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Source
apportionment of
submicron organic
aerosol

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Source apportionment of submicron organic aerosol at an urban background and a road site in Barcelona, Spain

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Abstract

This study investigates the contribution of potential sources to the sub-micron (PM₁) organic aerosol (OA) simultaneously detected at an urban background (UB) and a road site (RS) in Barcelona during the 30 days of the intensive field campaign of SA-PUSS (Solving Aerosol Problems by Using Synergistic Strategies, September–October 2010). 103 filters at 12 h sampling time resolution were collected at both sites. Thirty-six neutral and polar organic compounds of known emission sources and photo-chemical transformation processes were analyzed by Gas Chromatography-Mass Spectrometry (GC-MS). The concentrations of the trace chemical compounds analyzed are herein presented and discussed.

Additionally, OA source apportionment was performed by Multivariate Curve Resolution-Alternating Least Squares (MCR-ALS) and six OA components were identified at both sites: two were of primary anthropogenic OA origin, three of secondary OA origin while a sixth one was not clearly defined. Primary organics from emissions of local anthropogenic activities (Urban primary organic aerosol, Urban POA) contributed for 43 % (1.5 µg OC m⁻³) and 18 % (0.4 µg OC m⁻³) to OA in RS and UB, respectively. A secondary primary source – biomass burning (BBOA) – was found in all the samples (average values 7 % RS; 12 % UB; 0.3 µg OC m⁻³), but this component was substantially contributing to OA only when the sampling sites were under influence of regional air mass circulation. Three Secondary Organic Aerosol (SOA) components (describing overall 60 % of the variance) were observed in the urban ambient PM₁. Products of isoprene oxidation (SOA ISO), i.e. 2-methylglyceric acid, C₅ alkene triols and 2-methyltetrols, showed the highest abundance at both sites when the city was under influence of inland air masses. The overall concentrations of SOA ISO were similar at both sites (0.4 and 0.3 µg m⁻³, 16 % and 7 %, at UB and RS, respectively). By contrast, a SOA biogenic component attributed to α-pinene oxidation (SOA BIO PIN) presented average concentrations of 0.5 µg m⁻³ at UB (24 % of OA) and 0.2 µg m⁻³ at RS (7 %), respectively, suggesting that this SOA component did not impact the two monitoring

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site at the same level. A clear anti correlation was observed between SOA ISO and SOA PIN during nucleation days, surprisingly suggesting that some of the growth of urban freshly nucleating particles may be driven by biogenic α -pinene oxidation products but inhibited by isoprene organic compounds. A third SOA component was formed by a mixture of aged anthropogenic and biogenic secondary organic compounds (Aged SOA) that accumulated under stagnant atmospheric conditions, contributing for 12 % to OA at RS ($0.4 \mu\text{g OC m}^{-3}$) and for 18 % at UB ($0.4 \mu\text{g OC m}^{-3}$).

A sixth component, formed by C_7 – C_9 dicarboxylic acids and detected especially during daytime, was called “urban oxygenated organic aerosol” (Urban OOA) due to its high abundance in urban RS (23 %; $0.8 \mu\text{g OC m}^{-3}$) vs. UB (10 %; $0.2 \mu\text{g OC m}^{-3}$), with a well-defined daytime maximum. This temporal trend and geographical differentiation suggests that local anthropogenic sources were determining this component. However, the changes of these organic molecules were also influenced by the air mass trajectories, indicating that atmospheric conditions had an influence on this component although the specific origin on this component remains unclear. It points to a secondary organic component driven by primary urban sources including cooking and traffic (mainly gasoline) activities.

1 Introduction

Atmospheric aerosols influence on the atmospheric visibility (Watson, 2002), are relevant in climate forcing (Forster et al., 2007) and have several adverse effects on human health (Brunekreef et al., 2005). They contain a significant and variable fraction of organic material, ranging from 20 to 90 % of the submicron ($< 1 \mu\text{m}$ in particle size) particulate matter (PM_{10}) mass (Kanakidou et al., 2005). Such organic material divides into two broad categories termed primary and secondary. Primary organic aerosols (POA) in urban areas are emitted from combustion sources, including heavy and light duty vehicles, wood smoke, cooking activities, industries and others. Such primary particles can be modified in the presence of various atmospheric oxidants (Donahue et al., 2009)

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existing source apportionment techniques is relatively large, including Principal Component Analysis (PCA, Jolliffe, 2002), Chemical Mass Balance (CMB, US-EPA, 1987) and Positive Matrix Factorization (PMF, Paatero et al., 1994). PCA uses orthogonal constraints and environmental interpretation of score and loading profiles is sometimes cumbersome. CMB requires the previous knowledge of the emission source profiles, and therefore it is unable to identify unknown sources. PMF integrates natural constraints like non-negativity and uncertainty estimations in a rigorous non-linear optimization of the distribution and composition source profiles. In this work we deploy the Multivariate Curve Resolution Alternating Least Squares (MCR-ALS) method (Tauler et al., 1995; Tauler, 1995; Jaumot et al., 2005) that has previously been applied for environmental source apportionment (Salau et al., 1997; Terrado et al., 2009). MCR-ALS is based on an alternating linear least squares optimization under non-negativity constraints which produces physically better profiles than PCA and it has been shown to produce analogous results to PMF (Tauler et al., 2009; Staminirova et al., 2011).

The objective of this study is to characterize the submicron PM (PM_1) organic aerosol component sampled during the SAPUSS intensive field study conducted in Barcelona (Spain) during the period September–October 2010. This manuscript is part of the SAPUSS special issue (Dall’Osto et al., 2012a). The current study is unique in regards of a large dataset of more than 100 PM_1 filters collected simultaneously at an urban background site (UB) and an urban road site (RS). The urban study area of Barcelona has some unique features. It is characterized by one of the highest density of vehicles 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., 2008; Perez et al., 2010; Pey et al., 2009).

Past studies at an urban background site in Barcelona (same UB location used in this SAPUSS study), showed that a large fraction (56 %) of the OA consisted of oxygenated OA (Mohr et al., 2012). Moreover, radioactive carbon analysis showed that about 60 % of the organic carbonaceous atmospheric matter in this background site has a non-fossil origin (Minguillón et al., 2011). However, there are evidences that

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biomass burning contributes to only a small part ($\sim 15\%$) of the urban background OA which is mainly related to the winter season or wild fire events (Mohr et al., 2012; Reche et al., 2012; van Drooge et al., 2012a). This gives way to the hypothesis that other non-fossil sources should account for an important part of the OA. Indeed, Mohr et al. (2012) attributed 17% of the OA to primary food cooking emissions after AMS analysis in the UB site. Nevertheless, there is still a lack of information upon the chemical speciation of this source. Furthermore, the contribution of different types of SOA of both anthropogenic and biogenic origins is still highly uncertain in the urban area of Barcelona.

In summary, the simultaneous analysis of selected organic tracer compounds analyzed from the PM_1 filter samples collected at the UB and at the RS sites is herein presented. Furthermore, a source apportionment of the OA is also carried out and discussed.

2 Materials and methods

2.1 Sampling sites

Detailed information on the urban sites studied in Barcelona is given elsewhere (Dall'Osto et al., 2012a). The urban background site (UB; $41^\circ 23' 15''$ N; $02^\circ 07' 05''$ E; 80 m a.s.l.) was situated at the Western periphery of the city centre in a small park. The road site (RS; $41^\circ 23' 18''$ N; $02^\circ 09' 00''$ E; 40 m a.s.l.) was located in a car park next to Urgell Street within the square-grid street network (Eixample) (Fig. 1). The road, which cuts the city from South East to North West, is a street canyon composed by a two-way cycling path and a one-way four lane vehicle road. Vehicle intensity for the month of measurements was about 17 000 vehicles per day. The two monitoring sites are located within 3 km from each other.

The meteorological data were measured in the sampling sites by means of automatic weather stations (Dall'Osto et al., 2012a). Air mass back trajectories were calculated

daily during the sampling campaign. Four main air mass scenarios were identified during the SAPUSS field study (Dall'Osto et al., 2012a): Atlantic advection (2 periods; 7 days), North African-West (2 periods; 3 days), North African-East (1 period; 3 days), and Regional (2 periods; 8 days).

2.2 Organic compounds analyzed

The applied extraction method and instrumental analysis offers a selective sight on the total mass of the ambient air PM₁. The usage of organic solvent mixture allows the extraction of wide range of organic compounds with different polarities. Moreover, the instrumental analysis allows the detection of semi-volatile organics. During the years many of these compounds have been detected in emissions and ambient air samples, and therefore certain organic compounds can be used as tracers for sources and atmospheric processes. Table 1 shows the 36 organic compounds that were analyzed in the present study. They were selected based on their representativeness of primary organic aerosol emission sources and secondary organic aerosol formation. Briefly:

- Polycyclic aromatic hydrocarbons (PAH, 12 in total). They are toxic components of fossil fuels and primary products of incomplete combustion of fossil fuels and biomass (Rogge et al., 1993; Schauer et al., 2007).
- Hopanes (17(H) α -21(H) β -29-norhopane and 17(H) α -21(H) β -hopane). They are molecular markers for mineral oils, and their presence can be related to unburned lubricating oil residues from primary vehicles emissions (Rogge et al., 1993; Schauer et al., 2007).
- Nicotine. This alkaloid is present in high concentrations in environmental tobacco smoke. Although it is mainly present in the gas-phase due to its relatively high volatility, it can be detected at trace levels on PM filter samples (Rogge et al., 1994; Bi et al., 2005).

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- Levoglucosan, galactosan and mannosan. They are monosaccharide anhydrides generated by thermal alteration of cellulose and hemi-cellulose. They are emitted in large quantities during biomass burning (Simoneit et al., 2002; Fine et al., 2004).
- Dicarboxylic acids (DCA), hydroxy-DCA and aromatic-DCA (11 in total, Table 1). They can be emitted from various primary sources (mobile emission, meat cooking, etc.) although atmospheric photochemical formation is probably the main source (Jang et al., 1997; Kerminen et al., 2000; Heald et al., 2010; Sheesley et al., 2010; Paulot et al., 2011).
- *Cis*-pinonic acid, 3-hydroxyglutaric acid and 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA). They have been identified in aerosols and related to the photochemical oxidation of biogenic volatile compounds such as α -pinene (Claeys et al., 2007; Szmigielski et al., 2007). 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). It is worth to note that the most abundant monoterpene in the study area presented in this manuscript is α -pinene (Seco et al., 2011).
- 2-methylglyceric acid and polyols, such as C₅ alkene triols and 2-methyltetrols. They have been related to isoprene oxidation (Claeys et al., 2004; Hallquist et al., 2009), a major volatile organic compound emitted from land vegetation.

2.3 Analytical procedure

Digitel-DH80 HiVol samplers were used to collect 103 PM₁ filters (Pall Life Sciences; TISSUEQUARTZ 2500QAT-UP), each encompassing 12 h sampling hours, between 09:00 and 21:00 (UTC), at a sampling rate of 30 m³ h⁻¹. More information can be found elsewhere (Dall'Osto et al., 2012a). All filters were preheated at 450 °C overnight before sampling. 1/8 section of each filter was preserved for analysis of organic compounds.

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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 s⁻¹. The MS selective detector was operated in fullscan (m/z 50–650) and electron impact (70 eV) ionization modes.

Besides comparison of retention times, levoglucosan and mannosan were identified with ion m/z 204, galactosan with ion m/z 217 and nicotine with ion m/z 84. Acids, polyols and 2-methyltetrols were identified with the following ions: malonic acid (m/z 233), succinic acid (m/z 247), glutaric acid (m/z 261), 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), tartaric acid (m/z 292), phthalic acid (m/z 295), tricarballic acid (m/z 377), *cis*-pinonic acid (m/z 171), 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 to literature and library data (Claeys et al., 2007; Kourtchev et al., 2005; Cleemens et al., 2007). Quantification was performed with the external standard calibration curves. The concentrations were corrected by the recoveries of the surrogate standard succinic acid (m/z 251) and levoglucosan-d₇ (m/z 206).

PAH were identified by retention time comparison of the peaks with the following ions in SIM mode: 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). 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. Quantification was also performed by the external standard method and the calculated concentrations were

corrected for the recoveries of the above mentioned surrogates: anthracene-d₁₀ (*m/z* 188), benz[a]anthracene-d₁₂ (*m/z* 240), benzo[k]fluoranthene-d₁₂ (*m/z* 264) and benzo[ghi]perylene-D₁₂ (*m/z* 288).

In all cases the recoveries of the surrogate standards were higher than 70%. Field blank levels were between 1% and 30% of the sample levels. All concentrations were corrected for blank levels. 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 0.1 ng m⁻³ for the anhydrosaccharides, 0.06 ng m⁻³ for the acids and 0.005 ng m⁻³ for PAHs and hopanes.

2.4 Chemometrics

MCR-ALS method has been successfully used in the analysis of environmental datasets, both in contamination studies of surface waters (Terrado et al, 2009) and in air source apportionment studies (Salau et al., 1997; Tauler et al., 2009). One of the main advantages of MCR-ALS is that it decomposes the data matrix by applying more natural constraints than PCA, such as non-negativity, and, therefore, results interpretation is more straightforward.

MCR-ALS is based on a bilinear decomposition of the original data set. In matrix form, it is expressed as $\mathbf{D}(I \times J) = \mathbf{U}(I \times N)\mathbf{V}^T(N \times J) + \mathbf{E}(I \times J)$, where \mathbf{D} is the original data array, with I rows (samples) and J columns (compounds); \mathbf{U} is the matrix of scores of dimensions $I \times N$, where N is the reduced number of components; \mathbf{V}^T is the matrix of loadings with dimensions $N \times J$ and \mathbf{E} is the matrix of residuals not modelled by the N components. 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; Jaumot et al., 2005). The variance explained by the different components is overlapped and not orthogonal (non-overlapped) as in PCA (Jolliffe, 2002). Natural sources in the environment are rarely orthogonal, thus the MCR methods may have a physically sounder interpretation than orthogonal database decomposition methods.

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and such factor was found to be similar to the one of vehicle intensities near the two monitoring sites (1.4; Dall'Osto et al., 2012a).

3.1.2 Hopanes

Total hopanes concentrations were 0.75 ng m^{-3} and 0.50 ng m^{-3} at RS and at the UB sites, respectively (Table 1), reflecting – likewise the PAH concentrations – the strong influence of fossil fuel vehicles combustion at the former site. Temporal trends of hopanes were also found to be moderately correlated between the two monitoring sites ($r^2 = 0.65$, $P < 0.05$). There were no differences between day and night periods, likewise the PAH_low concentrations. The relationship between PAH_low and hopanes reflects the primary emissions of diesel vehicles (Rogge et al., 1993; Zielinska et al., 2004). Higher concentrations were observed during weekdays in comparison to week-ends/holidays (factor 1.6 at UB, 2 at RS; Table 1).

3.1.3 Nicotine

This alkaloid was found in all filter samples. Much higher concentrations (58 ng m^{-3}) were observed at the RS site than at UB (7 ng m^{-3}). This eight-fold difference points to a very strong outdoor cigarette consumption nearby RS which is situated next to a busy street and an exit of an underground metro station. The UB sampling station is situated in a local park and is away from streets and pedestrian people. It is worth to note that Spain rank among the countries of highest cigarette consumption in the European Union and in the World (WHO, 2010). High outdoor gas-phase nicotine concentrations were previously measured in Barcelona in summer 2010 between 0.5 and $1.5 \mu\text{g m}^{-3}$ (Sureda et al., 2012).

Nicotine concentrations showed a moderate correlation ($r^2 = 0.4$, $P < 0.05$) between the two monitoring sites, suggesting that the whole urban atmosphere of Barcelona was generally influenced by outdoor tobacco smoke. At RS nicotine concentrations had a day/night ratio of 1.5 ($P < 0.05$) at the RS, whereas a statistically difference was not

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found at the UB site. Significant higher nicotine concentrations were detected during weekdays than to weekends/holidays days (ratio of 1.8 and 2.5 at UB and RS, respectively, $P < 0.05$; Table 1). This indicates that the nicotine concentrations are more affected by anthropogenic working activities during daytime of the weekdays rather than leisure ones occurring during weekends. This result is in line with other SAPUSS studies of single particle Aerosol Time-Of-Flight Mass Spectrometry showing that nicotine concentrations correlate with traffic activities and not with gastronomic ones (Dall'Osto et al., 2012a).

3.1.4 Anhydro saccharides

In this group of compounds, mannosan and galactosan showed low concentrations (about $2\text{--}4\text{ ng m}^{-3}$), and also the levoglucosan concentrations were relatively low (9 and 5 ng m^{-3} at UB and RS, respectively, Table 1). These levels are similar to previous studies in the same region during the summer season (van Drooge et al., 2012b) and in European background sites with low influence of biomass burning (Puxbaum et al., 2007). In contrast, higher levoglucosan concentrations were found at the UB site in former studies conducted during wintertime ($35\text{--}60\text{ ng m}^{-3}$, Reche et al., 2012; van Drooge et al., 2012a). In the present study, these high levels were only observed at both sites at the end of the sampling period (about 35 ng m^{-3} , 15–20 October 2010). This increase was coincident with the legal permission of burning biomass waste in regional background fields from 15 October and onwards (DOGC, 1995) as well as with a stagnant regional anticyclonic conditions (Dall'Osto et al., 2012a). The temporal concentration changes of the anhydro saccharides compounds at both sites were very similar ($r^2 = 0.88$, $P < 0.05$).

However, the higher levels found at the UB site relative to the RS site (ratio 1.9; $P < 0.05$) are likely due to the higher exposure of the UB site from regional sources because the RS site is located within a network of streets that reduce natural ventilations. This difference between the two stations was more defined in the last period of the sampling when higher concentrations were detected.

3.1.5 Dicarboxylic acids (DCA), hydroxy-DCA and aromatic-DCA

Mean concentrations of individual DCA compounds were found ranging between 1 and 14 ng m⁻³ and between 1 and 10 ng m⁻³ at the UB and RS, respectively. The highest individual mean concentrations at both sites were observed for malic acid (14 ng m⁻³ at UB; 10 ng m⁻³ at RS) and succinic acid (7 ng m⁻³ at UB; 6 ng m⁻³ at RS). Such range of concentrations is similar to those measured during winter time at the UB site (Van Drooge et al., 2012a). The higher ratio of malic acid/succinic acid was previously observed in other sites influenced by anthropogenic emission sources (Yang et al., 2008a). Phthalic acid – a secondary organic tracer for fossil fuel combustion – showed similar mean concentrations at both sites (4 ng m⁻³, Table 1). As regard of the temporal trends of the DCA concentrations during SAPUSS, the majority of them were found similar between the two monitoring sites ($0.2 < r^2 < 0.8$, $P < 0.05$, Table 1).

Most DCA concentrations were found slightly higher at the UB site relative to the RS one (UB/RS about 1.2), with the exception of the C₇–C₉ dicarboxylic acids (pimelic, suberic and azelaic acids) which were found to possess a ratio UB/RS of 0.5. Moreover, in contrast to any of the other analyzed compounds, C₇–C₉ dicarboxylic acids showed a clear daytime maximum in their concentrations, especially at the RS site (Table 1). Among the C₇–C₉ DCA analyzed, azelaic acid showed the highest concentrations (3 ng m⁻³ and 6 ng m⁻³ at UB and RS, respectively). The presence of azelaic acid in ambient air PM has been related to fast oxidation of un-saturated fatty acids, i.e. oleic acid, by ozone (Gogou et al., 1994; Moise et al., 2002). The oxidation of biogenic precursors can also be an important source of C₇–C₉ dicarboxylic acids (Kawamura and Gagosian, 1987; Stephanou and Stratigakis, 1993; Mochida et al., 2003; Zhang et al., 2010; Ho et al., 2011). Oleic acid in the urban atmosphere may have many sources, such as food cooking, traffic and biogenic sources, including the marine environment (Fang et al., 2002; Schauer et al., 2002; Robinson et al., 2006). In the present study, oleic acid was identified in all samples (including field blank filters) at low concentrations (< 2 ng m⁻³). The lack of substantial oleic acid concentrations in the samples may

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be due to the chemical instability of this unsaturated fatty acid and/or a fast oxidation to other compounds in the urban atmosphere. Further considerations on possible sources and atmospheric processes responsible for the elevated azelaic acid concentrations detected are given in Sect. 3.2, where an aerosol source apportionment is attempted.

5 3.1.6 α -pinene SOA tracers: *cis*-pinonic acid, 3-hydroxyglutaric acid and MBTCA

Cis-pinonic acid, 3-hydroxyglutaric acid and MBTCA, the three biogenic SOA tracers for α -pinene oxidation, were detected in all samples. *Cis*-pinonic acid was found in two times higher concentrations at the UB sites (15 ng m^{-3}) than at RS site (8 ng m^{-3}).

10 The other two tracer compounds (3-hydroxyglutaric acid and MBTCA) showed lower average concentrations ($3\text{--}5 \text{ ng m}^{-3}$) (Table 1) but still statistically higher at UB. All the observed SOA pinene tracer concentrations are similar to the ones measured by El Haddad et al. (2011) in a nearby French Mediterranean urban area. There was no substantial correlation between the temporal concentration trends of *cis*-pinonic acid and the other two tracer compounds ($r^2 = 0.1$), whereas there was a very good correlation between 3-hydroxyglutaric acid and MBTCA in the two different monitoring sites ($r^2 = 0.65$; 0.75 , $P < 0.05$). The same correlations between these three biogenic SOA tracers were recently discussed by Ding et al. (2011). Oxidation of α -pinene – emitted mainly by coniferous trees – form pinic acid and *cis*-pinonic acid. Previous studies proposed that *cis*-pinonic acid and pinic acid could further photo-degrade to MBTCA (Claeys et al., 2007; Szmigielski et al., 2007). Although MBTCA has other precursors apart from α -pinene (Szmigielski et al., 2007), the significant correlations among MBTCA and 3-hydroxyglutaric acid suggest that α -pinene is probably its major precursor.

25 The ratio of *cis*-pinonic acid to MBTCA (P/M) can be employed to estimate the aging of α -pinene SOA (Ding et al., 2011). The P/M ratios at the UB and at the RS were 4.0 and 2.8, respectively, indicating that overall the α -pinene SOA tracers were relatively fresh during our campaign. It is important to note that *cis*-pinonic acid was found to

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possess the highest ratio between the two sites (UB/RS = 1.9) of all the 36 detected organic compounds in this study, implying this fresh SOA oxidation product may be further oxidized in the more urban city centre (RS site).

3.1.7 Isoprene SOA tracers: C₅-alkene triols, 2-methylglyceric acid, 2-methylthreitol and 2-methylerythritol

It is generally considered that the main atmospheric source of isoprenoid VOCs is the direct emission from vegetation (Guenter et al., 1995). However, tailpipe sources may also contribute a non-negligible amount of isoprene in urban areas (Borbon et al., 2001; Park et al., 2011). Indeed, previous studies in the metropolitan region of Barcelona described the human-related sources of isoprene (Seco et al., 2012). However, whilst the predominately anthropogenic origin is mainly seen in winter months, during the summer ones (including September and October, this study) a mainly biogenic origin is apportioned (Filella and Penuelas, 2006).

During SAPUSS, all the isoprene related markers concentrations were found higher at the UB site than the more anthropogenically influenced RS site (Table 1). Whilst it is not possible to uniquely attribute isoprene markers only to biogenic sources, previous urban air quality studies point suggests that the majority of isoprene SOA should be of biogenic origin. For example, Langford et al. (2010) concluded that as much as 80 % of isoprene in London has biogenic sources. Schneidmesser et al. (2011) concluded that isoprene does not have very important role in atmospheric chemistry in London or Paris. However, given the unknown anthropogenic contribution, we leave this SOA isoprene aerosol source without a clear biogenic labeling.

During this study, C₅-alkene triols concentrations (about 1 ng m⁻³) were slightly lower than those reported in other European sites (Kourtchev et al., 2005) and much lower than the levels of 300 ng m⁻³ in sites located in the southeastern USA (Lin et al., 2012). The 2-methylglyceric acid (2-MGA) concentrations were in the same range as those observed in Marseille (about 2 ng m⁻³, El Haddad et al., 2011), whereas the levels of 2-methyltetrols (2-MT) were higher in the present study (about 2 ng m⁻³).

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(97.2% of explained variance) did not show any further relevant environmental information.

Following the optimal number of components obtained by PCA, MCR-ALS was applied to the scaled column-wise data matrix (i.e. without mean-centering) and non-negativity constraints, resulting in six components which accounted for 96.2% of the total data variance.

Although many compounds were distributed between different MCR-ALS components for many of the chemical compounds, an insight of the contributions of the different OA sources can be seen in Fig. 2. The average organic carbon concentrations (OC, determined separately by the Sunset EC/OC instrument, Dall'Osto et al., 2012a) were found to be $3.5 \mu\text{g m}^{-3}$ at the RS and $2.1 \mu\text{g m}^{-3}$ at the UB site (Dall'Osto et al., 2012a). There was a very good correlation between the total OC concentrations of PM_{10} and \sum scores of component for each sampled days ($r^2 = 0.9$, $P < 0.05$), indicating that the selected organic components described in this study can be representative for the contributions to the organic fraction sampled during the SAPUSS project. The percentages of OA contribution of each of the six components obtained were calculated from the relative contribution of the individual MCR-ALS resolved component with respect to the \sum score of the six components. The mass contribution of OC per volume for each component (Fig. 2) was calculated by multiplying the relative contributions with the OC concentrations from Dall'Osto et al. (2012a). The following sections discuss the unique features of the six OA sources identified, as well as the temporal trend of the scores. The percentages presented in brackets after the molecular markers represent the proportion of such marker among all six MCR-ALS profiles, and not the percentage of such marker among the total signal of the individual MCR-ALS profile.

3.2.1 Urban Primary Organic Aerosol (POA Urban)

This component is defined by strong contributions from PAH (43%), hopanes (43%) and nicotine (79%) and account for 32% of the explained variance. The relative larger contribution to the component of LMW PAH in combination with the hopanes, points

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to diesel vehicles as an important emission source. Among the six components this is the one showing the best correlation with traffic intensity ($r^2 = 0.5$), pointing to traffic as a major contributor to this component. The temporal changes of this source between the two sites were correlated $r^2 = 0.5$ ($P < 0.05$). Urban POA accounted for 0.35 and $1.5 \mu\text{g m}^{-3}$ OC at UB (18 % of total OC) and RS (43 % of OC), respectively. This observation is consistent with a previous study (Mohr et al., 2012) in which 16 % of the OA was attributed to primary organic aerosol at UB. Urban POA was higher during weekdays, especially on Wednesday and Thursday, whilst the lowest values were recorded during weekends and holidays (Fig. 2). There was no clear day-night fluctuation for this component, which is in accordance with the absence of such fluctuation in the LMW PAH and hopanes. The scores of this component are nearly equally divided among the four main air mass scenarios (Fig. 3), suggesting that it is less dependent on regional air mass transport and that local emissions are mainly responsible for the presence of such primary atmospheric pollutants in the urban area.

3.2.2 Primary regional Biomass Burning Organic Aerosol (BBOA Regional)

This component is essentially formed by levoglucosan (68 %), mannosan (75 %) and galactosan (79 %), several markers of primary biomass burning. The component also contains an important part of glyceric acid (45 %), which could be emitted after biomass burning or formed during atmospheric transport. Moderate contributions (about 20 % of the total signal) from other DCAs and PAH are also observed (Fig. 2).

This component accounted for 15 % of the total variance and its values in the two sites were strongly correlated ($r^2 = 0.85$). The highest score values in both sites were observed in the last sampling period of the SAPPUSS campaign (15–17 October, Fig. 2) coinciding with regional recirculation air masses (Fig. 3, 70 %) as well as with the permission to burn litter from fields surrounding the urban area of Barcelona (DOGC, 1995).

Although the relative contribution of BBOA was higher at UB (12 %) than at RS (7 %), both monitoring sites presented roughly similar concentrations (about $0.3 \mu\text{g m}^{-3}$).

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the more aged character of this component, since the higher carbon numbered DCA tend to photo-chemically degrade to smaller DCA (Yang et al., 2008b). Further support from the high degree of “aging” of this component also comes from the trend seen for the isoprene SOA markers, with the 2-MGA score being the strongest among all isoprene markers. In other words, when comparing this SOA Aged component with the SOA ISO one (Fig. 2), whilst 2-MGA is found the least important tracer among the four main ones describing such component, the opposite trend is seen for SOA Aged.

This component accounted for 18% of the explained variance and was related to SOA tracers. Similar concentrations ($0.4 \mu\text{g m}^{-3}$ OC) were found at both sites (18% of OA at UB; 12% at RS). There was a good correlation between the scores of the two sampling sites ($r^2 = 0.5$), suggesting this SOA component is impacting the two sites at similar level. The temporal trend of this component (Fig. 2) was air mass dependent, with lowest values observed during windy North Atlantic advections (Fig. 3).

3.2.6 Oxidized Organic Aerosol of mainly urban origin (OOA Urban)

Contrary to the previously described five OA sources, it is not known at this stage if this OOA Urban source has a primary and/or a secondary component, hence the name does not include any specification on this regard. The unique feature of this aerosol source is the strong association with pimelic (65%), suberic (61%) and azelaic (55%) acids (C_7 – C_9 DCA). It is also interesting to note the presence of PAHs (21% of total PAH signal), with particular evidence for coronene (39%, strongest signal of all six sources) and minor ones from benzo[ghi]perylene (32%) and benz[a]anthracene (33%). This source has also the peculiarity to contain the remaining 20% of the nicotine signal which in this study is mainly apportioned by POA Urban (80%, see Sect. 3.2.1 and Fig. 2). OOA Urban was found to have an average concentration of $0.8 \mu\text{g m}^{-3}$ (23%) at the RS site and of $0.2 \mu\text{g m}^{-3}$ (10%) at the UB site. A temporal correlation of this OA source was not found between the two monitoring sites. The consistently higher abundance of this component at the city centre site (RS) with respect to the urban background site (UB), as well as a daytime maximum (Fig. 2), suggest

to gasoline vehicle emissions and cooking activities, and the different behaviors under different air masses suggest its abundance depend on the atmospheric conditions encountered during its emission.

4 Implications and conclusions

5 The application of MCR-ALS on a database generated from off-line GC-MS analysis of 36 organic tracer compounds in 103 PM₁ filter samples collected simultaneously in two sites from Barcelona during 30 successive days allowed the identification of six organic aerosol components in the two sites that explained 96 % of the total database variance. The specific study of these components provides information on the environmental
10 sources and processes responsible for the organic aerosol constituents.

Two of the aerosol components (POA Urban and BBOA Reg.) could be linked directly to primary anthropogenic emission sources. At the RS site, the primary emissions from anthropogenic sources explain 43 % of the variance of the OA, whereas only 28 % at the UB site. Overall, the regional BBOA component had little influence on the air quality
15 in the city.

The sum of the three SOA components (SOA Aged, SOA ISO and SOA BIO PIN) contributed to 60 % of the OA at the UB, in line with the 55 % calculated by Mohr et al. (2012) in the same location during winter 2009. At the RS, the SOA component was found to be only of 27 %. Two of them were represented by products of isoprene and α -pinene oxidation, while the third was composted by a mixture of more oxidized
20 compounds from anthropogenic and biogenic origin. Most of the SOA formed from biogenic sources are believed due to isoprene and monoterpenes emissions because of their high emission rates from various vegetated surfaces. Biogenic contributions to SOA were previously expected to be relatively low in urban areas. However, the complex emissions in urban settings have been shown to accelerate oxidation of biogenic
25 VOCs and thus production of biogenic SOA (Goldstein and Galbally, 2007; Liao et al.,

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2007). Our study suggests that the overall biogenic SOA component at the UB and RS was at least 42 % and 15 %, respectively, with a ratio ISO/PIN of about 3.

An unexpected sticking result of this work is the relationship between SOA ISO, SOA BIO PIN and the NPF events during the SAPUSS project. Briefly, a clustering analysis of aerosol size distributions data collected at a UB site in Barcelona revealed that ultrafine particles often fail to grow above 10 nm (Dall'Osto et al., 2012c). However, NPF originating within the city centre can grow to larger sizes while transported away from the city to the urban-regional background (Dall'Osto et al., 2013). Previous laboratory results showed that the high reactivity of isoprene with OH leads to suppression of new particle formation (Kiendler-Scharr et al., 2009). Large isoprene emissions can also suppress NPF formation in forests although the underlying mechanism for the suppression is unclear (Kanawade et al., 2011). Although the role of biogenic VOC in limiting oxidant levels is established, the influence of OH remains uncertain (Taraborrelli et al., 2012).

Figure 4 summarise a key finding of our study during the SAPUSS project. A clear anti correlation between SOA ISO and SOA BIO PIN can be seen for the plotted PM₁ daytime samples. Additionally, the five days characterised by NPF events are all distributed in the top left part of the panel. In other words, our results suggest that large isoprene emissions can suppress NPF formation in urban areas. Furthermore, the very high percentages of SOA BIO PIN in the PM₁ mass detected during the NPF events suggest that biogenic compounds could be partially responsible for the growth of ultrafine particles in the urban area of Barcelona. Such results goes in the same direction of recent finding in the same area showing that the majority of OA is of non fossil origin (Minguillón et al., 2011).

The third SOA component (SOA Aged) contains a mixture of both biogenic and anthropogenic SOA tracers. Therefore, it was not possible to estimate the contribution of non-fossil and fossil organic carbon in this component. By considering BBOA Reg., SOA BIO PIN of non-fossil origin, then this was about 37 % at the UB (0.8 µg m⁻³) and 15 % at the RS (0.5 µg m⁻³). It is likely that SOA ISO is mainly biogenic during the

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studied period although a possible influence of an anthropogenic contribution in the urban sites could not be excluded. Nevertheless, adding SOA ISO to the non-fossil OA would lead to contributions of 54 % and 22 % at UB and RS, respectively. The relative large contribution of non-fossil SOA in this study is in agreement with the isotopic carbon data from former studies in the same urban area (Minguillón et al., 2011).

What remains unclear in the present study is the exact meaning of the OOA Urban component. It is composed mainly of C₇–C₉ dicarboxylic acids, with contributions of PAH_{high} compounds. Our results suggest that the presence of this aerosol source of anthropogenic origin depends on a number of unknown conditions. When analyzing the MCR-ALS seven solution (see Supplement), two new components appears. POA Urban 1 (PAH_{high} and nicotine) and POA Urban 2 (PAH_{low} and hopanes) somehow take away all the primary OA component from Urban OOA, leaving it with only the C₇–C₉ signature (Fig. S1). Unfortunately, the solution with seven components worsen all other external correlations with all the other existing factors and therefore it cannot be chosen as the correct one. Nevertheless, this is suggesting that both Urban POA and Urban OOA somehow hide some unknown OA sources or processes not distinguishable in this study. The 12 h sampling time resolution used in this study does not allow us to fully apportion urban OOA to traffic or cooking emissions. Although the linkage of this component to traffic can not be excluded, the chemical composition formed by the C₇–C₉ dicarboxylic acids suggests that cooking activities could play an important role in this component. Nevertheless, the component is represented only by the less volatile products of the oxidation of unsaturated fatty acids (Moise and Rudich, 2002). The air mass dependence of the component indicates that its abundance cannot be directly linked to any emission source, but could be related to oxidation processes in the urban centre.

This study reveals that 66 % and 28 % of the OA detected at the RS and UB (respectively) has an urban origin, leaving a substantial contribution of biogenic components in the studied urban area. However, the urban atmosphere seems to be responsible for

the transformation of OA (Donahue et al., 2009) creating difficulties in fully assigning OA sources with the traditional definitions of primary and secondary organic aerosol.

Supplementary material related to this article is available online at:

<http://www.atmos-chem-phys-discuss.net/13/11167/2013/>

[acpd-13-11167-2013-supplement.pdf](#).

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Table 1. Summary of the concentrations ($\mu\text{g m}^{-3}$) of analyzed organic tracer compounds. The results indicated in bold showed significant (t-test, $p < 0.05$) differences between sites, day and night, or between weekday (WD) and weekends/holidays (WE).

		UB		RS		UB vs. RS		ratio day/night		ratio WD/WE	
		mean sd	(min–max)	mean sd	(min–max)	ratio	r^2	UB	RS	UB	RS
polycyclic aromatic hydrocarbons	phenanthrene	0.05 ± 0.02	(0.01–0.12)	0.09 ± 0.03	(0.04–0.17)	0.6	0.5	0.8	0.9	1.6	1.4
	anthracene	0.01 ± 0.00	(0.00–0.02)	0.02 ± 0.01	(0.01–0.04)	0.5	0.4	1.0	1.1	1.5	1.6
	fluoranthene	0.06 ± 0.03	(0.02–0.14)	0.13 ± 0.04	(0.06–0.21)	0.5	0.4	0.8	0.9	1.7	1.4
	pyrene	0.08 ± 0.05	(0.02–0.22)	0.20 ± 0.07	(0.10–0.38)	0.4	0.4	0.8	0.9	1.9	1.5
	benz[a]anthracene	0.05 ± 0.03	(0.02–0.12)	0.13 ± 0.05	(0.04–0.24)	0.4	0.4	0.9	1.3	1.7	1.8
	chrysene	0.07 ± 0.03	(0.02–0.14)	0.16 ± 0.07	(0.05–0.31)	0.4	0.5	0.9	1.2	1.6	1.7
	benzofluoranthenes	0.13 ± 0.07	(0.03–0.37)	0.17 ± 0.09	(0.03–0.48)	0.7	0.3	1.0	1.2	1.3	1.5
	benzo[e]pyrene	0.15 ± 0.08	(0.05–0.37)	0.33 ± 0.16	(0.07–0.73)	0.4	0.5	0.9	1.3	1.7	1.9
	benzo[a]pyrene	0.06 ± 0.04	(0.01–0.20)	0.18 ± 0.09	(0.03–0.40)	0.4	0.4	0.9	1.3	1.6	2.1
	indeno[123cd]pyrene	0.04 ± 0.03	(0.01–0.12)	0.11 ± 0.06	(0.02–0.27)	0.4	0.2	0.9	1.2	1.0	1.5
	benzo[ghi]perylene	0.12 ± 0.05	(0.04–0.26)	0.30 ± 0.13	(0.07–0.56)	0.4	0.4	0.9	1.4	1.4	1.9
	coronene	0.04 ± 0.02	(0.01–0.08)	0.09 ± 0.03	(0.03–0.17)	0.5	0.2	1.0	1.4	1.2	1.5
hopanes	17a(H)21β(H)-29-norhopane	0.52 ± 0.22	(0.20–1.11)	0.73 ± 0.37	(0.20–1.70)	0.7	0.5	1.1	1.1	1.5	2.0
	17a(H)21β(H)-hopane	0.46 ± 0.22	(0.19–1.16)	0.79 ± 0.41	(0.20–1.88)	0.6	0.5	1.0	1.1	1.6	2.0
alkaloid	nicotine	7.0 ± 5.6	(0.5–20.0)	58.1 ± 39.8	(9.2–164)	0.1	0.4	1.3	1.5	1.8	2.5
anhydro-sugars	levoglucosan	9.4 ± 9.4	(1.7–40.0)	5.3 ± 5.8	(0.6–30.5)	1.8	0.8	0.9	0.9	0.7	0.8
	galactosan	1.3 ± 1.6	(0.2–7.1)	0.7 ± 0.9	(0.1–4.4)	1.8	0.8	0.9	0.9	0.6	0.9
	mannosan	1.2 ± 1.4	(0.2–5.6)	0.6 ± 0.7	(0.1–3.8)	1.9	0.8	0.8	0.9	0.6	0.7
acids, polyols, methyltetrols	malonic acid C ₃	1.5 ± 1.5	(0.3–8.1)	1.6 ± 1.0	(0.4–4.9)	1.0	0.5	1.1	1.3	0.9	1.2
	succinic acid C ₄	7.3 ± 4.8	(3.1–24.7)	6.2 ± 3.0	(2.5–14.8)	1.2	0.3	1.1	1.0	0.9	0.9
	glutaric acid C ₅	2.0 ± 1.3	(0.6–7.5)	1.5 ± 0.7	(0.6–3.2)	1.3	0.3	1.3	1.2	1.0	1.0
	pimelic acid C ₇	0.6 ± 0.3	(0.2–2.1)	1.3 ± 0.6	(0.6–3.7)	0.5	0.5	1.3	1.6	0.9	1.0
	suberic acid C ₈	0.9 ± 0.5	(0.4–3.0)	1.7 ± 0.7	(0.7–3.9)	0.5	0.2	1.2	1.5	1.0	1.0
	azelaic acid C ₉	2.9 ± 1.3	(1.0–7.3)	6.1 ± 2.6	(2.4–13.0)	0.5	0.2	1.2	1.7	1.0	1.2
	glyceric acid	3.2 ± 2.9	(0.7–15.2)	3.4 ± 2.0	(1.1–9.8)	0.9	0.5	1.0	1.1	0.9	1.1
	malic acid	14.2 ± 14.3	(1.2–72.7)	9.9 ± 8.5	(1.2–33.6)	1.4	0.7	1.2	1.0	1.0	0.9
	tartaric acid	2.1 ± 2.8	(0.0–12.2)	1.8 ± 1.7	(0.1–7.0)	1.2	0.6	1.5	1.2	0.9	0.9
	tricarballic acid	3.9 ± 3.3	(0.3–15.3)	3.0 ± 2.4	(0.4–11.6)	1.3	0.6	1.2	1.2	1.1	0.9
	phthalic acid	3.9 ± 2.4	(0.9–11.4)	3.6 ± 1.6	(1.3–9.3)	1.1	0.7	1.4	1.2	1.1	1.1
	3-hydroxyglutaric acid	4.5 ± 3.5	(0.5–20.2)	3.1 ± 2.1	(0.8–8.6)	1.5	0.7	1.1	1.0	1.0	1.1
	MBTCA	5.5 ± 4.5	(1.0–23.5)	4.1 ± 2.4	(0.7–10.3)	1.4	0.6	1.3	1.3	1.2	1.2
	cis-pinonic acid	15.4 ± 8.4	(3.6–49.7)	8.0 ± 2.9	(3.1–18.4)	1.9	0.6	1.0	1.1	1.0	1.0
	C ₅ -alkene triols	1.0 ± 0.7	(0.1–3.0)	0.7 ± 0.5	(0.1–2.2)	1.4	0.7	1.1	1.0	1.2	1.4
	2-methylglyceric acid	2.1 ± 1.3	(0.4–6.4)	1.9 ± 1.1	(0.6–4.5)	1.1	0.5	1.2	1.1	1.1	1.3
	2-methylthreitol	2.8 ± 1.6	(0.6–7.8)	1.4 ± 0.9	(0.1–3.8)	1.9	0.6	1.1	1.0	1.2	1.1
2-methylerythritol	6.5 ± 4.1	(1.7–20.7)	3.5 ± 2.4	(0.6–9.5)	1.9	0.6	1.1	1.0	1.2	1.2	

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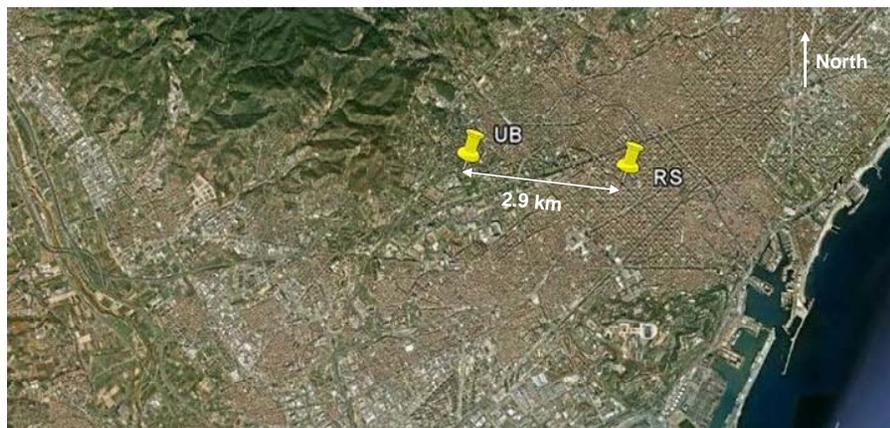


Fig. 1. Location of the sampling sites in Barcelona.

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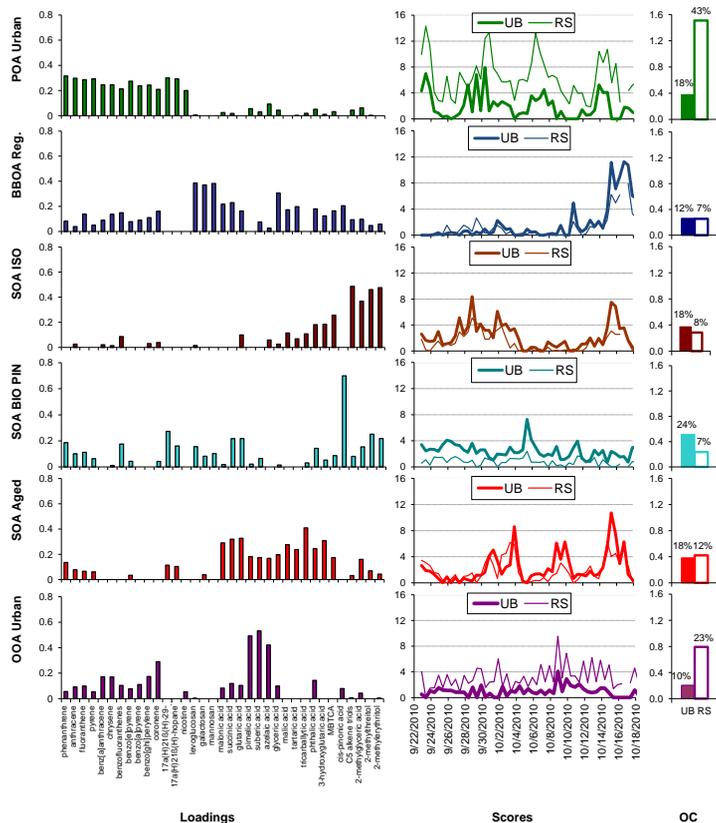


Fig. 2. MCR-ALS resolved profiles applying non-negativity constraints. Column on the left shows the loading organic compound composition of the six selected components. Column in the middle shows the temporal trend of the score values of the six components. Column on the right shows the relative contribution of the scores (%) as well as the estimated mass contribution of organic carbon to volume ($\mu\text{g OC m}^{-3}$).

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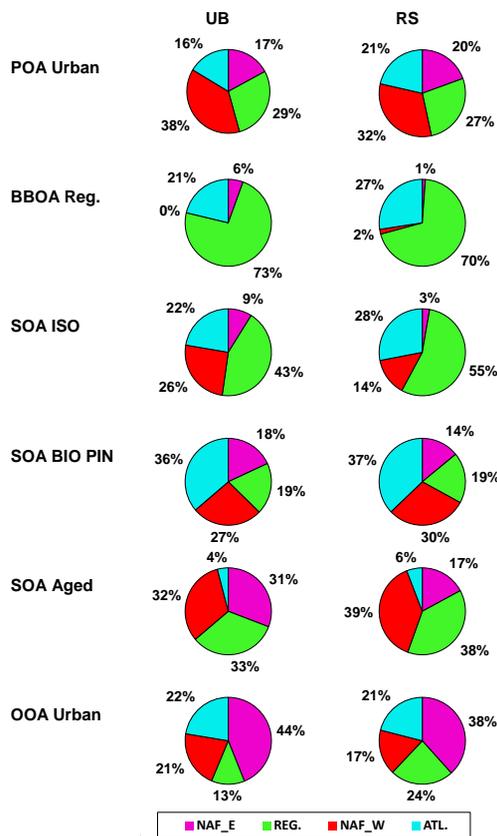


Fig. 3. Relative scores of the components in UB and RS in relation to the different air mass scenarios; NAF_W: north African air mass from the west; Atl.: Atlantic Advection; Reg.: Regional air circulation; NAF_E: North African from the East over the Mediterranean Sea (Dall’Osto et al., 2012a).

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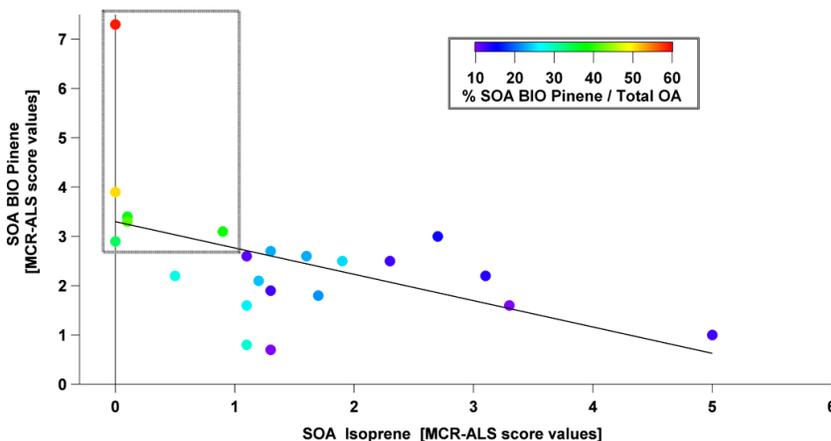


Fig. 4. MCR-ALS scores values for SOA Isoprene and SOA BIO Pinene for day time samples (09:00–21:00) collected during SAPUSS. Please note the rectangular in figure includes the five nucleation days seen during SAPUSS (25, 26, 27 September, 5 and 18 October 2010).