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Characterization of polycyclic aromatic hydrocarbon levels in the vicinity of a petrochemical complex located in a densely populated area of the Rio de Janeiro, Brazil

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ABSTRACT

The Petrochemical Complex of Duque de Caxias, Rio de Janeiro, is situated on a coastal strip between Guanabara Bay and a mountainous region covered with tropical forest. The complex comprises a refinery, a thermal power plant and several petrochemical industries. Higher rates of particulate–matter emissions are found in the region, mainly due to diesel emissions and the industrial activities of this area. In 2009 and 2010, samples were collected in three sites, and the 16 polycyclic aromatic hydrocarbons (PAHs) that are designated as priority pollutants by the US Environmental Protection Agency were determined. The sites are located in the vicinity of the Petrochemical Complex, one of them is on a roadside and the others are urban areas around the industrial complex. Multivariate analyses and diagnostic ratios show that the three studied areas were different, and the emissions seemed to be due to both gasoline and diesel vehicles. The carcinogenic PAHs represented the main fraction of the total PAHs determined in the particulate matter, and because the region is densely populated, these values may represent a health concern. The results indicate that regarding PAHs, the principal impact of the petrochemical complex is the high increase in the traffic of diesel vehicles and related tailpipe emissions.

Keywords: *Polycyclic aromatic hydrocarbons, particulate matter, petrochemical complex, vehicle emissions*

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous environmental contaminants and may represent a health hazard for humans. Sources related to energy production are the most important ones releasing PAHs. PAHs can be classified as either pyrogenic (mainly from the incomplete combustion of organic materials, such as coal, oil, vegetation or fossil fuels) or petrogenic inputs (Vasconcellos et al., 2003; Machado et al., 2009; Maioli et al., 2010). In areas under the influence of urban and industrial activities, the major contributors to anthropogenic emissions are vehicular sources, mainly due to the combustion of gasoline and diesel, and emissions related to industrial processes.

In Brazil, most of the studies on PAHs have been conducted in urban centers, and many reports have been published in the last few decades. Lopes and de Andrade (1996) reviewed the sources, reactivity and analytical methods used to determine PAH levels and the main results obtained up to that date. The PAH concentrations in total suspended particles (TSP), inhalable particles (PM_{10}) and, to a lesser extent, $PM_{2.5}$ were reported for the cities of Sao Paulo (De Martinis et al., 2002; Vasconcellos et al., 2003; Bourotte et al., 2005; Vasconcellos et al., 2010; Vasconcellos et al., 2011), Rio de Janeiro (Azevedo et al., 1999; Fernandes et al., 2002; Oliveira et al., 2002; Machado et al., 2009), Porto Alegre (Dallarosa et al., 2005; Dallarosa et al., 2008), Campo Grande (Re–Poppi and Santiago–Silva, 2005; Stroher et al., 2007), Niteroi (Pereira Netto et al., 2001; Pereira Netto et al., 2002a; Pereira Netto et al., 2002b; Pereira Netto et al., 2002c; Pereira Netto et al., 2006; Lima and Pereira Netto, 2009), Campos dos Goytacares (dos Santos et al., 2002; Maioli et al., 2009), and Salvador (Pereira et al., 2002; da Rocha et al., 2009).

The impact of industrial and biomass burning has also been studied for a few Brazilian regions. Results were obtained in different matrices for areas impacted by sugarcane–monoculture practices (Maioli et al., 2009; Maioli et al., 2010; Maioli et al., 2011). In 2007 (Vasconcellos et al., 2010), the levels of PAHs as well as other organic compounds and soluble ions were determined and compared in three sites with different characteristics in Sao Paulo State: an urban area with intense traffic of heavy and light vehicles, a clean area in the Mata Atlantica (Atlantic Forest) with primarily biogenic hydrocarbon emissions and a region characterized by intense sugar–cane burning during the dry season. The PAH abundances were higher in the urban area, but tracers of biomass burning were found in the site influenced by biomass burning and in the city, most likely due to long–distance air transport.

In 2008, measurements were taken of the 16 PAHs designated as priority pollutants by the US Environmental Protection Agency in the Cubatao industrial complex in southeast Brazil (Allen et al., 2008). Using the characteristic concentration ratios for emission sources, the authors concluded that tailpipe emissions from diesel vehicles were the main source of the compounds. Recently, PAHs were determined in fine ($PM_{2.5}$) and coarse particles ($PM_{2.5–10}$) in an urban and industrial area in the Metropolitan Area of Porto

Alegre (Teixeira et al., 2012). Based on the diagnostic ratios and principal component analysis, the authors concluded that the major contributors to the PAH levels were vehicular sources (diesel and gasoline), especially for the $PM_{2.5}$ fraction, as well as coal and wood burning.

To our knowledge, the PAH–concentration data for the metropolitan area of Rio de Janeiro (RJMA), Brazil, are in general related to urban areas where the main contribution to air pollution is due to vehicular emissions. In the present study, the PAH concentrations in a suburban area under the impact of an intensely trafficked road and industrial activities were characterized. The data required for the study were collected from different sampling sites to allow the comparison of areas with different emission characteristics.

2. Experimental Method

2.1. Sampling site

The sampling was conducted in the suburban area of Duque de Caxias near a petrochemical complex that is strongly affected by vehicular and industrial emissions. The area is located in the Air Basin III, which belongs to the Rio de Janeiro Metropolitan Area (RJMA). Air Basin III is located in the northern region, with an area of 700 km^2, and has the most severe air–pollution problems of the RJMA, mainly involving particulate matter levels. The highest rates of particulate matter emissions in Air Basin III are found in the downtown area of the city of Rio de Janeiro, mainly due to diesel emissions, and in the region of Campos Eliseos (Duque de Caxias), due to the industrial activities in this area. The most recent emission inventory for RJMA shows that approximately 58% of the particulate matter is emitted from stationary sources (INEA, 2009). According to Pires (2005), the refineries, energy plants and petrochemical industries account for 42%, 31% and 10%, respectively, of the total emissions from stationary sources. The particulate matter emission rates were estimated at 5–10 ton km^{-2} y^{-1} and 10–100 ton km^{-2} y^{-1} for the downtown area and Campos Eliseos, respectively.

The Petrochemical Complex comprises a refinery, a thermal power plant, and several petrochemical industries. The refinery, with an area of 13 km^2 and an installed capacity of 242 000 barrels d^{-1}, produces gasoline, lubricants, diesel fuels, aviation kerosene, liquefied petroleum gas, bunker and the petrochemical naphtha. This refinery was inaugurated in 1961 and since then has undergone modernization processes focusing on quality and environmental protection. The thermal power plant is natural gas–fired and generates 2 025 MW d^{-1}. The activities of the petrochemical plants comprise the development, manufacture and sale of plastics, rubber, resins, solvents, fluids and oils, specialty chemicals and intermediates.

Samples were collected at three monitoring stations located in Duque de Caxias that were implemented and are operated by ASSECAMPE (Campos Eliseos Companies Association): Federal Road Police (FRP), Cora Coralina State School (CC) and Adelina de Castro State School (AC). The FRP station (22°40' S, 43°17' W) is a roadside site, located by the Washington Luiz Highway, and is approximately 5 km from the Petrochemical Complex. The Washington Luiz Highway is the part of the BR–040 road that links the cities of Rio de Janeiro and Petropolis, and the vehicular traffic on this highway contributes approximately 3% of the particulate matter and volatile organic compounds (VOCs) emitted by mobile sources in the RJMA (Loureiro, 2005). The CC station (22°42' S, 43°18' W) is an urban area located in a neighborhood approximately 4 km from the Petrochemical Complex and 2.5 km from the Washington Luiz Highway. The AC station (22°42' S, 43°16' W) is a mixed urban–industrial area approximately 1.5 km from the Petrochemical Complex. It was not possible to perform a vehicular count, but clearly, the diesel (trucks and buses) and light–vehicle movement is very intense in the vicinity of this monitoring station. A map of the studied area is provided in the Supporting Material (SM) (Figure S1).

Climatological evaluations of the wind patterns near the city of Rio de Janeiro show a larger frequency of south–southeast to north–northwest winds in virtually every month of the year, with an average wind speed of 8 km h^{-1}. Data collected from the Aeronautical Meteorology Services Network website (REDEMET, 2010) during the sampling period showed a predominance of weak winds in the southeast and northwest directions. The frequencies of winds over the sampling period were plotted according to the wind directions to show the direction with the greatest frequency. The plots show that the AC and CC stations were heavily affected by the industrial emissions, mainly in the early hours of the day. Atmospheric trajectory models show that changes in wind directions occur due to the area's geographical location on a coastal plain at the base of a mountain range (Mata Atlantica), frequently, a sea breeze predominates from the south–southeast direction during the day, and air flows from the continent to the ocean at night (Godoy et al., 2009; INEA, 2009). Because the studied area is located near the coast, polluted air emitted by the vehicular and industrial facilities is carried into the continent during the daytime. The wind rose and some illustrative trajectories obtained with the NOAA HYSPLIT model are show in the SM (Figures S2 and S3).

2.2. Sampling

For the particulate matter, the selection of the points and the sampling procedures took into account the minimum sampler–siting criteria, calibration and filter–handling procedures recommended by the Environmental Protection Agency (U.S. EPA, 2007). Briefly, following the EPA recommendations, the height above ground should be 2 to 7 m, the distance from the samples to obstacles should be at least twice the height of the obstacle, and the air flow around the sampler inlet should be unrestricted. In this work, PM_{10} and $PM_{2.5}$ were collected over 24 h using high–volume samplers (Hi–vol–Energetica) that were equipped with an impactor–design size–selected inlet (Andersen, model G1200–2.5) and quartz–fiber filters (Millipore filters with an area of 20x25 cm and a thickness of 0.5 mm). The flow rate was 1.15 m^3 min^{-1}. The samplers were placed at a height of 3 m. Preceding the sampling, the filters were cleaned by thermal treatment (at 800 °C) for 24 h and weighed in an analytical balance after conditioning in a desiccator at constant temperature, (24±2) °C, and relative humidity, (55±3)%, conditions. The loaded filters were similarly conditioned and weighed for gravimetric determination of the particle mass concentration. Then, the filters were wrapped in aluminum foil and kept refrigerated (–20 °C), inside sealed plastic bags, until extraction and analysis (<4 days).

Samples were collected from June 2009 to August 2010 as indicated in Table 1. The samplings were done only on weekdays without rainfall. No attempt was done to collect samples during Saturdays and Sundays because it was not the objective of this study to assess comparisons between different periods such as weekdays and weekends. Because only two $PM_{2.5}$ samplers were available, simultaneous sampling in the three locations was not possible.

Additionally, PAHs in the gas phase were collected using XAD–2 cartridges (SKC 226–30–06, 400/200 mg) and an air pump with a flow rate of 1.0 L min^{-1}. These samples were collected at the FRP and CC monitoring stations during the same period as the $PM_{2.5}$ sample collection.

2.3. Extraction procedure and analysis

The levels of PM_{10} and $PM_{2.5}$ were determined by gravimetry using an electronic microbalance with a 1 μg sensitivity. Organic