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Speciation of organic compounds in aerosols from urban background sites in the winter season

Célia Alves *, Teresa Nunes, Ana Vicente, Cátia Gonçalves, Margarita Evtyugina, Telma Marques, Casimiro Pio, Frieda Bate-Epey

Centre for Environmental and Marine Studies, Department of Environment, University of Aveiro, 3810-193 Aveiro, Portugal

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ABSTRACT

Winter aerosol samples were daily collected during one-month long campaign in Oporto and Coimbra. The high-volume $PM_{2.5}$ samples were solvent extracted and their organic content separated into several functional groups, which were then analysed by gas chromatography–mass spectrometry. The organic compounds identified and quantified revealed some differences between samples from the two urban areas. In general, the levels of total hydrocarbons in the urban background station of Oporto were higher than those of Coimbra. Concentration ratios between specific compounds and the presence of molecular markers derived from petroleum, such as hopanes, pristane and phytane, point out vehicles as the main source of pollutants. The contribution of biogenic compounds, mainly hydrocarbons associated with the waxy cuticle of vegetation, is also observable in both cities. The benzo[a]pyrene equivalent daily values were frequently higher than 1 ng m^{-3} in Oporto suggesting an additional cancer risk for the population. The $PM_{2.5}$ mass attributable to vehicle emissions is higher in the background atmosphere of Oporto than in Coimbra. On weekends, biomass burning emissions could represent up to 74% of the organic carbon content of the urban aerosols.

1. Introduction

It has long been recognised that atmospheric aerosols interact both directly and indirectly with the Earth's radiation budget and climate (Carslaw et al., 2010) and may have detrimental effects on human health, such as impairment of pulmonary function (Islam et al., 2007; Riva et al., 2011). The organic content of aerosols accounts for a substantial fraction of the global aerosol burden (Zhang et al., 2011).

More than half of the world's population live in towns and cities. Thus, most of the aerosol characterisation and risk assessment studies have been carried out in urban areas (e.g. Bi et al., 2008; Herlekar et al., 2012; Schnelle-Kreis et al., 2005; Tsapakis et al., 2002; Wang et al., 2006). Among the target organic compounds, great efforts have been made to speciate, quantify, and understand the sources and reactivity of polycyclic aromatic compounds (PAHs), particularly due to their carcinogenic potential (Chen et al., 2011; Krumal et al., 2013; Mazquiarán and Pinedo, 2007; Wang et al., 2009a; Wei et al., 2012; Xie et al., 2009).

In Portugal, only a few reports have dealt with the organic composition of aerosols in urban environments (Alves et al., 2001; Oliveira et al., 2007). Comprehensive information on the chemical composition of atmospheric aerosols is useful to improve climate models, to propose emission abatement strategies and to estimate public health impacts. Aiming at better understanding the organic

* Corresponding author.
E-mail address: celia.alves@ua.pt (C. Alves).

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composition and sources of urban aerosols, a monitoring campaign was carried out in two cities: Oporto and Coimbra.

2. Methodology

2.1. Sampling

Fine ($PM_{2.5}$) and coarse ($PM_{2.5-10}$) aerosol samples were daily collected onto pre-fired quartz fibre filters with high volume samplers operating at 1.13 m^3 min^{-1}. Sampling was carried out during one-month long campaign, simultaneously in Oporto and Coimbra, between January 27 and February 27, 2007. Urban background sites of the air quality network were, respectively, selected: Ermesinde (41°12.40′N; 8°33.17′W) and Geophysical Institute of Coimbra (10°13.33′N; 8°24.65′W). The urban area of Oporto, which extends beyond the administrative limits of the city, has a population of about 1.3 million in an area of 389 km^2, making it the second-largest urban area in Portugal, after Lisbon. Coimbra is the third biggest and most important city in the country with an estimated resident population of 150,000. It plays a chief role in the northern-central littoral and interior of Portugal.

2.2. Analytical determinations

After gravimetric determination of particle concentration, small punches of the filters were analysed by a thermal–optical transmission technique to obtain the organic carbon (OC) content (Pio et al., 2011). The $PM_{2.5}$ samples were extracted for 24 h by refluxing dichloromethane and the nitrogen-dried extract was separated into 5 different organic fractions by flash chromatography with silica gel and various eluents of increasing polarity. The detailed description of the methodology for the extraction of organic compounds could be found in Gogou et al. (1998) and Alves et al. (2001). The fractionated extracts were analysed by gas chromatography–mass spectrometry (GC–MS). Before injection, the compounds with hydroxylic and carboxylic groups were converted into the corresponding TMS ether or TMS ester derivatives, respectively, by addition of a mixture of N,O-bis(trimethylsilyl)triflouroacetamide and trimethylchlorosilane (BSTFA/TMCS; 99:1), followed by 3 h in an oven at 70 °C. Extracts were injected within 24 h after the derivatisation procedure. Two quadrupole GC–MS were used, a HP 6890 MSD 5973 and a GC Trace Ultra, DSQ II from Thermo Scientific. Both instruments were operated with TRB-5MS 60 m × 0.25 mm × 0.25 μm columns. Helium was used as carrier gas at a constant flow of 1.2 mL min^{-1}. The heating programme was as follows: 60 °C (1 min); 60–150 °C (10 °C min^{-1}); 150–290 °C (5 °C min^{-1}); and 290 °C (27 min). The acquisition mode was electronic impact at 70 eV and the scanned masses ranged from 50 to 850 m/z. Calibration for GC–MS analysis was based on a total of more than 200 standards in five different concentration levels with relative response factors determined individually for the majority of compounds. For those compounds with no authentic standards available, relative response factors were obtained as an average from the overall homologous series or from compounds of similar chemical structure and retention time. Standards and samples were both co-injected with two internal standards: tetracosane-D50 and 1-chlorohexadecane or 1-chlorododecane. In the case of PAHs, an internal standard mix was used: 1,4-dichlorobenzene-D4, naphthalene-D8, acenaphthene-D10, phenanthrene-D10, chrysene-D12 and perylene-D12. Compound identification was based on comparison of resulting spectra with mass spectra libraries (Wiley and NIST), co-injection with authentic standards and analysis of fragmentation patterns. Quantification was performed by single ion monitoring and total ion chromatogram analysis.

3. Results and discussion

3.1. Meteorological conditions

Meteorological data from Oporto and Coimbra were obtained for the study period from the nearest airport weather stations, both located less than 10 km from the cities: Pedras Rubras and Cernache, respectively. In Coimbra, the temperatures varied from a minimum value of 1.6 to a maximum of 17 °C. Values ranging from −1 to 18 °C were registered in Oporto (Fig. 1). During the sampling campaign, the averages of the daily mean temperatures were similar for both cities: 11.4 °C (Oporto) and 10.7 °C (Coimbra).

Lower temperatures and almost no rainfall were registered in the first 11 days of the campaign. Both sites were under the influence of continental air masses, most of which originating and staying over Spain and Portugal, or maritime transformed air masses, when backward trajectories indicated an Atlantic origin, with a final re-circulation through the Iberian Peninsula (Supplementary Fig. A1 and Fig. 2). After this period, the regime was generally characterised by low-pressure systems centred to the west of the British Isles. This feature led to the prevalence of the westerlies and frontal systems over the country, which transported maritime air masses and established rain-generating conditions, milder temperatures and higher wind speeds.

3.2. Particulate matter concentrations and organic constituents

The daily mean (±standard deviation) $PM_{2.5}$ concentrations during the sampling campaign were 29.9 ± 25.0 and 19.3 ± 13.3 μg m^{-3}, in Oporto and Coimbra, respectively. $PM_{2.5}$ represented 66.7 ± 17.8% of the PM_{10} mass in Oporto, whilst the percentage was 70.6 ± 16.1% in Coimbra. On some days, in Oporto, the daily mean PM_{10} concentrations exceeded the limit value of 50 μg m^{-3} set by the Air Quality Directive 2008/50/CE. Organic carbon accounted for 32.5 ± 14.6% and 33.9 ± 18.5% of the $PM_{2.5}$ concentrations measured in Oporto and Coimbra, respectively. In general, the lowest concentrations of both $PM_{2.5}$ and OC were associated with rainy events and air masses from the Atlantic, whilst stagnant conditions, regional atmospheric circulation and/or continental air masses coincided with the most polluted days. The chromatographically resolved organic compounds encompassed aliphatic and aromatic hydrocarbons, carbonyls, methyl esters of carboxylic acids, alcohols, anhydrosugars and several types of acids.

3.2.1. Aliphatic compounds

The aliphatic fraction of particulate matter comprised *n*-alkanes (Fig. 3), *n*-alkenes, hopanes, the unresolved complex mixture (UCM) of cyclic branched and unsaturated hydrocarbons and acyclic isoprenoids (pristane and phytane). Levels