Polycyclic Aromatic Hydrocarbons and their Molecular Diagnostic Ratios in Airborne Particles (PM10) Collected in Rio de Janeiro, Brazil

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Abstract Atmospheric polycyclic aromatic hydrocarbons (PAHs) were determined in particulate matter (PM10) collected in a suburban area with industrial and vehicular emissions in the Metropolitan Area of Rio de Janeiro City (Brazil). A total of 22 samples were collected between March and August 2005 by means of a high volume PM10 sampler. The particulate matter contained in the filters was extracted ultrasonically with dichloromethane. The extracts were later analyzed by gas chromatography coupled to a mass spectrometer (GC/MS). The individual concentrations of PAHs ranged between the detection limit and 0.386 ng m\(^{-3}\). The PAHs concentrations observed in this study were towards the lowest end of the range of values reported for other European locations and also lower than values obtained for South America. PAHs concentrations and molecular ratios showed that light cars seem to be the main contributors to PM10 emissions, but diesel vehicles are clearly minor emission sources and industrial contributions should not be disregarded until more data are obtained.

Keywords PM10 · polycyclic aromatic hydrocarbons · diagnostic ratios · vehicular emissions · cluster analysis

1 Introduction

Polycyclic aromatic hydrocarbons (PAHs) are products of incomplete combustion and pyrolysis of organic matter such as coal, oil, wood, diesel oil and petroleum (Silva, 2005).

In urban areas, where the major contributors to anthropogenic emissions are vehicular sources, PAHs are predominantly due to the combustion of fuels, mainly gasoline and diesel (Velasco, Siegmann, & Siegmann, 2004). To our knowledge, PAHs concentrations data for the Metropolitan Area of Rio de Janeiro (RJMA), Brazil, are rather sparse and, in general, are related to total particulate matter (Oliveira, Fernandes, Moreira, & Ferreira, 2002; Pereira Netto, Barreto, Arbilla, & Moreira, 2001; Pereira Netto, Barreto, Moreira, & Arbilla, 2002a; Pereira Netto, Barreto, Moreira, & Arbilla, 2005; Pereira Netto, Cunha, Muniz, & Rego, 2004; Pereira Netto, Muniz, & Rego, 2002b). Since the high level of particulate matter is
considered to be the main air quality problem in the RJMA (Fundação Estadual de Engenharia do Meio Ambiente (FEEMA), 2004), and considering the biological properties of some PAHs, it is important to understand the abundance and potential sources of PAHs in order to improve the mechanisms for atmospheric pollution control.

In the Metropolitan Area of Rio de Janeiro, Bonsucesso is considered to be one of the most polluted suburbs. Values reported by FEEMA, the regulatory state agency for air quality, show that for the period of 1998–2003, PM10 levels in Bonsucesso were between 80 and 110 μg m$^{-3}$ [Fundação Estadual de Engenharia do Meio Ambiente (FEEMA), 2003]. These values are higher than 50 μg m$^{-3}$, the primary and secondary standards for Brazil [Commissão Nacional de Meio Ambiente (CONAMA), 1990].

In this work, the concentrations of the 16 PM10-bound PAHs included in the EPA’s Priority Pollutant list (TP PAHs, 1995) – naphthalene (Na), acenaphthene (Ace), acenaphthylene (Acy), fluoranthene (Fl), phenanthrene (Phe), anthracene (An), fluorene (Flu), pyrene (Py), benzo[a]anthracene (B[a]An), chrysene (Chry), benzo[b]fluoranthene (B[b]F), benzo[k]fluoranthene (B[K]F), benzo[a]pyrene (B[a]Py), dibenz[ah]anthracene (DB[ah]An), benzo[ghi]perylene (B[ghi]Pe) and indene[1,2,3-cd]pyrene (IPy) – will be reported.

2 Experimental

2.1 The area of study

The air samples were collected at the campus of the Oswaldo Cruz Foundation (FIOCRUZ), located in Bonsucesso, a suburban region of Rio de Janeiro where the most severe problems, regarding air quality, have been observed [Fundação Estadual de Engenharia do Meio Ambiente (FEEMA), 2003]. Figure 1 shows the sampling location.

For this purpose, a sampler was installed at FIOCRUZ in an area close to a football ground (distant of any building and trees), at approximately 100 m from Brazil Avenue and about 200 m from the Faria Timbo River, which has been polluted by industrial rejects. Brazil Avenue is the most important way connecting the downtown area of Rio de Janeiro with the Baixada Fluminense region. This area has 13 districts with a total population of 2,423,141 inhabitants and intense industrial and commercial activities. The Avenue has a flux of about 250,000 cars day$^{-1}$ and, according to FEEMA, accounts for 25%–30% of the total vehicular emissions in the RJMA and 22.9% of PM10 emissions [Fundação Estadual de Engenharia do Meio Ambiente (FEEMA), 2004].

Recent data shows that about 77% of total pollutant emissions in the RJMA are due to vehicular exhausts [Fundação Estadual de Engenharia do Meio Ambiente (FEEMA), 2004]. At rush time 20%–30% of the vehicular fleet in Brazil Avenue consists of diesel-fueled buses and trucks (Campos, Pimentel, Corrêa, & Arbilla, 1999), which are the major contributors to atmospheric particulate matter concentrations, since levels of emissions by light duty vehicles are controlled by the national government through a severe legislation (PROCONVE/IBAMA, 2005).

The climate, in the region, is mesothermal. The temperature and relative humidity averages for the sampling period were 24 °C and 76%, respectively. Total rainfalls were 370 mm, with an extremely dry month (August 2005).

2.2 Sampling

Sampling of ambient PM10 was conducted during the period of March 2005–August 2005, every six days. A total of 22 samples were taken.

PM10 sampling was achieved by using a high volume sampler operated according to the specifications for PM10 designated by the NBR 13412 specifications [Associação Brasileira de Normas Técnicas (ABNT), 2005]. A flow rate of aspiration of 1,600 m$^3$ (25 °C, 760 mmHg) and 24 h sampling periods of time were used. Borosilicate glass micro fiber filters were used. After sampling, filters were wrapped in aluminum foil and stored at −20 °C for no more than 14 days prior to extraction.

2.3 Extraction procedure and analysis

Sixteen PAHs specified on US EPA Method 610 in a mixture and surrogate, consisting of naphthalene-D8, acenaphthene-D10, phenanthrene-D10, chrysene-D12, and perylene-D12 standards, were obtained from AccuStandard.

In order to check the best extraction procedure, test samples were spiked with PAH standard mixture and surrogates and submitted to ultrasonic extraction,