Hopanes in particulate matter from two road tunnels of the São Paulo Metropolitan Area

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Keywords: Hopanes, Tunnel, $PM_{2.5}$
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Hopanes have been reported to be present in many sources, such as crude petroleum and source rocks (Mulabadal *et al.*, 2013), urban aerosols (Alves *et al.*, 2014) and engine lubricating oil (Kleeman *et al.*, 2008). Hopanes have an important role as specific biomarkers of coal and lubricating oil present in motor vehicle exhaust (Kleeman *et al.*, 2008).

Particulate matter samples were collected inside two road tunnel in the São Paulo metropolitan area: Jânio Quadros (JQ) tunnel and tunnel nº3 of the Beltway Rodoanel Mário Covas (RA). JQ tunnel is situated in the southwest region of the São Paulo city. The tunnel is 1900 m long and has two lanes with the traffic flowing in only one direction. The majority of the circulating traffic inside the JQ tunnel is composed of vehicles or motorcycles fuelled with gasohol (ethanol mixed with gasoline) and vehicles powered with ethanol (Brito *et al.*, 2013). The RA tunnel is a beltway with a radius of approximately 23 km, from the geographical centre of the city downtown area. The tunnel has four lanes, is about 1700 m long and the traffic also flows in only one direction (Brito *et al.*, 2013). Brito *et al.* (2013) reported the median values of traffic counts in the tunnels during the collection of the samples analysed in this study. On average, from 8 am to 20 pm, 1806 vehicles h^{-1} and 1152 vehicles h^{-1} light duty vehicles circulated in the JQ and RA tunnels, respectively. Diesel engines accounted for 4 vehicles h^{-1} in the JQ tunnel and 330 vehicles h^{-1} in the RA tunnel.

Using high-volume equipment, $PM_{2.5}$ sampling was carried out in both tunnels. The daily sampling programme, in 2011, took place between May 4th and 11th for JQ and July 11th and 13th for RA. The sampling was divided in two different periods of the day: i) 8 am to 14 pm and 14 pm to 20 pm; ii) 8 am to 14 pm and 14 pm to 8 am, for JQ and RA, respectively. Samples were solvent-extracted and analysed by gas chromatography and mass spectrometry.

Hopanes were detected and quantified by the key ion m/z 191. A series of hopanes, from C_{27} to C_{35} (excluding C_{28}), have been identified in aerosols from both tunnels, maximising at $C_{31}\alpha\beta S$ and $C_{30}D$, for JQ and RA, respectively.

Hopane average concentrations in both tunnels are in the range of values reported for Chinese megacites (3.1 ± 4.6 ng m^{-3}) (Wang *et al.*, 2006a) and New Zealand cities of Auckland (5.7 ± 4.3 ng m^{-3}) and Christchurch (2.0 ± 2.4 ng m^{-3}) (Wang *et al.*, 2006b). The highest concentration of hopanes was obtained in the RA tunnel, during the morning period (8 am - 14 pm). These results can be related to the intense traffic of heavy duty vehicles, responsible for the transporting of large payloads to and from the Santos harbour (Brito *et al.*, 2013).

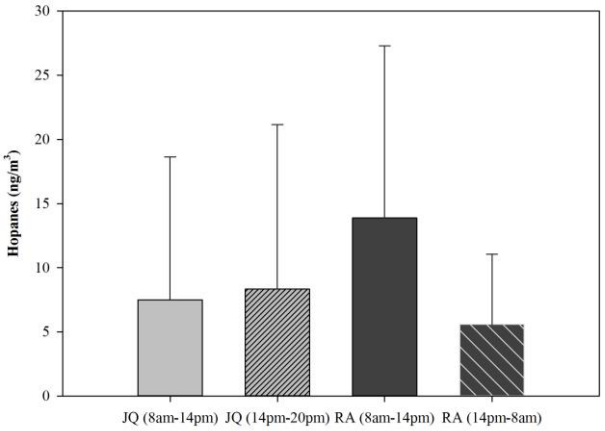

Figure 1 – Average concentrations of hopanes identified in the samples from JQ and RA in two different periods of the day.

This work was supported by the Research Foundation of the State of São Paulo (FAPESP, project 2008/58104-8) and by the National Council for Scientific and Technological Development (CNPq, project 402383/2009-5). Ana Vicente acknowledges the Postdoc grant SFRH/BPD/88988/2012 and the financing programme POPH/FSE. Perola thanks INCT-EEnergy and Environment.

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