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

Barend L. van Drooge [a,*], Michael Crusack [a], Cristina Reche [a], Claudia Mohr [b], Andres Alastuey [a], Xavier Querol [a], Andre Prevot [b], Douglas A. Day [c], Jose L. Jimenez [c], Joan O. Grimalt [a]

[a] Department of Environmental Chemistry, Institute of Environmental Assessment and Water Research (IDÆA-CSIC), Jordi Girona 18, 08034 Barcelona, Catalonia, Spain
[b] Paul Scherrer Institut (PSI), Villigen, Switzerland
[c] Department of Chemistry and Biochemistry and CIRES, University of Colorado Boulder, USA

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).

* Corresponding author. Tel.: +34 93 4006100; fax: +34 93 2045904.
E-mail address: barend.vandrooge@idaea.csic.es (B.L. van Drooge).

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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