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Road tunnel, roadside, and urban background measurements of aliphatic compounds in size-segregated particulate matter

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ABSTRACT

Particulate matter samples were collected in a road tunnel in Lisbon ($PM_{0.5}$, $PM_{0.5-1}$, $PM_{1-2.5}$, and $PM_{2.5-10}$) and at two urban locations representing roadside and background stations ($PM_{2.5}$ and $PM_{2.5-10}$). Samples were analysed for organic and elemental carbon (OC and EC), *n*-alkanes, *n*-alkenes, hopanes, some isoprenoid compounds, and steranes. Particulate matter concentrations in the tunnel were 17–31 times higher than at roadside in the vicinity, evidencing an aerosol origin almost exclusively in fresh vehicle emissions. $PM_{0.5}$ in the tunnel comprised more than 60% and 80% of the total OC and EC mass in PM_{10}, respectively. Concentrations of the different aliphatic groups of compounds in the tunnel were up to 89 times higher than at roadside and 143 times higher than at urban background. Based on the application of hopane-to-OC or hopanes-to-EC ratios obtained in the tunnel, it was found that vehicle emissions are the dominant contributor to carbonaceous particles in the city but do not represent the only source of these triterpenic compounds. Contrary to what has been observed in other studies, the Σhopane-to-EC ratios were higher in summer than in winter, suggesting that other factors (e.g. biomass burning, dust resuspension, and different fuels/engine technologies) prevail in relation to the photochemical decay of triterpenoid hydrocarbons from vehicle exhaust.

1. Introduction

Organic aerosols are composed of hundreds of individual compounds, some of which have adverse impacts on human health (Mauderly and Chow, 2008), with aliphatics being among the most ubiquitous. The homologous series of *n*-alkanes represent one of the dominant organic classes in ambient aerosols, and their distribution may indicate different pollution sources (Andreou and Rapsomanikis, 2009; Ladji et al., 2014; Tang et al., 2006). Their lipophilicity enables rapid penetration through membranes and into tissues. At low concentrations, alkanes can simply cause respiratory or skin irritation. At high concentrations, acute eczema of the skin and pulmonary edema may develop. Alkanes have also been found to penetrate rapidly into the fatty cells of the myelin sheath that surrounds nerve fibres, where they dissolve the cells and cause degeneration of the axons, interrupting the transference of impulses (Yu et al., 2011a). Alkenes are not found in crude petroleum but are present in some refined products, particularly in gasoline. Due to their unsaturation, they undergo addition reactions, yielding potentially more toxic metabolites. Hopanes are pentacyclic triterpanes commonly containing 27–35 carbon atoms in a naphthenic structure composed of four six-membered rings and one five-membered ring (Omar et al., 2001). Hopanes have been reported to be present in crude petroleum and source rocks (Enkhtsetseg et al., 2011; Hodairi and Philp, 2012; Mohialdeen et al., 2015; Mulabagal et al., 2013), particulate matter of vehicular exhaust (Fujita et al., 2007; Fushimi et al., 2011; Kleeman et al., 2008; Riddle et al., 2007a,b), engine lubricating oil (Kleeman et al., 2008), road dust (Rogge et al., 2012), smoke particles from biomass burning (Fang et al., 1999), and urban aerosols (Alves et al., 2014; Křůmal et al., 2013; Wang et al., 2006a,b, 2009). They have been used as specific biomarkers of coal and lubricating oil present in motor vehicle exhaust (Kleeman et al., 2008).

It is known that exhaust and non-exhaust vehicle emissions are large contributors to ambient aerosol concentrations, especially in urban areas (Pant and Harrison, 2013). Since the emitted particles and their organic constituents are serious environmental contaminants and detrimental to human health (Zhang et al., 2012), extensive studies have been performed on the chemical composition of particulate organics in urban areas (e.g. Andreou et al., 2008; Rushdi et al., in press; Wang et al., 2006a,b) and tunnels (El Haddad et al., 2009; Phuleria

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et al., 2006, 2007). Road tunnels are relatively confined traffic passages that are greatly exposed to the exhaust emission, providing a unique environmental setting to study the mixture of organic pollutants emitted from the fleet of gasoline- and diesel-fuelled vehicles (Song et al., 2005). So far, very few studies on urban (Almeida et al., 2006, 2007; Oliveira et al., 2010) and tunnel aerosols (Alves et al., 2015; Pio et al., 2013) in Portugal are available. However, all these studies were focused on inorganic constituents and only Alves et al. (2014) have recently reported the detailed organic composition, including aliphatics and hopanes, of aerosols collected in urban background sites of Oporto and Coimbra. Oliveira et al. (2011) presented concentrations of particle-bound polycyclic aromatic hydrocarbons in a roadway tunnel distributed by four aerodynamic size ranges.

The current study, conducted in three sampling sites differently impacted by road traffic in the Portuguese capital city (Lisbon), provides detailed information on lipophilic organic compounds in fine and coarse particles. The Lisbon metropolitan area has about 2.8 million residents and a population density of 6700 inhab. km^{-2}, involving a fleet of almost 3 million vehicles. It is estimated that more than 1 million citizens come into Lisbon area every day from the outskirts, leading to high traffic densities and intense traffic jams. The knowledge of carbonaceous aerosol constituents is often required to provide information for either source apportionment or for evaluating effects on public health. This work aims to contribute with new insights into the nature and sources of carbonaceous particulate matter, focusing especially the assignment of traffic emissions, in a metropolitan area with very limited information.

2. Methodology

2.1. Sampling

Atmospheric particulate matter was collected at 3 different locations: a road tunnel, a site strongly affected by nearby traffic (roadside), and an urban background station.

Sampling took place in Marquês de Pombal, the longest urban road tunnel in inland Portugal (1725 m). This infrastructure is open to traffic since 2007, connecting the city centre of Lisbon to a motorway leading to Cascais. The tunnel comprises three entrances and five exits, possesses a cross-ventilation system and accommodates two lanes in each direction. Due to the very steep slope (reaching 10%, with an average of 9%), some restrictions have been imposed, namely, a speed limit of 50 km h^{-1} and the prohibition of circulation of heavy-duty vehicles (HDV) or transportation of dangerous goods. The tunnel is prone to two daily periods of traffic congestion, when almost 90% of the vehicles circulate in the same direction: in the morning (8:00–10:00) descending towards the city centre and in the late afternoon (17:00–19:00) in the opposite direction. In these periods, the traffic density is about 2600 vehicles h^{-1} on weekdays and 1200 vehicles h^{-1} on weekends. At the time of the campaign, among passenger cars in Lisbon, 58% were gasoline powered, whereas diesel vehicles represented 42%. Only 10% of these had engine capacities higher than 2000 cm^{-3}. Commercial vehicles (diesel powered) accounted for 16% of the fleet (11% light duty and 5% HDV).

In the period between 9 and 21 October 2008, from Mondays to Fridays, sampling took place every 2 days, totalising 6 days of sampling. On weekends, a pooled schedule was followed by combining samplings from Saturday and Sunday on the same filters. In accordance with rush hours in both the descending and the ascending way, two daily sampling periods were selected, a first from 8:00 to 10:00 and the other from 17:00 to 19:00 (local time). Two high-volume samplers, one in each direction of the traffic flow, operating at 1.13 m^3 min^{-1}, were placed on the sidewalks, approximately in the middle of the tunnel. The sampler located in the descending way was connected during the morning periods, while the second one was connected during the afternoon. They were both equipped with a PM_{10} size selective inlet and a cascade impactor, from Tisch Environmental, Inc., with a three-stages impactor and a back-up filter (20.3 × 25.4 cm). Particles were collected in four size fractions: <0.49, 0.49–0.95, 0.95–2.5, and 2.5–10 μm, referred throughout the manuscript as approximately <0.5, 0.5–1, 1–2.5, and 2.5–10 μm. A total of 48 filters, corresponding to 12 sampling periods, was collected and analysed.

Additionally, daily sampling was carried out in parallel at two urban sites in the city centre, one main thoroughfares of Lisbon, directly impacted by fresh emissions from intense road traffic, considered a roadside (*Avenida da Liberdade*—Liberdade Avenue), and a residential area (Olivais), far enough to be considered by the Portuguese air quality monitoring network as an urban background. These two sites are equipped with continuous instruments for regulated air pollutants. Liberdade Avenue, a key point for those who enter or leave Lisbon by car, is today one of the most polluted roads in Europe. In 2008 and 2009, years in which the sampling campaigns took place, 80 and 92 exceedances of the daily limit (50 μg m^{-3}) have been registered, respectively. Two different intensive campaigns were performed, one of 35 consecutive days between June and July 2008 (summer campaign) and the other of 30 consecutive days between January and February 2009 (winter campaign). The high-volume samplers used in these two sites were those described for the tunnel. However, only two size fractions have been obtained: $PM_{2.5}$ and $PM_{2.5–10}$. Filters were changed simultaneously at 7:00 a.m., local time.

At the 3 sites, particulate matter collection was carried out onto pre-fired (500 °C for 6 h) quartz fibre filters from Whatman (QM-A). Before sampling, filters were pre-conditioned in a box with constant humidity (50%) for a minimum period of 24 h, and then weighted.

2.2. Chemical characterisation

After sampling, punches of the quartz filters were analysed for elemental and organic carbon (EC and OC) by means of a thermal–optical transmission method (Pio et al., 2011). Half of each filter was Soxhlet extracted with dichloromethane and the organic extract was concentrated in a rotary evaporator. The nitrogen-dried extract was separated into five different organic fractions (i) aliphatics, ii) aromatics, iii) carbonyls, iv) hydroxyl compounds, and v) sugars and acids) by flash chromatography with silica gel and various solvents of increasing polarity (Gogou et al., 1998; Alves et al., 2001). The fractionated aliphatic extracts were analysed in a Shimadzu QP5050A gas chromatography-mass spectrometer (GC-MS) with automatic injector, working under the following conditions: (a) 3 μL splitless injection with 2 min of sampling time and 290 °C of injection temperature; (b) column ZB-5MS, 30 m × 0.25 mm × 0.25 μm; (c) helium as carrier gas at a constant flow of 1 mL min^{-1}; (d) heating programme: 60 °C (1 min); 60–150 °C (10 °C min^{-1}); 150–290 °C (5 °C min^{-1}); 290 °C (27 min); (e) acquisition mode, electronic impact at 70 eV; (f) interface and ion source at 290 °C, (g) scanned masses from 33 to 800 m/z. Several *n*-alkanes and *n*-alkenes from Sigma–Aldrich and a 17β(H),21β(H)-hopane solution from Fluka were used to calibrate the GC-MS. Tetracosane-d50 (Aldrich) was used as internal standard. The relative response factors were determined individually for the majority of compounds. For those 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. Compound identification was based on the GC-MS spectra libraries (Wiley and NIST), co-injection with authentic standards and analysis of fragmentation patterns. Quantification was performed by both single ion monitoring (SIM) and total ion chromatogram (TIC) analysis, in two separate GC runs.

3. Results and discussion

3.1. Particulate matter concentrations and carbonaceous content

In accordance with the traffic patterns in the tunnel, on weekdays, the PM_{10} and $PM_{2.5}$ mass concentrations were in the 541–1340 and 450–1061 μg m^{-3} ranges, while on weekends, the levels varied from