyglutaric acid, MBTCA, C_5 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; Cleemens and Seinfeld, 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 standards, d_4-succinic acid (m/z 251) and d_7-levoglucosan (m/z 206).

PAHs 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 through a comparison to authentic standards using the following ions: fluorenone (m/z 180), phenanthrenequinone (m/z 208), anthraquinone (m/z 208), benzo[a]fluorenone (m/z 230), benzo[b]fluorenone (m/z 230) and benzanthrone (m/z 230). $17(H)\alpha,21(H)\beta$-29-Norhopane and $17(H)\alpha,21(H)\beta$-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: d_{10}-anthracene (m/z 188), d_{12}-benz[a]anthracene (m/z 240), d_{12}-benzo[k]fluoranthene (m/z 264), d_{12}-benzo[ghi]perylene (m/z 288) and d_{50}-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 MCR-ALS. The joint data set was imported into MATLAB 7.4 (MathWorks, Natick, USA) for subsequent calculations using MATLAB PLS 5.8 Toolbox (Eigenvector Research Inc., Manson, 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., 1995; Tauler, 1995). 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 S3.

3.1.1 Polycyclic aromatic hydrocarbons

PAH are toxic components of fossil fuels and primary products of incomplete combustion of organic materials (Iinuma 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 µm, while around 10 % was present in particles > 3 µm. The urban samples collected in the warm period constituted an exception since around 20 % of the sum of PAH was in the coarse fraction and only 50 % of these hydrocarbons was found in the < 0.5 µm 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 $\sum$PAH concentrations were 6.4 ng m^{-3} in the cold period and twice as low in the warm period (3.3 ± 1.0 ng m^{-3}). The $\sum$PAH 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 $\sum$PAH concentration was observed in the warm period at the rural site (1.2 ± 0.5 ng m^{-3}). In the cold period, this site exhibited 20 times higher average $\sum$PAH concentrations (22 ± 8 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. Nevertheless, exposure to PAH may be much higher in other urban areas such as Baoji in China, where the average $\sum$PAH concentrations were 470 and 140 ng m^{-3} in spring and winter, respectively (Wang et al., 2009), and the benzo[a]pyrene levels in these two seasons were 33 and 11 ng m^{-3}, respectively. In Chennai, India, the observed concentrations of $\sum$PAH were 25 and 6.1 ng m^{-3} in winter and summer, respectively (Fu et al., 2010), and the average benzo[a]pyrene concentrations in these periods were 3.0 and 0.54 ng m^{-3}, respectively. The high PAH concentrations observed in China are not only re-
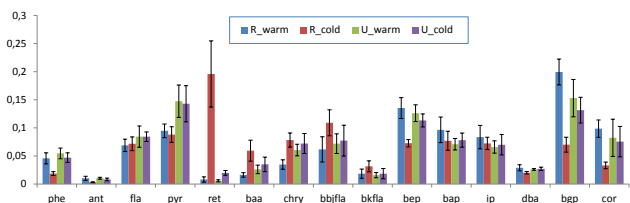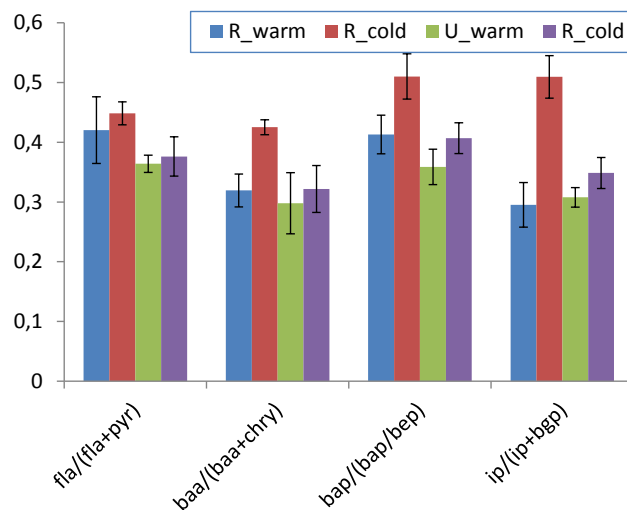
Figure 2. Relative composition of PAHs to $\sum$PAH for the different period (warm vs. cold) in the rural (R) and urban (U) sites.

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

stricted to urban areas. Thus, on Mount Tai (eastern China), the observed average $\sum$PAH concentrations were 51 and 9.1 ng m^{-3} in summer and spring, respectively (Wang et al., 2009), and the benzo[a]pyrene concentrations were 2.1 and 0.8 ng m^{-3} in these periods, respectively.

The assignment of PAH to wood burning in this site is consistent with the high concentrations of retene at the rural site of the present study in the cold period (3.2 ± 2.4 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 ± 0.002 ng m^{-3}, < 2 % of ΣPAH) than in the cold period (0.12 ng m^{-3}, 20–6 % of ΣPAH) (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; Simó et al., 1991, 1997). The baa / (baa + chry), bap / (bap + bep) and ip / (ip + bgp) ratios at the rural site, respectively 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 on 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; Simó 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 through a 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 S3). 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 $\sum$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 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. In this period, the average anto/pheno ratio is 6 and 2 at the rural and urban sites, respectively.

In the cold period, the $\sum$quinone concentration increases and anthraquinone loses predominance (Table S3). At the urban site, this is reflected by a proportion of 6 % quinone and an anto / pheno ratio of 1.1. Other compounds, such as benzofluorenones and benzanthrone, 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 an indicator of the 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 vehicle emissions (Rogge et al., 1993; Schauer et al., 2007). The compounds selected for quantification were $17\alpha(H),21\beta(H)$-29-norhopane and $17\alpha(H),21\beta(H)$-hopane, and they were found in all samples. At the urban site, $\sum$hopane average concentrations of 2–2.2 ng m^{-3} were observed in both warm and cold periods, whereas at the rural site the observed $\sum$hopane average concentrations were 0.9 and 0.5 ng m^{-3} 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 S3). In the former, they were highest in the fraction $< 0.5\,\mu$m; in the latter, 40 % of the compounds were present in the fraction $< 0.5\,\mu$m, whereas another 30–40 % were present in the coarse fraction between $3\,\mu$m and $> 7.2\,\mu$m. 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 a consequence of biogenic and anthropogenic emissions, such as plant waxes or fossil fuel residues (Mazurek et al., 1989; Schauer et al., 2002); 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 $\sum$n-alkane average concentration lowest at the rural site (12 ng m^{-3}) and highest at the urban site (43 ng m^{-3}; Table S3). In the cold period the mean concentrations were 35 and 29 ng m^{-3} 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 m^{-3}; Aceves and Grimalt, 1993b), probably as a consequence of the introduction of cleaner cars and natural gas for domestic heating
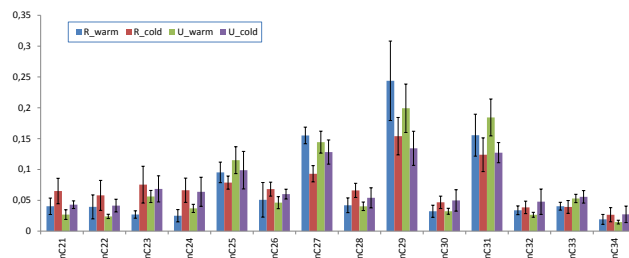
Figure 4. Relative composition of n-alkanes to $\sum$n-alkanes for the different period (warm vs. cold) in the rural (R) and urban (U) sites.

in the urban site over the past decades. Nevertheless, much higher average total n-alkane concentrations have been reported in other cities such as Baoji (China), with levels of 1700 and 490 ng m^{-3} in spring and winter of 2008, respectively (Wang et al., 2009). In Chennai (India), the measured average concentrations of total n-alkanes in 2007 were 140 and 190 ng m^{-3} in winter and summer, respectively (Fu et al., 2010). In rural sites in China, such as Mountain Tai, the observed concentrations of total n-alkanes were 130 and 41 ng m^{-3} in summer and spring of 2006, respectively (Wang et al., 2009).

At the rural site, during the warm period the n-alkanes were evenly distributed among all particle sizes (Table S3), with predominance of n-C_{29} followed by n-C_{31} and n-C_{27} (Fig. 4), while in the cold period they were predominantly in the fraction $< 0.5\,\mu$m (54 % $\pm$ 13 %). In this period, the relative composition of n-alkanes was dominated by n-C_{22} to n-C_{25}, although n-C_{29} and n-C_{31} were also present (Fig. 4). In general, the presence of n-C_{27}, n-C_{29} and n-C_{31} reflects contributions from waxes from terrestrial higher plants, while the n-alkanes in the range between n-C_{22} and n-C_{25} are more related to combustion sources (Mazurek et al., 1989).

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, 2002). 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 $\pm$ 1.3 in the warm period and 1.7 $\pm$ 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 the proportion of n-alkanes (47 % $\pm$ 3 %) found in the larger particles ($> 3\,\mu$m) during the warm period was higher than at the rural site, which is consistent with higher influence of biogenic inputs as also reflected in the high CPI, 3.5 $\pm$ 0.6, and the predominance of

n-C_{29} and n-C_{31} 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-C_{22} to n-C_{25} 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 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 $< 0.5 \, \mu m$. At the urban site, 80 and 90 % of total nicotine was 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 S3). At the rural site, the average concentrations were 0.6 and 1.7 ng m^{-3} in the warm and cold periods, respectively, and at the urban site they were about 1 order of magnitude higher, 13 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, including 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 the thermal alteration of cellulose and hemicellulose that are emitted in large quantities during biomass burning (Simoneit, 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 S3). These compounds predominated in the fraction $< 0.5 \, \mu m$ and their concentrations were significantly correlated ($r^2 > 0.90$). Those of levoglucosan were 3 times higher than the sum of galactosan + mannosan at the rural site and 5 times higher at the urban site, while galactosan and mannosan showed similar concentrations. Lowest and highest levoglucosan concentrations (8 vs. 1600 ng m^{-3}) were observed at the rural site in the warm and cold periods, respectively. These high levels at the rural site in the cold period can be directly related to the presence of local biomass burning for domestic heating or biomass waste removal as a consequence of the high abundance of cellulose in vegetation, as observed in other rural areas in the European and Asian continents (Puxbaum et al., 2007; Bi et al., 2008; Fu et al., 2010). At the urban site,

the higher concentrations of these compounds were also observed in the cold period (155 ng m^{-3}). The mean levoglucosan concentration in the warm period was about 1 order of magnitude lower (18 ng m^{-3}). 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 important constituents of soil organic matter and related to plant tissue and micro-organisms. Xylitol and mannitol are reduced saccharides that are generally associated with organic matter in soils. Mannitol is related to fungi (Simoneit et al., 2004). These compounds can enter into the atmosphere by wind erosion and upwhirling 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 S3). Higher concentrations were observed in the warm period ($\sum$ saccharides were 1150 and 810 ng m^{-3} at the rural and urban sites, respectively), which coincides with higher biological activities in soils, higher plant growth and possible contributions from pollen (Fu et al., 2012). 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 μm, 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 $\sum$ saccharides) and predominated in the coarse fractions between 1.5 and $> 7.2 \, \mu m$. Its concentration in the warm period, 411 ng m^{-3}, was about 1 order of magnitude higher than at the rural site, 46 ng m^{-3}, whereas the concentration of the other saccharides were about 2 times lower at the urban site, indicating the influence of different soil dust particles, plant species and pollen in the two studied sites.

In the cold period, the concentrations of saccharides and polyols in the different fractions decreased by 1 order of magnitude, which is consistent with the seasonal decrease of biological activities. An exception was observed for the fraction $< 0.5 \, \mu m$ 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 $< 0.5 \, \mu m$.

3.1.8 Carboxylic acids

C_{16}–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 (Iinuma et al., 2007; Medeiros and Simoneit, 2007).

The C_{16}–C_{21} straight-chain carboxylic acids were found in all samples (Table S3), with similar concentrations in the two sites and between periods. Palmitic acid ($C_{16:0}$) was the most abundant, followed by stearic acid ($C_{18:0}$). Over 50 % of the carboxylic acids were present in the coarse fractions between 1.5 µm and > 7.2 µm, except in the cold period at the rural site, when about 70 % were present in the fraction < 0.5 µm. 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., 1989). The presence of high proportions of unsaturated fatty acids, such as oleic acid ($C_{18:1}$), is consistent with contributions from food cooking, e.g., in $C_{18:1}$ / $C_{18:0}$ > 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 $C_{18:1}$ higher than $C_{18:0}$ 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 S3). As observed for the other biomass burning tracers, the concentrations were more than 1 order of magnitude lower in the warm period. Accordingly, average levels observed at the urban site were higher in the cold than in the warm periods: 23 and 5 ng m^{-3}, respectively. More than 75 % of this compound was predominantly found in the < 0.5 µm fraction, which is consistent with the size distribution of levoglucosan corresponding to pine wood combustion (Iinuma et al., 2007; Medeiros and Simoneit, 2007).

3.1.9 Dicarboxylic acids, hydroxydicarboxylic acids and aromatic-dicarboxylic acids

The formation mechanisms of these compounds is poorly understood. They are emitted from various primary sources (mobile emission, meat cooking, etc.) although photochemical processes have often been attributed to their occurrence in atmospheric samples (Jang and McDow, 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 S3) with predominance in the finest < 0.5 µm fraction in all cases except for terephthalic acid, which was evenly distributed among the different particle sizes. Malic, succinic, azelaic and terephthalic acids were the most abundant, which is in agreement with previous studies at the urban site (van Drooge et al., 2012; Alier et al., 2013).

The applied analytical methodology – the use of BSFTA+pyridine for derivation of COOH and OH groups into trimethylsilyl-esters and trimethylsilyl-ethers – allowed the detection and quantification of dicarboxylic acids from succinic (C_4) to sebacic acid (C_{10}). Malonic acid (C_3) could not be recovered satisfactorily and oxalic acid (C_2) was not detected (Fontal et al., 2015). Thus, oxalic acid and malonic acid were not included in the present study. Use of longer-chain reaction agents for derivatization, e.g., butanol, allows the quantification of oxalic and malonic acids; in these cases the observed distributions of aliphatic dicarboxylic acids are dominated by oxalic acid, with succinic acid as the second or third major compound (Kawamura and Ikushima, 1993; Mochida et al., 2003; Miyazaki et al., 2009; Ho et al., 2010; Pavuluri et al., 2010). It has been questioned whether these C_2–C_3 dicarboxylic acids could occur predominantly in the gas phase (Satsumabayashi et al., 1989). Comparison of results from high volume filtration and annular denuder sampling used in parallel led to conclude that these homologues are also in the aerosol fraction (Mochida et al., 2003).

In some studies, the relative distributions of oxalic, malonic and succinic acids have been observed to follow the same seasonal pattern (Kawamura and Ikushima, 1993). Good correlations between the concentrations of oxalic, malonic and succinic acids in urban aerosols have also been observed (Ho et al., 2010), which has been explained by the transformation of longer into shorter carbon chain acids (Kawamura and Ikushima, 1993). These antecedents suggest that the changes observed for succinic acid in the present study could also be reflected in the non-determined C_2 and C_3 homologues. The average concentration of succinic acid in the rural, 68–73 ng m^{-3}, and urban, 24–45 ng m^{-3}, sites (Table S3) is similar to that found in other urban areas such as Tokyo (37 ng m^{-3}: Kawamura and Ikushima, 1993; 36–47 ng m^{-3}: Satsumabayashi et al., 1989) or Beijing (49–50 ng m^{-3}: Ho et al., 2010) and lower than that found in sites located downwind of Los Angeles in periods of photochemical smog (200–500 ng m^{-3}: Grosjean et al., 1978), in New Delhi (270–330 ng m^{-3}: Miyazaki et al., 2009) and Shanghai (200 ng m^{-3}: Yao et al., 2002). It is higher than in Houston (16 ng m^{-3}: Yue and Fraser, 2004) or in Helsinki (6 ng m^{-3}: Timonen et al., 2008).

In all cases, the average concentrations of the aliphatic dicarboxylic acids in the rural site were higher than those in the urban site (Table S3). The average concentration of glutaric acid in the rural site of the present study, 9.1–21 ng m^{-3} (Table S3), is comparable to that found in Beijing (16–19 ng m^{-3}: Ho et al., 2010) and Tokyo (11 ng m^{-3}: Kawa-

mura and Ikushima, 1993; 8–21 ng m^{-3}: Satsumabayashi et al., 1989) and lower than that in New Delhi (51–66 ng m^{-3}: Miyazaki et al., 2009). The concentrations of this acid in the urban site are lower than in these cities. Similar differences between these cities and the presently studied sites are observed for the concentrations of pimelic acid. The average concentration of suberic acid in the rural site, 7.3 ng m^{-3}, is similar to those observed in these cities but much higher than those found in Beijing (0.77–0.85 ng m^{-3}: Ho et al., 2010).

Azelaic acid is an oxidation product of unsaturated fatty acids having the double bond at position C-9 from the carbonyl (Kawamura and Gagosian, 1987). As observed in Table S3, both in the urban and rural samples and in the warm and cold seasons, the concentrations of this dicarboxylic acid are higher than those of other homologues of similar carbon chain length, e.g., C$_8$ and C$_{10}$, which is due to its specific sources from the oxidation of oleic acid, C$_{18:1}$, and other longer carbon chain acids with unsaturation at C-9.

The average total concentrations of aliphatic dicarboxylic acids in the rural site were 130 and 210 ng m^{-3} in the warm and cold periods, respectively. At the urban site they were 64 and 110 ng m^{-3}, respectively (Table S3). As mentioned above, photooxidation is a likely source for the occurrence of these compounds in the aerosols but the higher abundance of these compounds in the rural site and in winter suggests that other sources such as combustion could also be relevant. In this respect, high concentrations of dicarboxylic acids have been reported in plumes from biomass burning (Narukawa et al., 1999; Graham et al., 2002; Rogge et al., 1991). Furthermore, the high average concentration of azelaic acid in the cold season of the rural site, 77 ng m^{-3} – which is higher than that in the warm season (21.5 ng m^{-3}) and at the urban site (17 and 19 ng m^{-3} in the warm and cold seasons, respectively) – is consistent with contributions from biomass burning. 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 about 30 % in the cold period.

Malic acid is a presumed product of the OH oxidation of succinic acid (Kawamura and Ikushima, 1993) as a consequence of photochemical aging. This is consistent with the observed distributions of dicarboxylic acids in the rural site. The average concentration of malic acid in the warm period was 99 ng m^{-3} and the malic / (malic + succinic) acid ratio was M / (M + S) = 0.57, whereas in the cold period the average concentration was 27 ng m^{-3} and the M / (M + S) ratio was 0.28. This contrast shows that malic acid is likely formed by photochemical reactions rather than combustion processes given the dominance of the latter in the cold period. In the urban environment, intermediate M / (M + S) ratios are observed, 0.45 and 0.42 in the warm and cold periods, respectively, and the respective concentrations are lower, 19.5 and 34 ng m^{-3}.

Phthalic acid esters are used as plasticizers in resins and polymers. They can be released into the air by evapora-

tion because they are not chemically bonded. Higher phthalic acid concentrations have been observed in summer because of the higher ambient temperatures (Ho et al., 2010). However, these compounds may also originate from combustion (Kawamura and Kaplan, 1987) or atmospheric oxidation of aromatic hydrocarbons (Kawamura and Ikushima, 1993; Kawamura and Yasui, 2005). The average phthalic acid concentration of the rural site was much higher in winter (33 ng m^{-3}) than in summer (20 ng m^{-3}) (Table S3), which suggests a preferential origin related to combustion sources. Conversely, in the urban site the average concentration of the warm period, 22 ng m^{-3}, was higher than that of the cold period, 18.5 ng m^{-3}. This difference is consistent with a predominance of plastic degassing at higher temperatures. The observed average concentrations of phthalic acid in the present study, 20–33 ng m^{-3}, are similar to those found in Tokyo, 15 ng m^{-3} (Kawamura and Ikushima, 1993) and 31–39 ng m^{-3} (Satsumabayashi et al., 1989), higher than those reported in Chennai (Fu et al., 2010) and lower than those found in New Delhi, 40–45 ng m^{-3} (Miyazaki et al., 2009), and Beijing, 68–78 ng m^{-3} (Ho et al., 2010).

The average concentrations of terephthalic acid were always higher in the cold period (180 and 170 ng m^{-3} in the rural and in the urban sites, respectively) than in the warm period (17 and 125 ng m^{-3}, respectively). A priori these differences also suggest an origin related to combustion processes. The average concentration range of this dicarboxylic acid is much higher than the concentration ranges reported in New Delhi (4–5 ng m^{-3}: Miyazaki et al., 2009), Tokyo (6–15 ng m^{-3}: Satsumabayashi et al., 1989), Santiago, Chile (0.5–3.2 ng m^{-3}: Simoneit et al., 2005), and Los Angeles (5.4 ng m^{-3}: Simoneit et al., 2005). With the exception of the samples collected during the cold period at the rural site, the average concentrations of the present study are also much higher than those observed in Chennai (28–43 ng m^{-3}: Fu et al., 2010; 45–68 ng m^{-3}: Kawamura and Pavuluri, 2010) and Beijing (32–41 ng m^{-3}: Ho et al., 2010). 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 and 7.2 µm. These concentrations were 1 order of magnitude higher than in the other rural samples, which indicated a primary emission contribution in that sampling period. Terephthalic acid has been found in high concentrations in smoke particles from open burning of plastic bags and landfill trash (Simoneit et al., 2005). It may also be formed by secondary oxidation reactions in the atmosphere but records relating this secondary mechanism with the occurrence of terephthalic acid in the aerosols are not available (Kawamura and Pavuluri, 2010). In the context of the rural and urban sites considered in the present study, no obvious source of plastic burning has been identified.

3.1.10   Tracers of α-pinene oxidation

Cis-pinonic acid, pinic acid, 3-hydroxyglutaric acid and 3-methyl-1,2,3-butanetricarboxylic acid are related to the photochemical oxidation of biogenic volatile α-pinene (Claeys et al., 2007; Szmigielski et al., 2007), which is the most abundant monoterpene 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 $< 0.5\,\mu m$, showing high average concentrations in the warm period at the rural site, $\sim 45\,ng\,m^{-3}$. In the cold period and at the urban site, the concentrations of these compounds were about $6\,ng\,m^{-3}$. Significant correlations 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 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-hydroxyglutaric 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). However, the concentrations of cis-pinonic acid showed a weak correlation with those of pinic acid and 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 $< 0.5\,\mu m$ 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.

3.1.11   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 a 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 S3) and the highest concentrations occurred in the fraction $< 0.5\,\mu m$. The highest con-

centrations were found in the warm period in the particles $< 0.5\,\mu m$ collected at the rural site, with mean values of 41, 123, 60 and $221\,ng\,m^{-3}$ for 2-methylglyceric acid, C5-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 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 3 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).

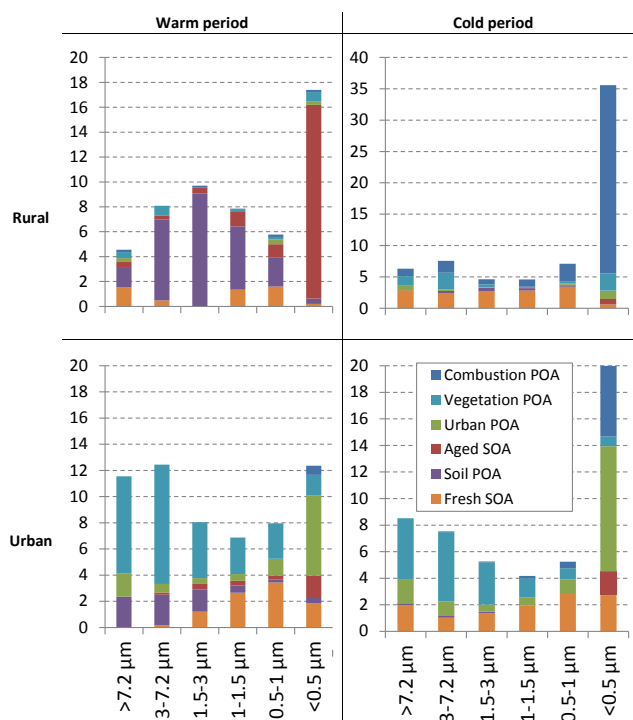## 3.2   Source apportionment of organic aerosol

MCR-ALS allowed the identification 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 dominant component and explains 40 % of the total variance. It was composed of primary biomass burning tracers, such as anhydrosaccharides, dehydroabietic acid, PAHs, quinones, C_{20}–C_{24} n-alkanes with low CPI index, carboxylic acids and dicarboxylic acids (Fig. 5a). This component was very abundant in the finest $< 0.5\,\mu m$ fraction of the fall–winter samples in both sites (Fig. 6). However, the rural site showed score values 3 to 6 times higher 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. However, the presence of dehydroabietic acid and retene indicates 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 the fall, while it hardly

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

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, both the former was lower in winter (2.7) than in fall (5.4) and the latter was lower in winter (370) than in 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 it in a six-component resolution (Fig. S1 in the Supplement). 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 (blue) 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 suggest that about 50 % of the biomass burning in the 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 $160\,\mathrm{ng\,m^{-3}}$ (Table S3), 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

Figure 6. The average $\sum$ score values of the six components for the different size fractions in the warm and cold period for the rural and urban site, obtained from the MCR-ALS resolved profiles for the organic compound composition.

fractions between > 7.2 and $> 1\,\mu m$ (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, because 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 $< 0.5\,\mu m$ 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 lifestyle, e.g., smoking and traffic. Thus, nicotine, hopanes and low-molecular-weight PAH, i.e., phenanthrene and anthracene, are significant compounds 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 a 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 $< 0.5\,\mu m$ 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 μm at the rural site during the warm period and, to a smaller extent, at the urban site during the warm period (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, when it is much drier than in the winter, 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 upwhirling 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 to 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 and 1.5 μm and sometimes up to $> 7\,\mu m$ (Fig. 6). This size distribution is very different from the other secondary aerosol constituents that essentially occurred in the $< 0.5\,\mu m$ 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 component of aged SOA
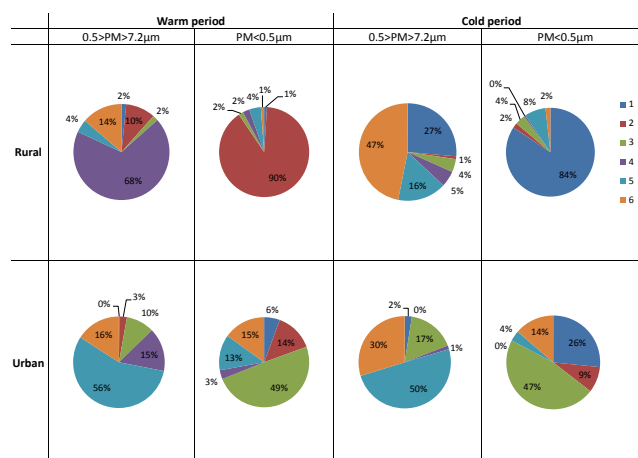
Figure 7. Relative scores of the components (%) in rural and urban site in relation to the warm and cold period: (1) combustion POA, (2) vegetation POA, (3) urban POA, (4) aged SOA, (5) soil POA and (6) fresh SOA.

(see Sect. 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 the exception of the rural sample collected in the fall, when biomass waste burning was contributing substantially 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 the combustion of plastic (Kawamura and Pavuluri, 2010) 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 latter compound has not been found in the aerosols of the present study. Another source for phthalic acid could be combustion or atmospheric oxidation of aromatic hydrocarbons (Kawamura and Kaplan, 1987; Kawamura and Ikushima, 1993; Kawamura and Yasui, 2005), which is consistent with the high concentrations of these compounds in the cold period samples collected in the rural site under intense biomass combustion.

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 (Figs. 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 ($22 \, \text{ng m}^{-3}$) at the rural site. That is nearly 3 times higher than at the urban site ($6.4 \, \text{ng m}^{-3}$). In this respect, the benzo[a]pyrene winter concentrations at the rural site exceeded the limit value of $1 \, \text{ng m}^{-3}$, indicating that rural communities undergo higher exposures to this carcinogenic compound as a 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 and Pérez-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 lasting 1 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) constituted 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

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

The particles $> 0.5\,\mu m$ showed a higher diversity of constituents. In 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). In 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 period (97 %).

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