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Molecular marker characterization of the organic composition of submicron aerosols from Mediterranean urban and rural environments under contrasting meteorological conditions

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HIGHLIGHTS

- Larger contributions of primary sources in urban site, leading to higher hydrocarbon levels.
- OA in the urban site is influenced by similar extent to biomass burning as the rural background site.
- Air pollution leads to formation of SOA, resulting in high OOA concentrations in BCN and MSY.
- Good correlations were observed between the off-line and the on-line data for the OA fractions.

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ABSTRACT

In Winter 2009 an intensive experimental campaign (DAURE) was conducted in an urban site (Barcelona) and in an elevated rural background station (Montseny) in the western Mediterranean basin. During this period three main scenarios were identified based on distinct meteorological conditions: A) temperature inversion, B) cloudy days in normal conditions, and C) intense sea breeze. Filter samples of the submicron fraction (PM_1) collected during these scenarios were analysed for organic tracer compounds to gain insight into the composition, sources, formation and processing of aerosol organic matter in the region under contrasting conditions. The results were compared to on-line Aerosol Mass Spectrometry (AMS) measurements. Scenario A conditions had the highest pollution concentrations in Barcelona (traffic and secondary aerosol formation) and lowest in Montseny whose sampling station remained above the mixing layer. Under scenario B the biomass burning contribution was highest in Montseny, reflecting nearby biomass burning sources. Under scenario C, the traffic-related contributions were highest in Montseny and lowest in Barcelona in comparison to the other samples, reflecting the enhanced pollution transport to Montseny and greater dilution in Barcelona. In this scenario, secondary organic aerosol was highest in Montseny. Molecular marker data and AMS source apportionment showed strong to moderate correlation for a) dicarboxylic acids and oxygenated organic aerosol, b) levoglucosan and biomass burning organic aerosol and c) Σn-alkanes and hydrocarbon-like organic aerosol.

1. Introduction

Particulate matter (PM) has been shown to cause numerous human health problems (Pope and Dockery, 2006), including case studies in the Mediterranean region (Pérez et al., 2009; Sunyer et al., 1989). In the Mediterranean countries densely populated cities are common and their inhabitants are frequently exposed to high levels of air pollution. PM in Barcelona is relatively high and with levels comparable to those found in other large metropolitan areas in Europe (Rodríguez et al., 2007). Furthermore, Mediterranean areas are often characterized by high solar radiation and anticyclonic conditions that enhance the development of sea breeze circulation which transport the air pollution inland from coastal cities (Millán et al., 1997; Rodríguez et al., 2003; Jorba et al., 2004). Conversely, in winter stagnant atmospheric conditions are common which results into the accumulation of pollution near the source locations (Pérez et al., 2008; Pey et al., 2009).

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In this study, the organic composition of PM in urban and rural areas is investigated to increase the knowledge on the processes that determine the concentrations of these pollutants under typical Mediterranean climate scenarios. Accordingly, during February and March 2009, an urban background site in Barcelona and an elevated rural background site in Montseny PM_1 concentrations (PM with aerodynamic diameter <1 μm) were measured as part of the DAURE campaign (Determination of the sources of atmospheric Aerosols in Urban and Rural Environments in the western Mediterranean). Meteorology and transport conditions during this campaign are described elsewhere (Jorba et al., 2011). The changes in total PM and the inorganic component of PM at these two sampling sites under dominant meteorological regimes have been described in previous studies (Jorba et al., 2011; Pérez et al., 2008; Pey et al., 2009). However, limited information is available on the organic component of PM in Barcelona (Aceves and Grimalt, 1993; Mohr et al., 2012) and none for Montseny. In this respect, the formation and transport of secondary organic species must also be considered to better understand their role in organic aerosol formation and accumulation and distribution of submicron PM (Jimenez et al., 2009).

PM_1 filter samples collected during selected days with contrasting atmospheric conditions (temperature inversion, cloudy days and normal conditions with strong sea breeze; scenarios A, B and C) were analysed for organic molecular tracers to gain insight into the organic composition of PM_1, the transport of pollution between these two areas, and their ability to be used to differentiate between different primary pollution sources and formation of secondary organic aerosol. The compounds analysed included polycyclic aromatic hydrocarbons (PAH), hopanes and aliphatic hydrocarbons, as tracers of primary emissions from traffic and other anthropogenic combustion sources, levoglucosan, as a primary tracer of biomass burning emissions, and dicarboxylic acids, as tracers of secondary organic aerosol concentrations (Bi et al., 2008; Schauer et al., 2007; Simoneit, 2002).

2. Methods and materials

2.1. PM_1 filter sample analysis

From February 25 to March 27 2009, PM_1 was sampled simultaneously in an urban background site from the metropolitan area of Barcelona (41°23′24″N, 02°6′58″E, 80 m a.s.l.) and in an elevated rural background station in the mountainous area of Montseny (41°46′44″N, 02°21′18″E; 720 m.a.s.l.). This mountain site is situated 48 km north-northeast of the sampling site in Barcelona.

PM_1 filter samples collected on February 26–27 (A scenario), March 3–4 (B scenario) and March 18–19 2009 (C scenario) were selected for study of molecular tracers. At both sites, samples were collected with 12-h resolution at local time from 9:00 h to 21:00 h (daytime) and from 21:00 h to 9:00 h (night time) using a Digitel-DH80 Hivol-sampler (Digitel Elektronic AG, Switzerland) (Table 1). After sampling, filters were weighted and divided in four parts and stored in aluminium foil at −4 °C for further analysis.

A quarter of each filter was ultrasonically extracted with 3 × 20 mL of (1:1, v/v) dichloromethane-methanol (Merck, Germany) for 15 min. Before extraction 25 μL of surrogate standards consisting of d_4-succinic acid (Sigma–Aldrich, Germany), d_7-levoglucosan (Cambridge Isotopic Laboratories, UK), d_{50}-n-C_{24} (Cambridge Isotopic Laboratories, UK), d_{10}-anthracene, d_{12}-benz[a]anthrancene, d_{12}-benzo[k]fluoranthene, and d_{12}-benzo[ghi]perylene (Dr. Ehrenstorfer, Germany) were added to samples and blanks. Insoluble particles from the extracts were removed by filtration over 0.45 μm Teflon membranes (Whatman, USA) and the solvent solutions were concentrated by rotovap to 1 mL.

n-Alkanes, PAH and hopanes were analysed using a 0.5 mL aliquot of this extract that was cleaned up by adsorption column chromatography on 2 g of aluminium oxide (Merck, Germany), previously activated at 120 °C overnight. The analytes were eluted with 5 mL of (9:1 v/v) hexane-dichloromethane and 15 mL of (1:2 v/v) hexane-dichloromethane, respectively (Merck, Germany). The collected fractions were concentrated by rotovap to 0.5 mL and further concentrated until almost dryness under a gentle stream of N_2 and diluted in 50 μL of iso-octane (Merck, Germany). An injection standard of d_{10}-pyrene was added before gas chromatographic analysis.

Anhydro-saccharides and dicarboxylic acids were analysed as described elsewhere (Medeiros and Simoneit, 2007). Briefly, 25 μL aliquots of the extract were evaporated under a gentle stream of N_2 until dryness. 25 μL of bis(trimethylsilyl)trifluoroacetamide + 1% trimethylchlorosilane (Supelco, USA) and 10 μL of pyridine (Merck, Germany) were added for overnight derivatization at room temperature. Then, the solvent mixtures were evaporated until dryness and diluted in 50 μL iso-octane. Before gas chromatographic analysis, an injection standard of d_{10}-pyrene was added.

Instrumental analyses were performed by gas chromatography coupled to mass spectrometry. Samples were injected into a Thermo GC/MS (Thermo Trace GC Ultra − DSQ II) equipped with a 60 m fused capillary column (HP-5MS 0.25-mm × 0.25-μm film thickness). The oven temperature program started at 60 °C where it was held for 1 min, then it was increased to 120 °C at 12 °C min^{-1}, and to 310 °C at 4 °C min^{-1}, where it was held for 10 min. The injector, ion source, quadrupole and transfer line temperatures were 280 °C, 200 °C, 150 °C and 280 °C, respectively. Helium was used as the carrier gas (0.9 mL s^{-1}). Ionization was performed using electron ionization (70 eV) and the quadrupole mass spectrometer was operated in full scan (*m/z* 50–650) mode.

Aliphatic hydrocarbons (n-C_{23} to n-C_{34}) were identified by the ions *m/z* 57, 71 and 85, at the corresponding GC retention times. PAH were identified by retention time comparison at the following ions: phenanthrene (*m/z* 178), anthracene (*m/z* 178), fluoranthene (*m/z* 202), pyrene (*m/z* 202), benz[a]anthracene (*m/z* 228), chrysene + triphenylene (*m/z* 228), benzo[b]fluoranthene (*m/z* 252), benzo[k]fluoranthene (*m/z* 252), benzo[e]pyrene (*m/z* 252), benzo[a]pyrene (*m/z* 252), indeno[1,2,3-cd]pyrene (*m/z* 276) and benzo[ghi]perylene (*m/z* 276). Quantification was performed using the external standard calibration curves. The resulting concentrations were then corrected by the recoveries of the following surrogates: d_{50}-n-C_{24} (*m/z* 66) for aliphatic hydrocarbons and d_{10}-anthracene (*m/z* 188), d_{12}-benz[a]anthrancene (*m/z* 240), d_{12}-benzo[k]fluoranthene (*m/z* 264) and d_{12}-benzo[ghi]perylene (*m/z* 288) for the PAHs. Hopanes, 17(H)α-21(H)β-29-norhopane and 17(H)α-21(H)β-hopane, were identified from the *m/z* 191 fragmentogram. Levoglucosan, mannosan and galactosan were identified in their derivatized form from the *m/z* 204 fragmentogram. Succinic, glutaric, malic and phthalic acids were identified in their derivatized form from the *m/z* 73 and 147 fragmentograms, as well as the individual *m/z* 247, 261, 233, and 295 ions, respectively. Quantification was performed using the external standard calibration curves of levoglucosan and succinic acid. These concentrations were corrected by the recoveries of the surrogate standards d_4-succinic acid (*m/z* 251) and d_7-levoglucosan (*m/z* 206).

In all analyses 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 concentrations. Limits of Quantification (LOQ) were calculated by dividing the lowest measured levels in the standard calibration curves by the volumes of the analysed sample fraction. These were

Table 1
Concentrations of PM_1, organic tracer compounds (ng m^{-3}), organic aerosol fraction concentrations and values for meteorological variables.

	A scenario: temperature inversion				B scenario: cloudy day				C scenario: sea breeze			
	MSY Feb. 26 night	BCN Feb. 26 day	MSY Feb. 27 day	BCN Feb. 27 day	MSY March 3 day	BCN March 3 night	MSY March 4 night	BCN March 4 day	MSY March 18 day	BCN March 18 night	MSY March 19 night	BCN March 19 night
PM1 (μg m^{-3})	6	42	13	41	24	16	17	12	21	32	25	32
HOA (μg m^{-3})	0.1	2.1	0.3	4.7	1.2	1.9	0.7	0.5	1.5	1.5	1.0	2.1
OOA (μg m^{-3})	0.5	8.2	0.7	10.4	2.9	4.9	1.6	3.3	3.9	6.1	2.9	5.1
BBOA (μg m^{-3})	0.2	1.0	0.6	0.9	1.4	0.6	0.5	0.4	0.6	0.3	0.4	0.4
OA (μg m^{-3})	0.8	11.3	1.6	16.0	5.5	7.4	2.8	4.2	6.0	7.9	4.3	7.7
PBL LIDAR (m)		250		555		1300		1100		1068		–
Temperature (°C)	8.6	16.1	14.1	11.1	6.7	9.8	5.4	8.2	14.1	15.7	10.3	11.8
Relative humidity (%)	32	44	35	73	94	79	89	83	56	54	57	58
Wind speed (m s^{-1})	0.3	1.8	0.4	0.8	0.3	0.4	0.6	1.9	2.0	2.9	0.6	1.5
Wind direction (°)	250	262	145		106	266	301	296	121	222	305	280
Phenanthrene	0.03	0.19	0.04		0.04	0.06	0.04	0.05	0.05	0.07	0.03	0.05
Anthracene	0.01	0.05	0.02		0.02	0.02	0.01	0.02	0.01	0.02	0.01	0.02
Fluoranthene	0.02	0.35	0.06		0.09	0.06	0.09	0.04	0.05	0.11	0.03	0.11
Pyrene	0.03	0.37	0.05		0.09	0.08	0.04	0.05	0.05	0.13	0.03	0.15
Benz[a]anthracene	0.01	0.26	0.06		0.08	0.08	0.01	0.07	0.03	0.10	0.02	0.13
Chrysene	0.03	0.53	0.15		0.20	0.19	0.07	0.17	0.07	0.21	0.05	0.22
Benzo[b+j] fluoranthene	0.04	0.38	0.13		0.19	0.17	0.06	0.17	0.09	0.13	0.06	0.17
Benzo[k]fluoranthene	0.04	0.30	0.10		0.20	0.13	0.04	0.14	0.08	0.10	0.04	0.16
Benzo[e]pyrene	0.06	0.49	0.16		0.20	0.27	0.11	0.25	0.14	0.18	0.11	0.22
Benzo[a]pyrene	0.05	0.30	0.08		0.11	0.13	0.05	0.14	0.08	0.10	0.05	0.16
Perylene	0.03	0.06	0.03		0.04	0.04	0.02	0.03	0.03	0.02	0.02	0.03
Indeno[123cd]pyrene	0.06	0.46	0.16		0.23	0.26	0.08	0.17	0.13	0.17	0.09	0.21
Benzo[ghi]perylene	0.05	0.58	0.12		0.18	0.34	0.08	0.20	0.14	0.21	0.08	0.25
ΣPAH	0.46	4.31	1.17		1.67	1.81	0.70	1.48	0.94	1.54	0.61	1.87
IP/(IP + BGP)	0.51	0.44	0.57		0.56	0.43	0.51	0.45	0.48	0.45	0.53	0.46
17α(H)21β(H)-29-norhopane	0.27	0.92	0.31		0.16	0.49	0.19	0.39	0.37	0.42	0.23	0.35
17α(H)21β(H)-hopane	0.49	0.99	0.43		0.23	0.64	0.28	0.56	0.54	0.45	0.43	0.44
ΣHopanes	0.76	1.90	0.74		0.39	1.13	0.47	0.94	0.90	0.88	0.65	0.79
n-C_{23}	3.9	15.7	1.7		5.2	10.0	5.1	9.6	10.9	15.9	9.1	3.6
n-C_{24}	5.3	10.3	1.7		6.3	8.7	5.2	8.4	9.9	5.1	5.5	6.7
n-C_{25}	3.7	8.8	1.1		5.2	7.7	4.2	7.1	7.0	7.4	4.6	6.0
n-C_{26}	1.9	5.5	1.1		3.3	5.9	3.4	3.2	4.1	4.6	5.4	3.0
n-C_{27}	2.8	7.1	1.2		5.9	8.6	4.6	6.3	7.1	7.2	6.3	5.3
n-C_{28}	1.5	4.3	0.5		3.5	3.9	2.1	3.2	3.2	2.3	5.9	2.4
n-C_{29}	3.0	6.6	1.3		7.2	7.5	3.5	4.5	6.9	5.3	9.1	5.9
n-C_{30}	1.5	3.8	0.7		3.3	6.4	2.1	4.5	4.4	2.5	4.9	3.3
n-C_{31}	2.5	5.4	1.2		4.7	8.8	3.9	5.9	6.9	5.6	8.3	5.4
n-C_{32}	1.5	2.5	0.6		1.7	4.3	2.1	4.3	3.4	2.8	2.9	2.9
n-C_{33}	0.8	2.6	0.4		3.3	7.5	2.1	6.4	4.0	2.9	3.3	3.1
n-C_{34}	0.6	1.8	0.3		2.9	7.0	2.0	6.1	3.5	0.5	2.5	2.2
Σn-alkanes	28.8	74.4	11.7		52.5	86.4	40.4	69.5	71.3	61.9	67.9	49.9
CPI	1.5	1.4	1.4		1.6	1.4	1.4	1.4	1.5	1.9	1.4	1.6
Galactosan	1.6	3.7	5.2		13.8	6.8	2.5	4.3	2.2	2.9	1.7	3.2
Mannosan	1.0	3.9	5.0		16.2	4.4	2.1	3.4	1.9	2.1	0.9	2.1
Levoglucosan	16.1	31.1	48.7		119.8	49.6	23.1	36.4	24.7	22.8	20.7	26.3
Succinic acid	3.4	24.2	5.4		14.5	12.9	6.2	9.2	16.9	22.5	10.4	16.3
Glutaric acid	1.7	7.8	2.8		6.3	5.9	3.5	3.2	6.9	7.0	4.6	8.6
Malic acid	2.8	21.4	5.8		12.5	17.7	4.3	8.0	23.8	22.5	24.9	17.0
ΣDiacids	7.9	53.4	14.0		33.3	36.4	14.0	20.5	47.7	52.1	39.9	41.8
Phthalic acid	4.3	10.9	3.0		6.2	9.7	3.5	6.9	9.6	7.2	6.3	8.5

CPI = (Σn-C_{25}–n-C_{33}/Σn-C_{24}–n-C_{32}) + (Σn-C_{26}–n-C_{34}/Σn-C_{25}–n-C_{33})/2.

0.1 ng m^{-3} for sugars, 0.06 ng m^{-3} for n-alkanes and 0.005 ng m^{-3} for PAHs and hopanes.

2.2. Complementary data

PM_1 was gravimetrically measured on quartz filters (Pall Scientific, USA). Local meteorological data (temperature, relative humidity, wind speed and direction) were obtained from Barcelona and Montseny meteorological stations. Radiosoundings for Barcelona were used to estimate the height of the mixed layer (Jorba et al., 2011). Two HR–ToF–AMS instruments (Aerodyne High-Resolution Time-of-Flight Aerosol Mass Spectrometer) instruments were operated in Barcelona and Montseny. The methodology is described elsewhere (Mohr et al., 2012). They provided semi-continuous measurements of the non-refractory submicron aerosol chemical composition. Factor analysis (Positive Matrix Factorization, PMF; Ulbrich et al., 2009) of the organic mass spectral matrix measured by AMS was used to quantify the fractions of oxygenated organic aerosol (OOA), hydrocarbon-like organic aerosol (HOA) and biomass burning organic aerosol (BBOA), and was compared to the molecular tracers. Only the primary fraction of BBOA is thought to be captured in the AMS BBOA factor, while secondary species in biomass burning smoke are typically apportioned to the OOA factor (e.g. Jimenez et al., 2009; Cubison et al., 2011).

All statistical calculations were performed using the SPSS v. 17 package (SPSS Inc., Chicago, Ill.). Unless otherwise noted, significance levels of the linear correlations were set at $p < 0.05$.

3. Results and discussion

3.1. PM_1 and OA concentrations

The highest PM_1 levels during the DAURE-winter campaign were observed in Barcelona (41–42 μg m^{-3} for night and daytime) under temperature inversion (A scenario; 26–27/2/2009; Table 1). In these conditions Montseny was situated above the regional mixed layer and showed the lowest PM_1 concentrations (6–13 μg m^{-3} for night and daytime) of the entire DAURE-winter campaign. The PM_1 levels in Barcelona were rather constant for both sampling intervals, reflecting the PM peak hours around 7:00 h (night time sample) and around 19:00 h (daytime sample) (Pérez et al., 2010; Rodríguez et al., 2007).

During the cloudy days (3–4/3/2009), with Montseny station situated within the mixed layer (B scenario), PM_1 levels were very similar at both sites or even slightly higher in Montseny (17–24 μg m^{-3}) than in Barcelona (12–16 μg m^{-3}). Under these meteorological conditions, the solar radiation and the sea-land breeze were reduced, e.g. low wind speed (Table 1), and the transport of air pollution from the urbanized coast to the valley inland was reduced.

In C scenario (18–19/3/2009), the sunny day with active sea breeze conditions, e.g. high wind speed (Table 1), the transport of air pollution towards Montseny was potentially high. Furthermore, the mountain station was situated within the mixed layer. PM_1 levels in Barcelona were 32 μg m^{-3} both in the day and night time samples and in Montseny they were 21 μg m^{-3} and 25 μg m^{-3} for the day and night samples, respectively.

The OA concentrations in the different scenarios showed similar trends to those of PM_1. Under A scenario (26–27/2/2009) OA concentrations were 11.3 and 16.0 μg m^{-3} in Barcelona during night and daytime, respectively, and much lower in Montseny, 0.8 and 1.6 μg m^{-3}, respectively. Under B scenario (3–4/3/2009) OA concentrations in Montseny were 5.5 and 2.8 μg m^{-3} for the day and night time, respectively, and 8.0 and 4.4 μg m^{-3} in Barcelona, respectively. Under C scenario (18–19/3/2009) OA concentrations in Barcelona were 8.8 and 8.7 μg m^{-3} for the day and night samples, respectively, and 6.0 and 4.3 μg m^{-3} in Montseny, respectively.

3.2. Primary organic tracers

3.2.1. Aliphatic hydrocarbons

n-Alkanes were found in all samples (12–86 ng m^{-3}; Table 1). These compounds are emitted to the atmosphere by a large variety of sources, such as fossil fuel vehicle emissions, biomass combustion, and by resuspension of vegetative detritus (Schauer et al., 2007). The lower molecular weight n-alkanes (n-C_{23} to n-C_{25}) that were measured are more related to traffic emissions, while the higher molecular weight n-alkanes, and particularly the odd carbon numbered n-alkanes: n-C_{27}, n-C_{29} and n-C_{31}, are almost entirely related to vegetation detritus as they are present in large quantities in epicuticular wax from higher plants (Aceves and Grimalt, 1993; Simoneit et al., 1991). The carbon preference index of n-alkanes (CPI; Table 1) is useful for identification of vegetation detritus since high index values indicate higher plant contributions and low values correspond to traffic emissions.

Under scenario A, the ∑n-alkanes in PM_1 filter samples was 75 ng m^{-3} in Barcelona, and 12–29 ng m^{-3} in Montseny (Table 1). The CPI was around 1.4–1.5 in both sites, indicating modest contributions of vegetation detritus. Under scenario B the concentrations were 40–53 ng m^{-3} in Montseny and 70–86 ng m^{-3} in Barcelona (Table 1). Under scenario C the n-alkanes showed higher concentrations in Montseny, 68–72 ng m^{-3}, than in Barcelona, 50–62 ng m^{-3}. The highest CPI was observed in the daytime sample from Barcelona under sea breeze conditions (scenario C), 1.9, whereas all the other sample values range between 1.4 and 1.6. This high CPI value indicates a higher contribution of vegetation detritus in this Barcelona sample, which could be caused by resuspension of organic material as a consequence of the higher wind speed due to the sea breeze. The rather constant and low CPI values in Montseny, 1.4–1.6, indicate that the PM_1 fraction observed at this station has a large proportion of background traffic inputs, either from Barcelona or from other urban areas.

3.2.2. Polycyclic aromatic hydrocarbons

PAHs are generated as consequence of incomplete combustion of organic matter, either fossil fuel or biomass. These compounds were higher in Barcelona (∑PAH = 4.3 ng m^{-3}) than in Montseny (∑PAH = 0.5–1.2 ng m^{-3}) during scenario A. The concentrations of benzo[a]pyrene during Scenario A, the only PAH that is regulated by law due to its carcinogenicity (European Council Directive, 2004), were 0.3 ng m^{-3} and 0.05–0.08 ng m^{-3} in Barcelona and Montseny, respectively. These concentrations were the highest and lowest observed, respectively. This is consistent with the trends in PM_1, OA, n-alkanes and other PAH indicating that under scenario A the differences in PM_1 loading between the coastal urban areas and inland rural sites were highest. The observed values were always under 1 ng m^{-3} which is the legal limit.

The relative concentrations of the individual PAH species were similar among all samples, with slightly higher values of benzo[ghi]perylene (BGP) and chrysene (CHR) in Barcelona and benzo[e]pyrene (BeP) and indeno[123-cd]pyrene (IP) in Montseny. The isomeric ratio of IP/(IP + BGP) was 0.44 in Barcelona and 0.51 and 0.57 during day and night time in Montseny, respectively. BGP concentrations are higher in traffic emissions while IP concentrations are higher in biomass combustion (Schauer et al., 2001, 2002). Accordingly, these ratios indicate that primary traffic emission sources are more significant in the atmosphere of Barcelona, while there is a higher contribution of biomass burning in the atmosphere of Montseny.

Photochemical degradation may also influence these ratios, involving higher decomposition rate of BGP than IP (Esteve et al., 2006; Galarneau, 2008). However, paired comparison of the IP/(IP + BGP) ratios between day and night samples does not show significant differences. Furthermore, the variations observed do not correspond to a systematic loss of BGP in the day samples which indicates that this photochemical effect was not significant in the studied PM_1 samples.

Under scenario B the ∑PAH levels during daytime were 1.8 ng m^{-3} and 1.7 ng m^{-3} in Barcelona and Montseny, respectively. Despite this similarity in concentrations, the relative PAH composition was different with IP/(IP + BGP) = 0.43 in Barcelona and 0.56 in Montseny, indicating again larger influence of direct traffic emissions in Barcelona. During night time the concentrations in Montseny decreased to levels which were about half those in Barcelona. Under scenario C the concentrations of ∑PAH were 1.5–1.9 ng m^{-3} in Barcelona and 0.61–0.94 ng m^{-3} in Montseny. The nighttime concentrations in Barcelona were higher than the daytime concentrations, while this was the opposite in Montseny. The higher daytime concentrations in Montseny may reflect higher transport rate of air pollution from the polluted coastal areas inland towards Montseny. This is also consistent with the lower IP/(IP + BGP) ratio of 0.48 in the day sample, than in the night sample, 0.53, indicating a higher proportion of traffic PAH during the day and similar to the ratios in Barcelona, 0.45–0.46. In Barcelona the higher PAH concentrations in the night sample, 1.9 ng m^{-3}, vs. the day sample, 1.5 ng m^{-3}, may also be explained by higher dispersion as a consequence of higher

mixed layer and higher wind speeds during sea breeze conditions (Table 1).

3.2.3. Hopanes

Hopanes, 17α(H)21β(H)-29-norhopane and 17α(H)21β(H)-hopane, are constituents of lubricating oils and may also reflect vehicular emissions. These compounds were found in all samples with their sum ranging between 0.4 and 1.9 ng m^{-3} (Table 1). The observed ∑hopane concentrations in Barcelona were in the upper range of those found in urban areas, such as Pittsburgh or Los Angeles (0.1–2.5 ng m^{-3}; Subramanian et al., 2006; Ning et al., 2007). A significant correlation between concentrations of hopanes and PAH was observed, $r^2 = 0.7$, which is consistent with the above assignment of traffic as an important PAH emission source for these sample periods. The lowest hopane concentrations were observed in Montseny on the cloudy day with calm winds (B scenario), suggesting that in these conditions the influence of traffic was lowest in this site. Under C scenario higher hopane concentrations were observed in the day sample, 0.90 ng m^{-3}, than in the night sample, 0.65 ng m^{-3} (Table 1) which was consistent with the higher transfer of pollutants in this site as discussed for PAHs under significant sea breeze.

3.2.4. Levoglucosan

Levoglucosan is a tracer for primary biomass burning. This compound had concentrations that ranged between 16 and 120 ng m^{-3}, and are in the same range as those found in European urban and rural areas (5–500 ng m^{-3}; Fabbri et al., 2008; Puxbaum et al., 2007; van Drooge and Pérez-Ballesta, 2009). In those studies, higher concentrations were observed in the winter season, when wood burning for domestic heating and biomass waste burning in fields and forests was practiced in the vicinity of the sampling sites. In the present study, the highest levoglucosan concentration was observed in Montseny suggesting larger influence of primary biomass burning in this elevated rural background site.

The contribution of biomass burning to OA can be estimated from the levoglucosan (LG) concentrations using the ratios between this compound and the concentrations of organic carbon found in biomass combustion smoke (Puxbaum et al., 2007). These ratios vary according to wood type and combustion conditions, e.g. in wood stove experimental combustion ratios have been observed to be between 0.04 and 0.3 (average ratio 0.14; Fine et al., 2001, 2002) and in experimental wildland fires in the Mediterranean region the average ratio was 0.09 (Alves et al., 2010). Levoglucosan may also partially evaporate or be oxidized by photochemical reactions (Hennigan et al., 2010; Cubison et al., 2011) although these effects may be limited in winter. To estimate the contribution of the biomass burning contribution to OA in Barcelona and Montseny, a ratio of 0.1 was used, assuming that wood types and conditions were similar in both sites and through time, and assuming limited impact of levoglucosan evaporation or photodegradation during this period. Conversion of OC into OA was performed using a OA/OC ratio of 1.4 that has been calculated from wood stove experiments (Fine et al., 2001, 2002). Accordingly, the transformation of levoglucosan and OA data from Table 1 following this method shows higher relative contributions of biomass burning in Montseny (5.8–43%) than in Barcelona (4–12%). This difference can be attributed to higher biomass burning activities inland in comparison to other emission sources. In Montseny, the biomass burning contributions to OA were highest under A scenario (28–43%) and under B scenario (11.5–31%) while they were lowest under C scenario (5.8–6.8%). In this last case (Scenario C), the proportions were very similar to those found in Barcelona (4.1–4.7%). This latter atmospheric conditions involving transport of atmospheric pollutants from coastal urbanized areas may have decreased the relative impact of the inland biomass burning activities in the Montseny station.

3.3. Secondary organic tracers: dicarboxylic acids

Dicarboxylic acids have been related to the formation of secondary organic aerosol (Bunce et al., 1997; Grosjean et al., 1978; Jang and McDow, 1997; Heald et al., 2010; Sheesley et al., 2010). Although, some dicarboxylic acids are emitted in small quantities from traffic and vegetation (Kawamura and Kaplan, 1987; Grosjean et al., 1978; Rogge et al., 1993), in most locations secondary reactions are primarily responsible for their ambient concentrations (Heald et al., 2010; Paulot et al., 2011). In particular, succinic acid and malic acid have been identified as some of the most abundant dicarboxylic acids in aerosols (Yu et al., 2005; Satsumabayashi et al., 1990; Helmi Rozaina and Brimblecomb, 2009). These compounds also have a role in the production of cloud condensation nuclei due to their tendency to increase the hygroscopicity of OA (Kerminen et al., 2000).

Under scenario A the concentrations of dicarboxylic acids in Barcelona were about 5 times higher than in Montseny. The highest concentrations were observed for succinic and malic acid (24 and 21 ng m^{-3}), followed by phthalic acid and glutaric acid (11 and 8 ng m^{-3}; Table 1). These levels were in the range of concentrations found in urban and rural sites reported elsewhere (Takegawa et al., 2007; Helmi Rozaina and Brimblecomb, 2009 and references therein). The low concentrations observed in Montseny when this site is situated above the mixed layer were related to the absence of air pollution and also possibly partly due to the low relative humidity (Table 1), which may reduce in-situ aqueous phase reactions that can form oxidized secondary organic aerosol (Ervens et al., 2011).

Under B scenario the ∑dicarboxylic acid concentrations in Montseny were substantially high during daytime (33 ng m^{-3}) and lower at night (14 ng m^{-3}; Table 1). A similar trend was observed in Barcelona with daytime concentrations of 36 ng m^{-3} and nighttime concentrations of 20 ng m^{-3}. Nevertheless, the highest dicarboxylic acid concentrations in Montseny were observed under scenario C, 40–47 ng m^{-3}, when the levels were similar to those in Barcelona, 52–42 ng m^{-3}. These high concentrations were probably a consequence of enhanced oxidation processes within the mixed layer and atmospheric transport towards this elevated rural site.

3.4. Off-line filter analyses data vs. on-line aerosol mass spectrometer data

Comparison of the estimates of primary biomass burning contributions to OA resulting from filter analyses and from AMS analyses (Mohr et al., 2012) showed a good correlation (slope = 1; $r^2 = 0.6$; Fig. 1). Primary biomass burning OA (P-BBOA) concentrations ranged from 0.2 to 1.4 μg m^{-3} in Montseny and from 0.3 to 1.0 μg m^{-3} in Barcelona. Highest levoglucosan and P-BBOA concentrations in Montseny were observed under B scenario when this station was situated within the mixed layer and regional biomass burning from inland could reach the site. BBOA contributions in the other days may reflect levels after long-distance atmospheric transport. A significant correlation was observed between the PAH ratio IP/(IP + BGP) and BBOA/OA, $r^2 = 0.7$, which reflects that in conditions of low traffic contributions (high IP/(IP + BGP) ratios) the BBOA contribution increased.

Another correlation was found between the concentrations of n-alkanes and the HOA concentration from the AMS PMF analysis ($r^2 = 0.5$; Fig. 2). The lower HOA concentrations (~0.5 μg m^{-3}) were observed in Montseny under A scenario. When Montseny was within the mixed layer (scenarios A and B) the HOA levels and the

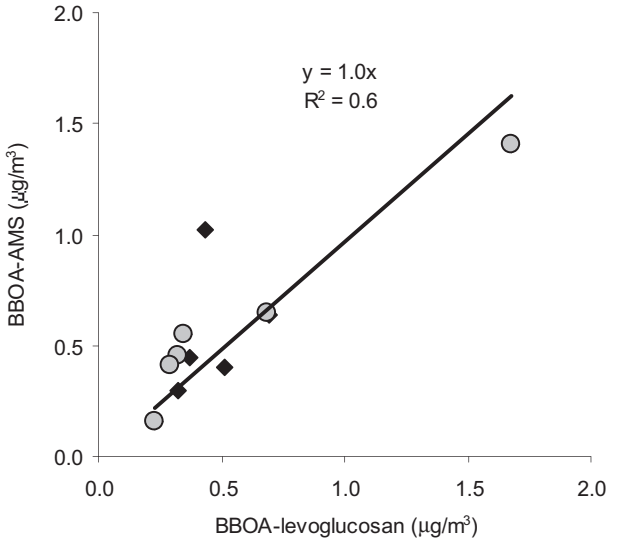

Fig. 1. Organic aerosol concentrations (μg m^{-3}) from biomass burning in MSY (grey dots) and in BCN (black squares) from PM_1 filter sample analyses and the application of levoglucosan/OC_{source} ratio = 0.1 and OA/OC_{source} = 1.4 vs. BBOA from the AMS.

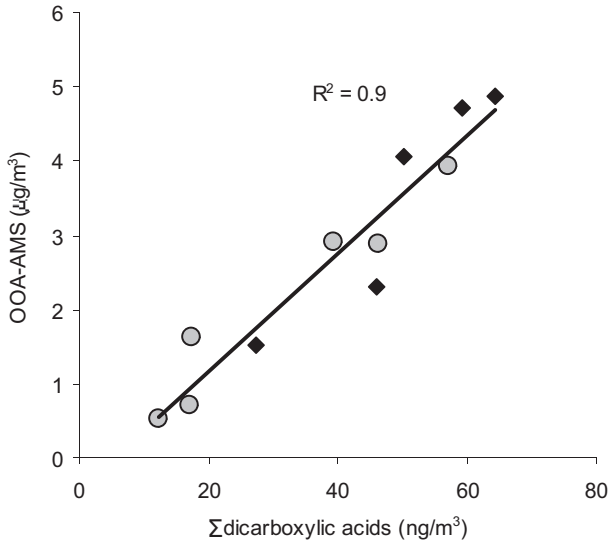

Fig. 3. ∑dicarboxylic acid + phthalic acid concentration (ng m^{-3}) from MSY (grey dots) and BCN (black squares) from PM_1 filter sample analyses vs. OOA from the AMS.

n-alkane concentrations were similar to those observed in Barcelona (HOA ~ 1.3 μg m^{-3}; Table 1).

The oxygenated chemical species play an important role in the composition of the OA (Jimenez et al., 2009; Sun et al., 2011). In all samples, and under all circumstances, this OOA fraction represented 60 ± 9% of the organic aerosol mass. The dicarboxylic acids analysed in this study showed a good correlation with the OOA concentrations of the AMS (r^2 = 0.9) (Fig. 3). In fact, the linear correlation allows estimating that the contribution of these three compounds is about 1.4% to the total OOA. This indicates that likely many other oxygenated organic compounds, that have not been identified here, compose the remaining fraction of secondary organic aerosol.

The lowest OOA concentrations were observed in Montseny, when this site was situated above the mixing layer (scenario A), particularly during night time. The highest OOA concentrations were found in Barcelona and Montseny during daytime, when this latter station was situated within the mixed layer (scenarios B and C).

Significant correlations between sulphate (data will be published elsewhere) and OOA (r^2 = 0.7) and ∑dicarboxylic acids (r^2 = 0.6) were found, consistent with the regional secondary nature of these species. In contrast, there was no correlation between OOA and BBOA or dicarboxylic acids and levoglucosan (r^2 < 0.09), indicating that the contribution of primary biomass burning aerosol to OOA and dicarboxylic acids was low, and that the OOA in this study was related to the formation of secondary organic aerosol. A good correlation (r^2 = 0.8) was observed between HOA and OOA, which reflects the fast formation of secondary organic aerosols compared to the transport time between the pollution sources and Montseny (DeCarlo et al., 2010).

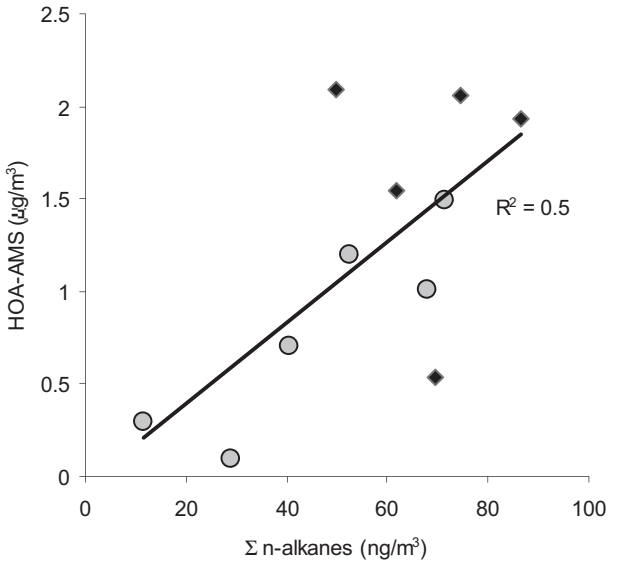

Fig. 2. ∑n-alkanes concentration (ng m^{-3}) from MSY (grey dots) and BCN (black squares) from PM_1 filter sample analyses vs. HOA from the AMS.

4. Conclusions

The highest pollution levels were observed in Barcelona during scenario A when maximum concentrations were observed for PM_1, OA, Σn-alkanes, Σhopanes and ΣPAH and n-alkane CPI was lowest. In these conditions the markers of secondary oxygenated aerosols were also highest, e.g. dicarboxylic acids and OOA. However, despite these conditions of secondary aerosol formation, the relative PAH composition was not altered significantly. The lowest pollution levels in this city were observed under scenario C which was characterized by strong sea breeze circulation that probably diluted local emissions and transported inland the pollutants generated by the urban activities. Despite this effect, the markers of secondary aerosol such as dicarboxylic acids and OOA remained high.

The highest PAH levels in Montseny were observed during scenario B reflecting local contributions from biomass burning, as supported by high levoglucosan concentrations. Conversely, the highest traffic pollution observed at this rural station was under scenario C when high concentrations of Σhopanes and Σn-alkanes with low CPI index were observed. In this scenario, the concentrations of dicarboxylic acids and OOA were also highest, reflecting the formation of secondary aerosol. At the Montseny station, the lowest organic levels were observed during scenario A when this station remained above the mixed layer.

Formation of secondary organic aerosol was monitored by concentration changes in dicarboxylic acids and OOA. Those markers were strongly correlated. Levoglucosan concentrations were also correlated with BBOA-AMS and Σn-alkanes with HOA-AMS, demonstrating the consistency of these independent indicators of contributions from biomass combustion and vehicular traffic, respectively.

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