Seasonal and spatial variation of organic tracers for biomass burning in PM_1 aerosols from highly insolated urban areas

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Abstract PM_1 aerosol characterization on organic tracers for biomass burning (levoglucosan and its isomers and dehydroabietic acid) was conducted within the AERTRANS project. PM_1 filters ($N=90$) were sampled from 2010 to 2012 in busy streets in the urban centre of Madrid and Barcelona (Spain) at ground-level and at roof sites. In both urban areas, biomass burning was not expected to be an important local emission source, but regional emissions from wildfires, residential heating or biomass removal may influence the air quality in the cities. Although both areas are under influence of high solar radiation, Madrid is situated in the centre of the Iberian Peninsula, while Barcelona is located at the Mediterranean Coast and under influence of marine atmospheres. Two extraction methods were applied, i.e. Soxhlet and ASE, which showed equivalent results after GC-MS analyses. The ambient air concentrations of the organic tracers for biomass burning increased by an order of magnitude at both sites during winter compared to summer. An exception was observed during a PM event in summer 2012, when the atmosphere in Barcelona was directly affected by regional wildfire smoke and levels were four times higher as those observed in winter. Overall, there was little variation between the street and roof sites in both cities, suggesting that regional biomass burning sources influence the urban areas after atmospheric transport. Despite the different atmospheric characteristics in terms of air relative humidity, Madrid and Barcelona exhibit very similar composition and concentrations of biomass burning organic tracers. Nevertheless, levoglucosan and its isomers seem to be more suitable for source apportionment purposes than dehydroabietic acid. In both urban areas, biomass burning contributions to PM were generally low (2 %) in summer, except on the day when wildfire smoke arrive to the urban area. In the colder periods the contribution increase to around 30 %, indicating that regional biomass burning has a substantial influence on the urban air quality.

Keywords Biomass burning aerosol · Organic tracers · Analytical methods · Urban air · PM_1 · Levoglucosan

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Introduction

Atmospheric particles have several adverse effects on human health (Pope et al. 2002) and atmospheric visibility, and partly compensate climate forcing by greenhouse gases (Forster et al. 2007). In urban environments, traffic is one of the major sources and is in many cases responsible for the exceedances of European air quality limit values for particulate matter (PM) (Pérez et al. 2010). Another important anthropogenic source for PM is biomass burning for residential heating after combustion of wood (Szidat et al. 2007), especially during the colder periods of the year (Puxbaum et al. 2007). Other indoor biomass burning sources that have influence on the outdoor PM are cooking activities, when charcoal was used as fuel (He et al. 2004; Hou et al. 2008). Additionally, the influence of wildfires (Phuleria et al. 2005; van Drooge et al. 2012) and removal of biomass waste from agricultural fields (Lee et al.

2008) can be very significant. Biomass burning can degrade the air quality as a primary pollution source in rural, but also in urban areas. During biomass combustion a very large quantity of organic compounds are emitted into the atmosphere; however, the composition of these organic compounds depends on many factors, such as the fuel composition, combustion and ambient air conditions (Simoneit 2002; Fine et al. 2004; Gonçalves et al. 2011; Vicente et al. 2013). It is therefore not an easy task to find suitable tracer compounds for biomass combustion (Simoneit 2002). Levoglucosan (L;1,6-anhydro-β-D-glucopyranose), a thermal degradation product of cellulose, is emitted in large quantities during almost any biomass combustion and has been proposed as organic tracer for this source (Simoneit et al. 1999). Besides levoglucosan, smaller quantities of other stereoisomeric anhydro-saccharides, i.e. mannosan (M;1,6-anhydro-β-D-mannopyranose) and galactosan (G;1,6-anhydro-β-D-galactopyranose) are normally emitted alongside. These later products result from burning of hemicelluloses. Dehydroabietic acid (DHA) is also emitted in large quantities during combustion of coniferous wood, and can therefore serve as an indicator for this specific fuel combustion (Simoneit 2002). Coniferous wood is an important fuel in the studied area for both residential heating as well as for wildfires, since coniferous tree species represent an important fraction of the regional forest composition (Gonçalves et al. 2011; Vicente et al. 2013).

Levoglucosan is easily detected in PM samples (Fabbri et al. 2008) and mainly associated to the fine aerosols after long-range atmospheric transport (Fraser and Lakshmanan 2000). In fact, many studies reported levoglucosan levels in different areas and different periods of the year (see references in Table 1). In the Northern European countries biomass burning is mainly linked to wood smoke from fireplaces and related to the colder periods in the year, while in the Southern European countries wildfires and biomass waste removal can also be important biomass burning sources (see reference Table 1). Recently, the impact of wildfires on the Iberian Peninsula was studied, and the results show that this source can have an important influence on the regional and local air quality (Vicente et al. 2012; 2013; van Drooge et al. 2012).

The organic tracer compounds must be relatively stable in the atmosphere to be used for source apportionment purposes. Although levoglucosan and its isomers have been detected in PM samples from remote areas, and can therefore be considered as useful tracer compounds for biomass burning (Fraser and Lakshmanan 2000), they may be less stable under conditions of high temperatures and oxidation by free hydroxyl radicals under high relative humidity conditions (Hennigan et al. 2010; Hoffmann et al. 2010). These depletion pathways may be more important in summer and practically irrelevant in winter, as observed in other studies (Fraser and Lakshmanan 2000; Mochida et al. 2010). The

Table 1 Average values and standard deviation for the different variables analysed in the study

		T	P	PM_1	PM_{10}	G	M	L	DHA	L/(M+G)	L/DHA	L/PM1	L/PM10
		°C	mbar	µg/m³	µg/m³	ng/m³	ng/m³	ng/m³	ng/m³			mg/g	mg/g
Summer	BCN_street	25±3	1,013±3	22±10	38±18	1.9±0.8	1.2±0.6	15.8±7.6	3.4±2.0	5.3±1.9	5.8±3.4	0.8±0.3	0.5±0.2
	MRD_street	25±5	939±4	14±5	34±11	1.6±1.6	0.8±0.9	11.4±17.9	0.7±0.5	4.0±1.4	15.7±7.8	0.8±1.0	0.3±0.4
	BCN_roof	24±2	1,014±3	16±7	–	1.6±1.1	0.7±0.5	9.3±5.8	0.7±0.3	4.6±1.9	15.5±8.0	0.6±0.3	–
	MRD_roof	28±5	933±3	8±4	–	1.7±1.9	1.0±1.0	11.9±17.3	0.6±0.6	3.9±1.1	18.5±6.5	0.8±0.2	–
Autumn-winter	BCN_street	13±1	1,016±4	24±8	32±14	26.8±16.1	26.2±16.7	209±124	21.6±14.4	4.1±1.1	10.3±2.4	8.8±5.0	6.9±3.7
	MRD_street	14±6	935±21	14±6	26±14	9.9±8.7	12.3±12.7	94±86	15.2±16.9	4.9±2.1	10.6±7.2	7.0±6.1	3.9±3.0
	BCN_roof	12±1	1,016±5	20±5	–	26.2±18.5	29.6±19.4	205±109	24.1±15.5	4.0±1.1	9.4±3.3	10.3±5.0	–
	MRD_roof	13±6	935±8	10±5	–	9.9±9.2	12.5±19.4	91±102	14.9±24.7	4.8±1.9	10.3±5.5	15.9±10.4	–

Autumn–winter includes samples collected in October, February and March in the case of Madrid, while in the case of Barcelona they include those collected in December. For the calculation of the values in BCN_roof, the sample collected during a wildfire event was not included. Compound identification: G galactosan, M mannosan, L levoglucosan, DHA dehydroabietic acid

– not available

urban areas studied here are located in the Mediterranean region, which is characterized by relatively high solar radiation. Moreover, Barcelona (BCN) situated along the Mediterranean coast, is characterized by high atmospheric humidity, while on the contrary Madrid (MRD), situated on the higher plains in the centre of the Iberian Peninsula, presents dry atmospheric conditions. These geographical characteristics and atmospheric conditions may be relevant for the investigation of organic biomass burning tracer stability in different seasons. In both urban areas, biomass burning for residential heating and cooking is not expected to be significant considering the data of the local councils. Nevertheless, in order to investigate whether biomass burning aerosols arrive to the urban areas after regional atmospheric transport or from possible local sources, the PM_1 filter samples were collected simultaneously at street and roof level (50 m above street sites). Similar ambient air concentrations of the studied organic tracers would indicate that regional sources are responsible for the biomass burning aerosols in these urban areas (Caseiro and Oliveira 2012).

A total of 90 PM_1 samples were collected in street and roof sites in BCN and MRD during different seasons (summer and autumn–winter). Two different extraction methods, i.e. Soxhlet extraction and ASE, were applied in order to analyse the organic tracer compounds by gas chromatography coupled to mass spectrometry (GC-MS). The efficiencies of both extraction methods will be handled here. The ambient air PM_1 concentrations of the tracer compounds are discussed in terms of their source and the data is used to estimate the contribution of biomass burning to the urban PM.

Material and methods

Reagents and analytical standards

Methanol and dichloromethane were of high purity SupraSolv® and UniSolv®, respectively (Merck KGaA, Darmstadt, Germany). Bis-(trimethylsilyl)-trifluoroacetamide and trimethylchlorosilane (BSTFA/TMCS, 99:1) were supplied by Supelco (Bellefonte, PA, USA). Pyridine was obtained from Fluka (Steinheim, Germany).

All standards were of the highest purity commercially available: 1-phenyldodecane was obtained from Fluka (Steinheim, Germany), deuterated D7-levoglucosan was provided from Cambridge Isotope Laboratories (Andover, MA, USA).

Calibration curves were constructed by injecting individual solutions from 0.01 to 600 ng/μL of levoglucosan prepared in methanol. Stock individual standard solutions were stored at −20ºC, while the BSTFA and pyridine reagents were stored at 4°C.

Sampling

Sampling was conducted in Madrid (MRD) from August 2010 to July 2011 and in Barcelona (BCN) from July 2012 to December 2012.

PM_1 samples were collected with a high volume air sampler (Digitel-DH80, Digitel Elektronic AG, Switzerland) equipped with pre-heated (450ºC) quartz filters with a 12-h resolution (08:00 to 20:00 UT and 20:00 to 08:00 UT) in the centre of Barcelona (Balmes street=BCN_street) 10 m above sea level (asl) and 50 m above ground level (agl) (Via Laietana=BCN_roof). In Madrid, samples were collected at a street site (Escuelas Aguirre=MRD_street) and a roof site 50 m agl (Av. de America=MRD_roof). After sampling, filters were weighted for PM_1 mass determination and stored in aluminium foil at −20 °C for further analysis.

Extraction

Extraction of aerosols samples was performed by Soxhlet extraction and by Accelerated Solvent extraction ASE (Dionex, ASE 150) using in both cases a mixture of dichloromethane and methanol (2:1 v/v). In the case of Soxhlet extraction, the filters were spiked with deuterated D7-levoglucosan, folded with tweezers and placed into the Soxhlet. Extraction was performed with 60 mL solvent mixture for 6 h. In the case of ASE, spiked filters were folded and placed into 10-mL stainless steel extraction cells end-closed with a glass-fibre filter (Dionex, Idstein, Germany). Sample extraction was performed by a 5-min preheat time, followed by three static cycles of 5 min at 1,500 psi and 100 °C, respectively. Flush volume was 60 % and purge time 100 s. The equivalence of these two methods will be discussed below.

Filtration

All extracts were filtered prior to evaporation through a pre-washed (three times with 4 ml of dichloromethane methanol, 1:1 (v/v)) 25-mm diameter glass–microfibre membrane filter (Sartorius, France) using a 25-mm Swinny stainless steel syringe filter holder (Sartorius, France) and a 30-ml glass syringe with Luer tip (Fortuna, Aldrich). The tube containing the extract was rinsed three times and the solvent washings were recovered together with the extract filtrate through the same membrane filter. Then, the filtrate was first concentrated by rotary evaporator to about 1.5 mL and to 1 mL using a gentle stream of high-purity nitrogen.

Derivatization

The derivatization procedure is similar to that described by Medeiros and Simoneit (2007). A 25-μL aliquot of the sample

extract was evaporated under a gentle stream of N_2 to dryness before the derivatization. Then, extracts were treated with 25 μL BSTFA/TMCS and 10 μL of pyridine at 70ºC during 1 h in order to obtain the corresponding trimethylsilyl esters of the saccharides and acid. Before gas chromatographic analysis, 1-phenyldodecane was added as injection standard to correct for instrumental instability.

GC-MS analysis and quantification

Samples were injected in a Thermo gas-chromatograph coupled to a mass spectrometer (Thermo Trace GC Ultra–DSQ II) equipped with a 60-m fused capillary column (RXi 5Si MS 0.25 mm × 0.25 μm film thickness). The MS was operated at 70eV electron ionization and the quadrupole was operated in full scan (m/z 50–650) mode. The column temperature program started at 60ºC during 1 min followed by an increase at 10 °C/min up to 120 °C, and to 310ºC (25 min) at 6 °C/min. The samples were analysed in the splitless mode (splitless time, 0.8 min). The injector, ion source and transfer line temperatures were 280, 250 and 270 °C, respectively. Helium was used as the carrier gas (0.9 mL/s).

Compound identification was performed by comparison with the chromatographic retention characteristics and mass spectra of levoglucosan standard reported mass spectra and the mass spectral library of the GC–MS data system. Levoglucosan, mannosan and galactosan were identified at the retention time of levoglucosan in the chromatogram in their derivatized TMS form with the m/z 204 fragmentogram in the case of levoglucosan and mannosan, and with m/z 217 in case of galactosan. Dehydroabietic acid was identified by m/z 236. Compounds were quantified by the internal standard method, response factors referred to the internal standard in the calibration curves. The concentrations were corrected by the recoveries of the surrogate standard D7-levoglucosan (m/z 206). The reproducibility of the method was assessed by of the quantified concentrations in triplicate analyses of blank and sample filters. Field blank levels were between <1 and 30 % of the sample levels and all reported concentrations are corrected for blank levels.

Complementary information

Meteorological data and PM concentrations were obtained from the local or regional authorities that run meteorological stations and air quality monitoring station near the ground-level sampling sites. The mean temperatures and PM concentrations for the samples are presented in Table 1.

Air mass backtrajectories were calculated for all samples using the HYSPLIT4 software from the NOAA-ARL (USA) (Rolph 2003). Here, the GDAS1 data used for the model calculation for the air mass trajectories were based on isentropic surfaces. The calculations were performed for 72 h in 6 h consecutive steps. For the sampling sites the isentropic surfaces were related to the potential temperature at 500 m above ground level. These data is provided in the supplementary information.

Results and discussion

Extraction method

In order to study the equivalence of Soxhlet extraction and ASE for the analysis of anhydro-saccharides in the urban air samples, a PM_1 filter was divided into four parts. Two parts were separately extracted by Soxhlet, while the other two parts were extracted by ASE. The concentration of levoglucosan varied from 26±2 ng/m^3 in Soxhlet extracts to 29±3 ng/m^3 in samples extracted with ASE. These concentrations were not statistically significant different and the overall relative standard deviation (RSD) was less than 8 %, which is small enough to consider these two extraction methods equivalent and suitable for the analysis of levoglucosan.

ASE extraction method for the determination of levoglucosan and its isomers was further validated by participating in an intercomparison exercise between 13 laboratories. Aliquots of blank and two sampled filters were analysed by triplicate. The obtained results were within the accepted analytical uncertainty of the test according to ISO 13528. Average recovery of deuterated D7-levoglucosan in these analysis was 72 %±15, which is similar to the average recovery obtained in the ambient air samples (N=90) collected in Barcelona and Madrid (67 %±14). The reproducibility of the analytical procedure was assessed through the RSD of the triplicate measurements. The RSD values were 31 % for the blank filter (<2 ng/cm^2=limit of quantification (LOQ)), 7 % for the sample with 2,900 ng/cm^2, and 4 % for the sample with 11,000 ng/cm^2. These values demonstrated satisfactory extraction efficiencies and acceptable reproducibility of the analytical method. LOQ of 2 ng/cm^2 was determined as the average concentration in the blanks plus three times the standard deviation.

Organic biomass burning tracers analysis in urban PM_1 samples

Concentrations of organic biomass tracers

Levoglucosan (L), mannosan (M), galactosan (G) and dehydroabietic acid (DHA) were detected in all samples above the analytical LOQ. This contrasts with a former study conducted in BCN by Reche et al. (2012) where levoglucosan could not be detected in 95 % of the PM samples in summer. In that study, high-performance anion-exchange

chromatography was used for levoglucosan determinations, which generally have higher LOQ than the organic-solvent GC-MS method used in the present study.

Table 1 summarizes the average ambient air concentration of the organic biomass burning tracer compounds in the PM_1 filter samples. Samples collected in July, August or September were considered "summer" samples, based on the season and the similar high ambient air temperature (approximately 25ºC; Table 1). On the other hand, samples collected in the other months were considered "autumn–winter" samples (approximately 13ºC). At both sites, lowest concentrations were observed in summer, with average levels of 2 ng/m³ for G and M and 10 ng/m³ for L (Table 1). The concentration of DHA was 1 ng/m³ in all sites, except at BCN_street where the level was 3 ng/m³ (Table 1). Autumn–winter concentrations were substantially higher, with average levels of G and M around 30 and 10 ng/m³ in BCN and MRD, respectively. Concentrations of L were around 200 and 100 ng/m³ in BCN and MRD, respectively, while DHA concentrations were around 20 and 15 ng/m³ (Table 1). These levels are comparable to those observed in other studies that include urban and rural areas in the Mediterranean Basin (Table 2). For example, Puxbaum et al. (2007) reported L-concentrations of 32 ng/m³ in summer at a rural site in Aveiro (Portugal), while high levels (1,290 ng/m³) were observed in winter. On the other hand, Reche et al. (2012) reported summer levels in BCN below their limit of

Table 2 Concentrations of levoglucosan (ng/m³) in different studies of northern and southern European countries

Study	Site	Specification	Levoglucosan (ng/m³)
Puxbaum et al. 2007	Azores (P)	Remote maritime	5
	Aveiro (P)	Rural	517
	Puy de Dome (F)	Remote continental	17
	Schauinsland (D)	Rural	24
	Sonnblick (A)	Remote continental	8
	K-Puszta (H)	Rural	309
Oliveira et al. 2007	Oporto (P)	Urban	120
	Copenhagen (DK)	Urban	40
Sillanpää et al. 2005[a]	Amsterdam (NL)	Urban	360
	Athens (G)	Urban	45
	Barcelona (ES)	Urban	60
Reche et al. 2012	Barcelona (ES)	Urban	60
Alier et al. 2013	Barcelona (ES)	Urban	8
This study	Barcelona (ES)	Urban	110
	Madrid (ES)	Urban	50

[a] Sum of levoglucosan, galactosan and mannosan

detection (2 ng/m³), while the average winter L-concentration was 60 ng/m³.

Generally, in those studies including samples from both summer and winter seasons showed the highest concentrations in winter. This seasonal difference can be explained by (1) larger emissions of the biomass burning tracers towards the atmosphere as a result of increased combustion for residential heating and biomass waste removal from gardens forests and field in autumn–winter, and (2) increased removal of the organic tracers by enhanced oxidation (Hennigan et al. 2010; Hofmann et al. 2010). In the present study the winter concentrations of the analysed compounds are between six and 40 times higher than in summer.

Biomass burning tracers in the studied urban areas are not expected to be emitted into the atmosphere from local sources, but arrive to the cities after regional atmospheric transport. A good example of such transport was observed in BCN_roof in summer 2012. During the daytime of 23 July smoke from a wildfire situated 120-km north-east entered the city (see supplementary information (SI) for air-mass backtrajectories). Briefly, wildfire smoke was detected in the morning until the afternoon, with the highest biomass organic tracer concentrations observed during the whole study (van Drooge et al., in preparation). They were about two orders of magnitude higher than those observed in the previous and posterior days of the wildfire in summer in BCN (Fig. 1). The air-mass backtrajectories of these other periods followed partly the same track (see SI), however, without passing any wildfires on their way. Compared to the autumn–winter samples, the L-concentration in the wildfire sample was about one order of magnitude higher (Fig. 1). The samples collected in BCN in December 2012 correspond to a period of calm and sunny weather with air-mass backtrajectories flowing from the Iberian Peninsula (see SI). For the calculation of the average summertime concentrations in Table 1, these wildfire event data was not included. Unfortunately, no samples were collected at the street site, but it is likely that similar high concentrations would have being detected at that site, since the regional wildfire smoke was distributed relatively homogeneously within planetary boundary layer. For MRD, largest contrast between L-concentrations is observed between samples that were collected in August and February (8 vs. 178 ng/m³, respectively), while these periods had very similar air-mass backtrajectories (i.e. origin on the North-Atlantic and transport over the western Iberian Peninsula; SI). Another contrast is observed for the two sampling periods in October; the tracer concentrations were not significantly different while the origins of the sampled air-masses were in opposite direction. These results suggest that in summer the influence of biomass burning aerosols in the studied urban areas was more related to emission events, such as wildfires, in combination with air-mass trajectories, while in autumn–winter the general increase of biomass burning emissions in
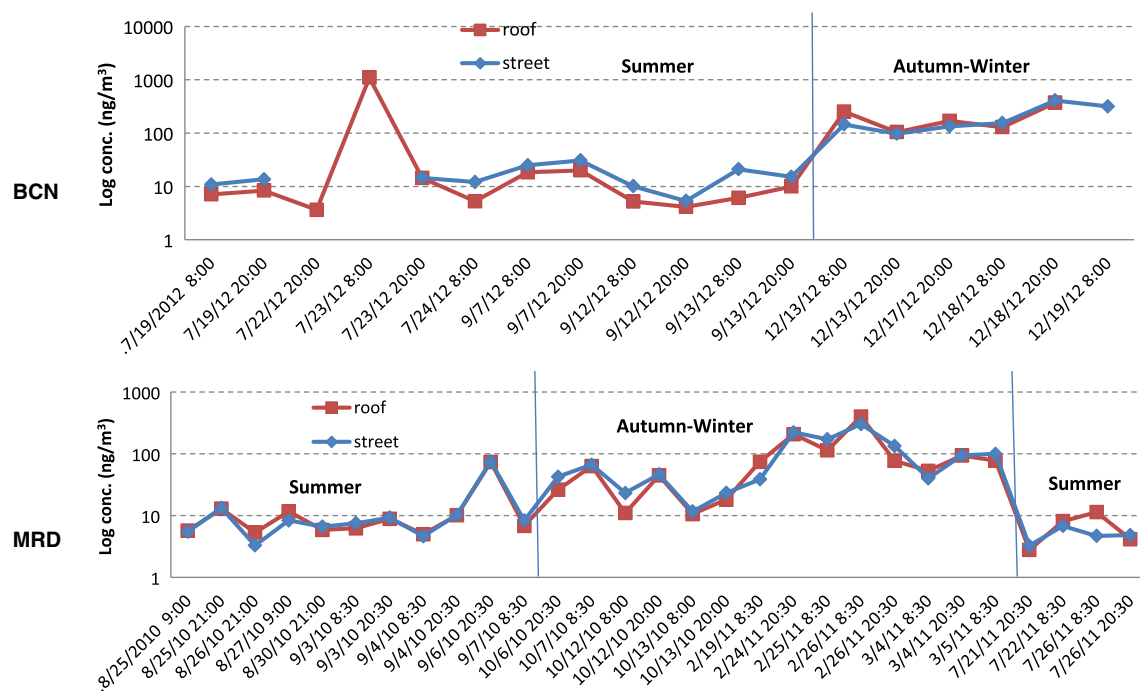
Fig. 1 Log-transformed concentrations of levoglucosan (ng/m^3) in Barcelona (*BCN*) and Madrid (*MRD*) in the street and roof sites

the region reduces the influence of the origin and track of the air mass.

The influence of biomass burning aerosols from regional sources to the studied urban areas is further indicated by the very similar L-concentrations at the street and roof sites (Fig. 1). This uniform vertical distribution was not observed for PM concentrations that showed 40 % lower roof site levels than the corresponding street sites, due to local PM emissions from other sources at street level. These findings would be in agreement with data from the local councils that indicate that wood burning is not a significant energy source in these urban areas.

*Relationship between anhydro-saccharides
and dehydroabietic acid*

The chemical composition of the biomass burning aerosol depends on many factors, such as biomass/wood type and combustion conditions (Fine et al. 2004; Engling et al. 2006), as well as atmospheric conditions, such as the oxidation potential of the atmosphere. As a consequence, the emission factors for G, M, L and DHA differ from source to source. On the other hand, it is unlikely that oxidation processes in the atmosphere have the same effect on the anhydro-saccharides and dehydroabietic acid. Therefore, regression analysis between concentrations of the different compounds as well as their ratios for the sampled days were performed in order to observe and discuss the variations. Statistically significant correlations among the individual compounds ($0.9 < r^2 < 1$; Fig. 2) were observed at all sites, pointing to similar origin

of these compounds. Table 1 shows the average L/(M+G) and L/DHA ratios in the different sites, while the ratios for the individual samples are shown in Fig. 3. The L/(M+G) are similar between the street and roof sites in both urban areas, indicating that the anhydro-saccharides analysed on the same day have the same regional origin. There is no clear temporal trend and the ratios oscillate between 2 and 10 (Fig. 3), with average values around 4.5. These values were also observed in wintertime samples in BCN (Reche et al. 2012) and are in the range of those determined in softwood combustion emissions (Fine et al. 2004; Engling et al. 2006). When the wildfire smoke affected directly the urban area of BCN the ratio was 3.1, which could be considered as a representative ratio for a summertime wildfire aerosol after regional atmospheric transport. During these fires, besides wood also leaves and grasses are burnt, resulting in a complex atmospheric mixture. Analysis of direct wildfire smoke on the Iberian Peninsula in 2010 (Vicente et al. 2013) showed L/(M+G) ratios between 1 and 3, which is close to the one observed in summer 2012 in BCN.

Although the anhydro-saccharides could be affected by oxidation in the atmosphere, especially in summer due to the higher oxidation potential of the atmosphere, the similar isomeric ratios for the different seasons (Table 1, Fig. 3) indicates that this process is probably not very relevant in the studied urban areas. Therefore, the small fluctuations of the isomeric ratios are likely related to changes in source emissions and atmospheric mixing. In both urban areas the highest ratios were observed in September and October, which may reflect such a type of change.
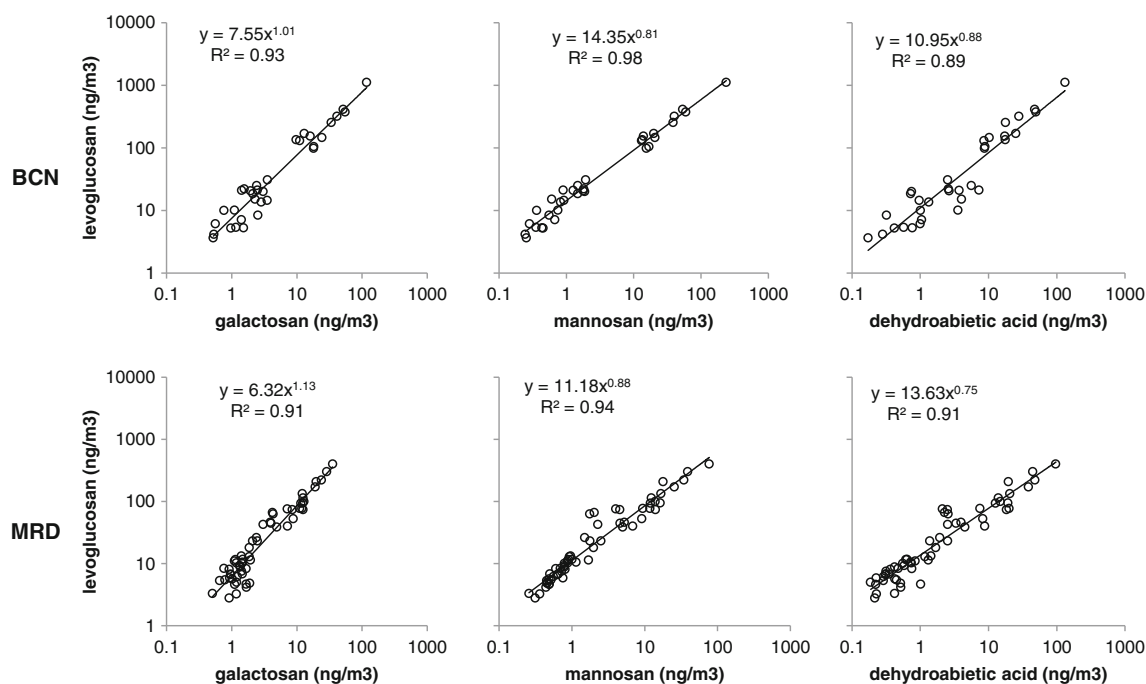
Fig. 2 Log–log correlations among the organic tracer compounds in Barcelona (*BCN*) and Madrid (*MRD*)

The ratios of L/DHA show more in situ fluctuations than the L/(M+G). The L/DHA ratio is smallest in BCN_street (5.8) in summer, while the other sites show average values between 15 and 18 (Table 1). In autumn–winter, all sites show values around 10. The ratios in the individual samples in BCN_street are substantially lower than BCN_roof in summer (Fig. 3). In winter, on the other hand, the ratios in the street and

roof sites are very similar in BCN and MRD. These results indicate that on certain summer days the street site of BCN is exposed to additional unidentified sources for DHA, as further indicated by the higher concentrations of DHA in BCN_street with respect to BCN_roof and MRD (Table 1). On the other hand, the good correlations between the L/DHA ratios in street and roof sites in BCN in winter and generally in
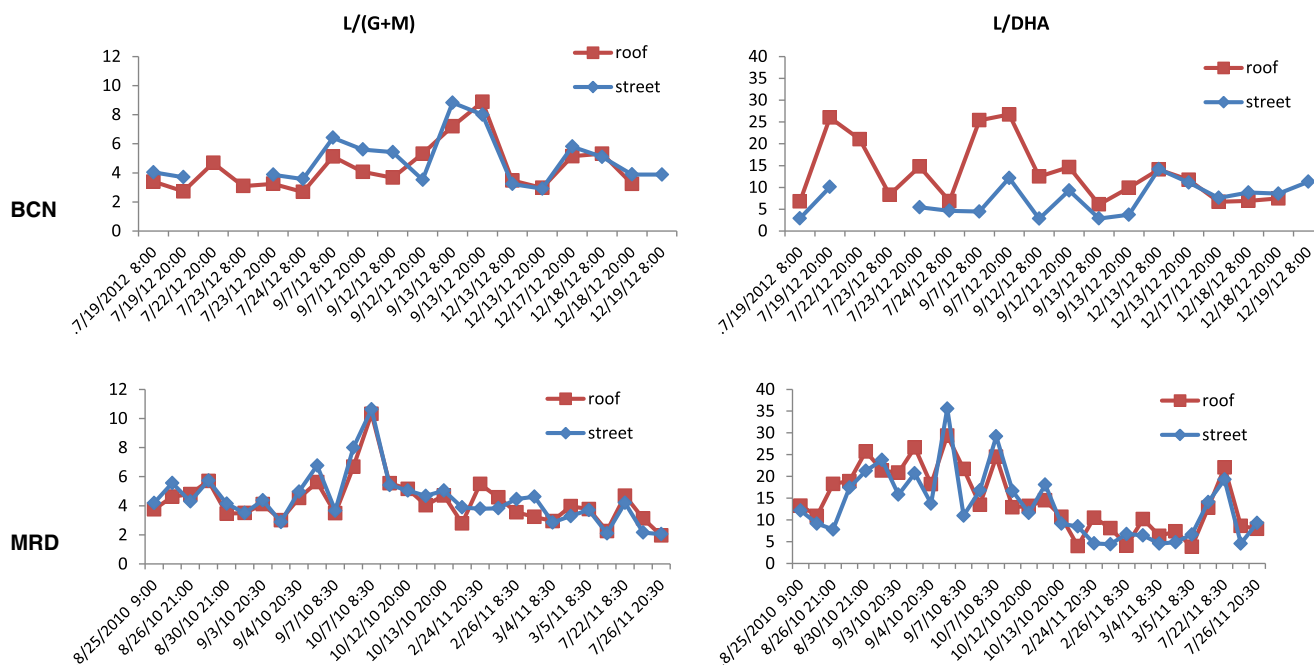

Fig. 3 Isomeric ratios of levoglucosan/(mannosan+galactosan) (L/M+G) and the ratio between levoglucosan/dehydroabietic acid (*L/DHA*) in Barcelona (*BCN*) and Madrid (*MRD*) in the street and roof sites

Madrid suggest that in these cases the sampled air masses were under influence of similar biomass burning sources and/or atmospheric processes. The autumn–winter ratios in both sites areas are around 10 while those in summer are 15. Moreover, Fig. 3 shows that there is a substantial decrease of L/DHA ratio in Madrid from the days in September–October (19±6) towards the sampling days in February–March (7±2). This indicates a relative decrease of DHA, i.e. coniferous wood combustion, in September–October with respect to the winter days.

Lower contributions of coniferous wood combustion to the overall biomass burning are also evident in BCN_roof site in summer (i.e. higher L/DHA ratios; Fig. 3). An exception can be observed on 23 July when the wildfire event affects the urban area of BCN; then the L/DHA is 8, which is similar to the autumn–winter ratios in this site. These results may also be interpreted as an increase of coniferous wood burning contributions in comparison to other combustion fuels during the wildfire event and colder period. On the other hand, the ratios in wildfire emission on the Iberian Peninsula in 2010 (Vicente et al. 2013) were ranging from 0.7 to 5.5, so much smaller than those observed in the urban atmospheres. It is therefore also possible that DHA in the ambient air is affected by oxidation during regional atmospheric transport at faster rates than levoglucosan, resulting in generally higher L/DHA ratios. The moderate negative correlations of L/DHA vs. log-DHA concentrations in BCN_roof and MRD in general (r^2=0.3) further support the faster depletion of DHA in ambient air compared to levoglucosan. Besides possible depletion of DHA during atmospheric transport, other DHA sources in urban areas could be responsible of the observed L/DHA ratios, which deserve further investigation. In any case, these uncertainties make DHA less suitable for source apportionment studies than anhydro-saccharides that seem to be stable enough for this purpose.

Source apportionment

The chemical analyses of the PM_1 filter samples in this study shows that the concentration of the biomass burning organic tracers increases from summer to autumn–winter by a factor 6 to 40, with an exception of the wildfire event in summer 2012 in BCN. On the other hand, the PM concentrations fluctuate along sampling periods, but no seasonal trend can be observed (Table 1). Average PM_1 levels at BCN_street were 23 μg/m^3, while the MRD_street levels were 14 μg/m^3. PM_{10} concentrations were 38 and 30 μg/m^3 in BCN and MRD, respectively. At both sites there was a positive correlation between the PM_1 and PM_{10} concentration (BCN_street: r^2=0.8; PM_1/PM_{10}=0.7; MRD_street: r^2=0.6; PM_1/PM_{10}=0.5), and the relatively high ratios indicate the importance of the submicron fraction in particulate matter in these urban areas. PM concentrations and PM_1/PM_{10} ratios are in range of those

observed in other studies in the same sites (Querol et al. 2009; Dall'Osto et al. 2013). The PM_{10} levels are close to the legislative annual limit value of 40 μg/m^3, and emphasize the impact that PM can have on health in the studied areas.

However, based on the mass concentrations in the samples, it is obvious that the biomass burning contributions to the PM increase in the colder season, or on specific days when the urban areas are under influence of biomass burning smoke, such as a regional wildfire. These changes in biomass burning contribution can be reflected by the L/PM_1 and L/PM_{10} ratios for the analysed samples as shown in Table 1 and Fig. 4. In summer, the L/PM_1 ratios are 0.6–0.8 mg/g, while in winter they increase ten to 20 times to values between 7 and 16 mg/g, with higher ratios at the roof sites (Table 1). These winter values were higher than those observed by Reche et al. (2012) in winter 2009 in BCN. The roof site value for the summer day when BCN was under influence of wildfire smoke is 35 mg/g (Fig. 4). The L/PM_{10} ratio at the street sites also increases in winter (4–7 mg/g) with respect to summer (0.3–0.6 mg/g).

As mentioned in the introduction, the PM in urban areas is subject to the apportionment of several local sources, such as traffic and industrial emissions as well as regional sources, which include the formation of secondary aerosols (Pérez et al. 2010; Alier et al. 2013). The detected organic biomass burning tracers are transported to the urban areas after regional atmospheric transport. A further indication of this transport is the higher night time L/PM_1 values in BCN in winter (11 mg/g) with respect to daytime (7 mg/g), which reflects the transport of air from the inland towards the city during the night. The anti-cyclonic conditions in this period normally activates a seabreeze during daytime, diluting the influence of biomass burning, while during night time an air flow from the inland affects the urban area in BCN. This phenomenon is very typical in BCN and was also observed in former studies (Reche et al. 2012; Alier et al. 2013).

The exact contribution of biomass burning to PM is uncertain partly because of the large variability of the L/PM ratio in the biomass burning aerosol (Puxbaum et al. 2007; Vicente et al. 2012). As an example, Vicente et al. (2012) found L/$PM_{2.5}$ values ranging from 0.8 to 11 mg/g in wildfire smoke, while Gonçalves et al. (2011) reported 31 mg/g in residential wood burning. Although an additional contribution of PM_1 to $PM_{2.5}$ particle mass could result in a small decrease of the L/PM values in the present study, the results here indicate that on the day of the wildfire event in BCN the contribution of biomass burning to the urban aerosol was exceptionally high.

For the rough estimation of the biomass burning contributions to PM (%BB-PM) the highest reported ratio was applied. This results in average %BB-PM of 15 % in BCN and 19 % in MRD. The summer %BB-PM values are similarly low in both urban areas (around 2 %) with little difference between street and roof sites. Autumn–winter %BB-PM was 30 % in BCN
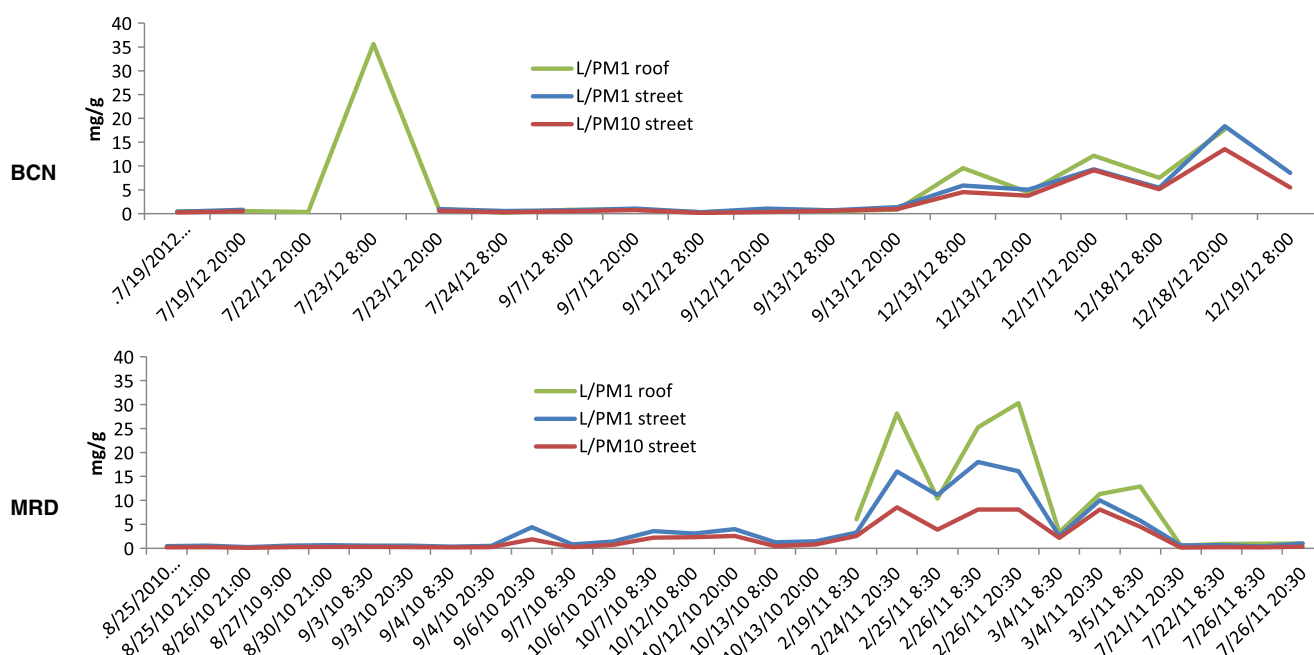
Fig. 4 Levoglucosan/PM ratios (*L/PM*; mg/g) in Barcelona (*BCN*) and Madrid (*MRD*) in the street and roof sites

and 33 % in MRD. Although the summertime %BB-PM contributions observed in the present study in BCN are lower than the 9 % calculated by Reche et al. (2012), the autumn–winter contributions were much higher than the 7 % winter-time contribution estimated in this previous study from a source-apportionment model using other inorganic and organic source tracers.

It is clear that the contribution calculations may suffer high uncertainties due to the large variability in the L/PM source ratios; however, they can serve to indicate that biomass burning can be a significant source of PM on specific days when the urban areas are exposed to biomass burning smoke.

Implications and conclusions

Organic tracers for biomass burning (levoglucosan, mannosan, galactosan and dehydroabietic acid) were detected in all PM$_1$ filter above the LOQ using organic solvent extraction methods and GC-MS analysis. The two extraction methods applied in this study, i.e. Soxhlet and ASE, provided equivalent results.

Ambient air PM concentrations for the tracer compounds were an order of magnitude higher in autumn–winter than in summer in both Barcelona and Madrid, except on specific days in summer when Barcelona was under direct influence of wildfire smoke. Good correlations were observed between the individual tracer compounds over the wide concentration range, although

changes in compound ratios in September–October could be interpreted as combustion fuel changes in this period of the year, which could be related to biomass waste removal in agricultural fields.

Concentrations of individual organic tracers were very similar between street and roof sites in Barcelona and Madrid which is consient with a dominance of regional biomass burning emissions arriving to these urban areas. Nevertheless, dehydroabietic acid showed higher concentrations in summer in the street site in Barcelona, pointing to an additional unidentified local source. Moreover, there were indications that dehydroabietic acid is more susceptible to oxidation in the atmosphere than saccharides. On the contrary, levoglucosan and its isomers seem to be stable enough to suite for source apportionment purposes.

Estimation of the biomass burning contributions to PM indicates low contributions in summer (2 %), while they were around 30 % in autumn–winter in both urban areas. These contributions are larger than found in former studies. Although the estimations have relatively large uncertainties, it is clear that regional biomass burning have an influence on the urban air quality. Levoglucosan and its isomers are relatively easily detectable in PM$_1$ samples and could therefore be included in routine analysis in air quality monitoring.

References

Alier M, van Drooge BL, Dall'Osto M, Querol X, Grimalt JO, Tauler R (2013) Source apportionment of submicron organic aerosol at an urban background and a road site in Barcelona (Spain) during SAPUSS. Atmos Chem Phys 13:10353–10371. doi:10.5194/acp-13-10353-2013

Caseiro A, Oliveira C (2012) Variations in wood burning organic marker concentrations in the atmosphere of four European cities. J Environ Monit 14:2261–2269. doi:10.1039/c2em10849f

Dall'Osto M, Querol X, Alastuey A, Minguillon MC, Alier M, Amato F et al (2013) Presenting SAPUSS: solving aerosol problem by using synergistic strategies at Barcelona, Spain. Atmos Chem Phys 13: 8891–9019. doi:10.5194/acp-13-8991-2013

Engling G, Carrico CM, Kreidenweis CM, Collet JL Jr, Day DE, Malm WC et al (2006) Determination of levoglucosan in biomass combustion aerosol by high-performance anion exchange chromatography with pulsed amperometric detection. Atmos Environ 40:299–311. doi:10.1016/j.atmosenv.2005.12.069

Fabbri D, Modelli S, Torri C, Cemin A, Ragazzi M, Scaramuzza P (2008) GC-MS determination of levoglucosan in atmospheric particulate matter collected over different filter materials. J Environ Monit 12: 1519–1523. doi:10.1039/b808976k

Fine PM, Cass GR, Simoneit BRT (2004) Chemical characterization of fine particle emissions from the fireplace combustion of wood types grown in the Midwestern and Western United States. Environ Eng Sci 21(3):387–409. doi:10.1089/109287504323067021

Forster P, Ramaswamy V et al. (2007) Changes in Atmospheric Constituents and in Radiative Forcing. In: IPCC, 2007, Climate Change 2007: The Physical Science Base. Contribution of Working Group I to the fourth Assessment Report of the IPCC, ISBN: 978 0521 88009–1

Fraser MP, Lakshmanan K (2000) Using levoglucosan as a molecular marker for the long-range transport of biomass combustion aerosols. Environ Sci Technol 34:4560–4564. doi:10.1021/es991229I

Gonçalves C, Alves C, Fernandes AP, Monteiro C, Tarelho L, Evtyugina M, Pio C (2011) Organic compounds in PM2.5 emitted from fireplace and woodstove combustion of typical Portuguese wood species. Atmos Environ 45:4533–4545. doi:10.1016/j.atmosenv.2011.05.071

He L, Hu M, Huang X, Yu B, Zhang Y, Liu D (2004) Measurement of emissions of fine particulate organic matter from Chinese cooking. Atmos Environ 38:6557–6564. doi:10.1016/j.atmosenv.2004.08.034

Hennigan CJ, Sulivan AP, Collett JL, Robinson AL (2010) Levoglucosan stability in biomass burning particles exposed to hydroxyl radicals. Geophys Res Lett 37, L09806. doi:10.1029/2010GL043088

Hoffmann D, Tilgner A, Iinuma Y, Herrmann H (2010) Atmospheric stability of levoglucosan: a detailed laboratory and modeling study. Environ Sci Technol 44:694–699. doi:10.1021/es902476f

Hou X, Zhuang G, Lin Y, Li J, Jiang Y, Fu JS (2008) Emission of fine organic aerosol from traditional charcoal broiling in China. J Atmos Chem 61:119–131. doi:10.1007/s10874-009-9128-3

Lee JL, Engling G, Lung SC, Lee KY (2008) Particle size characteristics of levoglucosan in ambient aerosols from rice straw burning. Atmos Environ 42:8300–8308. doi:10.1021/es902476f

Medeiros PM, Simoneit BRT (2007) Analysis of sugars in environmental samples by gas chromatography–mass spectrometry. J Chromatogr A 1141:271–278. doi:10.1016/j.chroma.2006.12.017

Mochida M, Kawamura K, Fub P, Takemura T (2010) Seasonal variation of levoglucosan in aerosols over the western North Pacific and its assessment as a biomass-burning tracer. Atmos Environ 44:3511–3518. doi:10.1016/j.atmosenv.2010.06.017

Oliveira C, Pio C, Alves C, Evtyungina M, Santos P, Gonçalves V et al (2007) Seasonal distribution of polar organic compounds in the urban atmosphere of two large cities from the North and South of Europe. Atmos Environ 41:5555–5570. doi:10.1016/j.atmosenv.2007.03.001

Pérez N, Pey J, Cusack M, Reche C, Querol X, Alastuey A, Viana M (2010) Variability of particle number, black carbon and PM10, PM2.5 and PM1 levels and speciation: influence of road traffic emissions on urban air quality. Aerosol Sci Technol 44:487–499. doi:10.1080/02786821003758286

Phuleria HC, Fine PM, Zhu Y, Sioutas C (2005) Air quality impacts of the October 2003 Southern California wildfires. J Geophys Res 110: D07S20. doi:10.1029/2004JD004626

Pope CA III, Burnett RT, Thun MJ, Calle EE, Krewski D, Ito K, Thurston GD (2002) Lung cancer, cardiopulmonary mortality, and long-term exposure to fine particulate air pollution. JAMA 287:1132–1141

Puxbaum H, Caseiro A, Sánchez-Ochoa A, Kasper-Giebl A, Cleays M, Gelencsér A, Legrand M, Preunkert S, Pio C (2007) Levoglucosan levels at background sites in Europe for assessing the impact of biomass combustion on the European aerosol background. J Geophys Res 112:D23S05. doi: 10.1029/2006JD008114.

Querol X, Alastuey A, Moreno T, Viana MM, Castillo S, Pey J, Rodríguez S, Artiñano B, Salvador P, Sánchez M, Garcia Dos Santos S, Herce Garraleta MD, Fernandez-Patier R, Moreno-Grau S, Negral L, Minguillón MC, Monfort E, Sanz MJ, Palomo-Marín R, Pinilla-Gil E, Cuevas E, de la Rosa J, Sánchez de la Campa A (2009) Spatial and temporal variations in airborne particulate matter (PM10 and PM2.5) across Spain 1999–2005. Atmos Environ 42: 3964–3979. doi:10.1016/j.atmosenv.2006.10.071

Reche C, Viana M, Amato F, Alastuey A, Moreno T, Hillamo R, Teinilä K, Saarnio K, Seco R, Peñuelas J, Mohr C, Prévôt A, Querol X (2012) Biomass burning contributions to urban aerosols in a coastal Mediterranean city. Sci Tot Environ 427–428:175–190. doi:10.1016/j.scitotenv.2012.04.012

Rolph GD (2003) Real-time Environmental Applications and Display sYstem (READY) Website (http://www.arl.noaa.gov/ready/hysplit4.html). NOAA Air Resources Laboratory, Silver Spring, MD

Sillanpää M, Frey A, Hillamo R, Pennanen AS, Salonen O (2005) Organic, elemental and inorganic carbon in particulate matter of six urban environments in Europe. Atmos Chem Phys 5:2869–2879

Simoneit BRT (2002) Biomass burning—a review of organic tracers for smoke from incomplete combustion. Appl Geochem 17:29–162. doi:10.1016/S0883-2927(01)00061-0

Simoneit BRT, Schauer JJ, Nolte CG, Oros DR, Elias VO, Fraser MO et al (1999) Levoglucosan, a tracer for cellulose in biomass burning and atmospheric particles. Atmos Environ 33:173–182

Szidat S, Prévôt ASH, Sandradewi J, Alfarra MR, Synal H-A, Wacker L et al (2007) Dominant impact of residential wood burning on particulate matter in Alpine valleys during winter. Geophys Res Lett 34, L05820. doi:10.1029/2006GL02832

van Drooge BL, Lopez J, Grimalt JO (2012) Influences of natural emission sources (wildfires and Saharan dust) on the urban organic aerosol in Barcelona (Western Mediterranean Basis) during a PM event. Environ Sci Pollut Res 19:4159–4167. doi:10.1007/s11356-012-0890-4

Vicente A, Alves C, Monteiro C, Nunes T, Mirante F, Cerqueira M, Calvo A, Pio C (2012) Organic speciation of aerosols from wildfires in central Portugal during summer 2009. Atmos Environ 57:186–196. doi:10.1016/j.atmosenv.2012.04.030

Vicente A, Alves C, Calvo A, Fernandez A, Nunes T, Almeida SM, Pio C (2013) Emission factors and detailed chemical composition of smoke particles from the 2010 wildfire season. Atmos Environ 71: 295–303. doi:10.1016/j.atmosenv.2013.01.062