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# Atmospheric distribution of organic compounds from urban areas near Olympic games sites in Rio de Janeiro, Brazil



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## ABSTRACT

The hydrocarbon composition of atmospheric particulate matter (PM) and Volatile Organic Compounds (VOC) from urban areas of Rio de Janeiro City were studied to assess different pollution levels. PM samples were acquired using a standard high-volume air sampler (Hi-Vol), extracts were prepared and fractionated into aliphatic and aromatic compounds, and VOC compounds were collected in adsorbent tubes. High-resolution gas chromatography and GC coupled to mass spectrometry (GC-MS) were used to analyze the organic compounds from the PM and VOCs. The results showed that all samples contained *n*-alkanes, but the distribution was different for each sample, which reflects both biogenic (vascular plant wax input) and fossil fuel contamination sources (vehicular exhaust). Fossil fuel biomarkers, such as hopanes, were observed in all samples, but steranes were not detected in Marina da Gloria. The presence of benzo[*a*]pyrene was observed, and all measured concentrations were below the upper permissible limit. Benzene was also observed, and the upper limit value (5  $\mu$ g/m<sup>3</sup>) was exceeded in Jacarepagua (JP) and Maracanã (MC) according to the Ambient Air Quality and Cleaner Air for Europe limit value (EC, 2008). Regarding the Ambient Air Quality Criteria (AAQCs), all analyzed samples had concentration values above the limit of 2.30  $\mu$ g/m<sup>3</sup>. A decrease in pollution level was observed in the following order: Maracanã (MC), Guadalupe (GP), Jacarepagua (JP), Barra da Tijuca (BT), Vila Militar (VM) and Marina da Gloria (MG).

# 1. Introduction

Brazil hosted the XXXI Summer Olympic Games and Paralympic Games in the city of Rio de Janeiro. The metropolitan region of Rio de Janeiro (RMRJ), Brazil, is the second largest region in the country, with approximately 12 million people; thus, it also has the largest population density and an approximate vehicle fleet of 2.5 million. Like other cities, most of the pollutants emitted to the atmosphere are related to industrial development, population growth and vehicular emissions, which may be the most important source of anthropogenic pollution in urban areas. In the RMRJ, light-duty vehicles are mainly fueled by gaso-line, ethanol and compressed natural gas. Flexible-fuel vehicles using mixtures of gasoline and ethanol of random compositions are also found in the RMRJ [1].In recent years, few studies have been performed to characterize the air quality of Rio de Janeiro [1–13].

The main emission sources of environmental pollution in the urban area are the activities in industries, construction, and vehicle traffic, which emit particles and/or gases that can significantly affect air quality [1,2,3,4,6,10,14].

\* Corresponding author. *E-mail address:* celesteyara@iq.ufrj.br (C.Y.S. Siqueira). The levels of some compounds and the temperature and relative humidity should be controlled at Olympic Games venues because of the emissions of different compounds from different sources and the inadequate temperature and relative humidity values. Considering the necessity to monitor the air quality during the Olympic Games, studies on the air quality were shown to be fundamental in the analysis of health risks for human exposure to toxic compounds, such as polycyclic aromatic hydrocarbons (PAH), in the air.

#### 2. Experimental

#### 2.1. Sampling site description

**Barra da Tijuca** (BT) is in the western portion of Rio de Janeiro City near the Atlantic Ocean (Fig. 1). Barra is well known for its beaches, many lakes and rivers, and lifestyle. Although it has only 4.7% of the city population and 13% of the total area of Rio de Janeiro, the demographic data indicate that the region is the fastest growing county in Rio: 98,851 in 1991, 174,353 in 2000, and 300,823 in 2010. Barra da Tijuca hosted competitions such as badminton, basketball, boxing, road cycling, track cycling, diving, golf, gymnastics, handball, judo, swimming, table tennis, taekwondo, tennis and water polo.



**Fig. 1.** Rio de Janeiro area with the locations of the air-sampling sites. MC = Maracanã, MG = Marina da Gloria, JP = Jacarepagua, GP = Guadalupe, VM = Vila Militar and BT = Barra da Tijuca.

**Maracanã** (MC) is a middle-class neighborhood in the Northern Zone of Rio de Janeiro City (Fig. 1). The Maracanã Stadium and Ginásio do Maracanãzinho are located in this neighborhood. The estimated neighborhood population was 25,256 according to the 2010 census. The UERJ, which is one of the main universities in Rio de Janeiro, is near these venues, and the area is crossed by several avenues. Maracanã hosted competitions, such as football and volleyball, in addition to the opening and closing ceremonies.

**Marina da Glória** (MG) is in the southern part of the city of Rio de Janeiro (Fig. 1) in the Guanabara Bay next to Santos Dumont Airport. It is also a tourist place with a bike lane, decks and restaurants. Marina da Glória hosted the sailing competitions at the 2016 Rio Olympic Games.

**Jacarepaguá** (JP)/Rio Centre is a middle- to high-class neighborhood in the Western Zone of the city (Fig. 1). It is currently the sixth largest neighborhood in the state of Rio de Janeiro with a population of 157,326 people according to the 2010 census. Jacarepaguá is bordered and crossed by many busy highways. JP hosted competitions such as badminton, boxing and table tennis.

**The Military Village** (MV) is a specifically planned neighborhood in the Western Zone of the city of Rio de Janeiro (Fig. 1). It is bordered by neighborhoods such as Deodoro, Realengo and Jardim Sulacap. According to the 2010 census, its estimated population is 13,184 people. The area is crossed by one of the busiest highways in the city of Rio de Janeiro, the Avenida Brasil. The village uses a large open green area for military training. In addition, many types of sports can be practiced in this neighborhood. The Olympic Centre, which hosted horseback riding, shooting, bicycle motocross (BMX) and grass hockey, is located there.

**Guadalupe** (GP) is in the northern part of the city of Rio de Janeiro near the Military Village (Fig. 1). It is cut across by the Avenida Brasil, a highway with the greatest traffic flow of the city. Guadalupe used to be a significant industrial park but is currently characterized by commercial enterprises, supermarkets and Guadalupe malls. Guadalupe hosted the competitions in horseback riding, mountain biking, BMX cycling, modern pentathlon, sport shooting, slalom canoeing, grass hockey, and rugby.

## 2.2. Sampling

Aerosol samples were collected from six urban sites (Maracanã-MC, Guadalupe-GP, Jacarepagua-JP, Barra da Tijuca-BT, Vila Militar-VM and Marina da Gloria-MG) by filtering the ambient air through a high-volume air sampler ("Hi-Vol") fitted with quartz fibers ( $20 \times 25$  cm surface, Gelman Sciences Inc., Ann Arbor, MI) at a flow rate of 1.5 m<sup>3</sup>/min. The filters were extracted using ultrasonic agitation for four 20-min periods with 50 mL of fresh methylene chloride: methanol (9:1-Omnisolv, Merck) each time. The filtrate was first concentrated to a reduced volume on a rotary evaporator and subsequently by a stream of nitrogen gas [15].

#### 2.3. Particulate matter

The extract was fractionated using an activated silica gel column (kieselgel 60, Merck; column size of  $15 \times 1$  cm). The chromatographic column was eluted with 10 mL of hexane to obtain the aliphatic hydrocarbon fraction. Further elution was with 10 mL of hexane/dichloromethane (8:2) to obtain the PAHs.

Then, the fractions were subjected to gas chromatographic (GC) and gas chromatograph–mass spectrometric (GC–MS) analyses. The GC and GC–MS operating conditions were as follows: Hewlett-Packard (Avondale, USA) 5890 gas chromatograph and HP5972 mass spectrometer; electron impact ionization of 70 eV; 30 m × 0.25 mm i.d. fused silica capillary column coated with DB-5;  $d_f = 0.25 \text{ mm}$  (J & W Scientific, Folsom, CA); temperature program 60–300 °C/min at 6 °C/min; isothermal held at 300 °C for 20 min; helium as the carrier gas for GC–MS; and hydrogen for GC. Whenever possible, molecular assignments were performed by comparing the spectra with authentic standards or using the Wiley 138 standard library of mass spectra; the mass spectrometric

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