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Passive air sampler-derived concentrations and carcinogenic potential of PAHs in oil/gas production city (Macaé, Brazil)

Concentrações e potencial carcinogênico de hidrocarbonetos policíclicos aromáticos derivados de amostradores passivos atmosféricos em uma cidade produtora de óleo/gás (Macaé, Brasil)

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ABSTRACT

Urban centers cause atmospheric pollution and suffer the most from their emissions. Polycyclic aromatic hydrocarbons (PAHs) are persistent toxic substances (PTS) that can be air transported at urban sites and impact human health, causing skin allergies, respiratory diseases, and cancer. Macaé is a southeastern Brazilian coastal city that had an intense process of urbanization and population growth due to the installation of oil companies in the 1970s. The study aimed to evaluate Macaé's air quality regarding atmospheric PAH occurrence, measured using polyurethane foam passive air samplers (PUF-PAS). PUF disks were deployed along environmental gradients during the 2018–2019 spring/summer in Macaé city and its surroundings. In total, 22 individual PAHs were analyzed by gas chromatography coupled with mass spectrometry. Total PAH air concentrations ranged from 0.3 to 3.3 ng.m^{-3}, pointing out three- to four-membered ring compounds as the most abundant (76%). Among them, phenanthrene, anthracene, and fluoranthene had the highest air concentrations, especially at sampling sites where fossil fuel combustion seemed more prominent. Compared to other cities worldwide, the lower PAH air levels reported in this study may be linked to the influence of marine air masses. As the most carcinogenic PAH compound is benzo[a]pyrene, the results are also given in benzo[a]pyrene-equivalent (BaPeq). BaPeq ranged from 0.02 to 0.10 ng.m^{-3}. This study indicated an environmental trend along urban-industry-background spatial transects. Even though a prominent marine air mass might contribute to efficient air pollution dispersion, in urban/industrial areas, human exposure to carcinogenic chemicals is higher, probably due to local PAH sources inside the urban perimeter of Macaé.

Keywords: polycyclic aromatic hydrocarbons; passive sampler; air pollution; benzo[a]pyrene-equivalent; urban coast areas.

RESUMO

Os centros urbanos causam poluição atmosférica e são os que mais sofrem com suas emissões. Os hidrocarbonetos policíclicos aromáticos (HPA) são substâncias tóxicas persistentes que podem ser transportadas por longas distâncias e impactar a saúde humana, causando alergias, doenças respiratórias e câncer. Macaé é uma cidade litorânea do sudeste brasileiro que teve um intenso processo de urbanização e crescimento populacional, associado à instalação de companhias petrolíferas. O estudo teve como objetivo avaliar a qualidade do ar de Macaé quanto à ocorrência de HPA, medidos com amostradores passivos de espumas de poliuretano (EPU). Os discos EPU foram implantados ao longo de gradientes ambientais durante o período primavera/verão 2018–2019 na cidade de Macaé e arredores. Vinte e dois HPA individuais foram analisados por cromatografia gasosa acoplada a espectrômetro de massas. A concentração total de HPA atmosféricos variou de 0,3 a 3,3 ng.m^{-3}, sendo os compostos de três e quatro anéis aromáticos os mais abundantes (76%). Fenantreno, antraceno e fluoranteno apresentaram as maiores concentrações, especialmente em locais onde a queima de combustível fóssil parece ser mais proeminente. Comparando com outros centros urbanos, as baixas concentrações de HPA atmosféricos encontradas no presente estudo podem ser explicadas por retrotrajetórias marinhas de massa de ar. Os resultados também são expressos em benzo[a] pireno-equivalente (B[a]Peq), HPA altamente carcinogênico. O B[a]Peq variou de 0,02 a 0,10 ng.m^{-3}. Este estudo indicou uma tendência decrescente no transecto urbano-industrial-controle (ou de fundo). Apesar de uma massa de ar marinha possivelmente contribuir para a eficiente dispersão de poluentes atmosféricos, áreas urbanas/industriais aumentam a exposição humana a compostos carcinogênicos, provavelmente por fontes de HPA, dentro dos perímetros urbanos de Macaé.

Palavras-chave: hidrocarbonetos policíclicos aromáticos; poluição atmosférica; amostradores passivos; Benzo[a]Pireno-equivalente; áreas costeiras.

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Introduction

Since the Industrial Revolution, atmospheric pollution has intensified. During the early 20th century, urban centers became responsible for most of the atmospheric pollution emissions due to their high density of humans and vehicles (WHO, 2016; Shafie and Mahmud, 2020), suffering the most from atmospheric pollution (Shafie and Mahmud, 2020). Many studies suggest an association between human diseases and atmospheric pollution exposure, mainly in highly industrialized countries and/or highly populated countries (Clark et al., 2019; Jaganathan et al., 2019; Ilango et al., 2020; Yang et al., 2021). Indeed, 90% of the world's population is exposed to atmospheric conditions that do not meet the World Health Organization Air Quality Guidelines (WHO, 2016). Moreover, approximately 30% of liver cancer deaths and more than 50% of children's deaths from pneumonia are associated with atmospheric pollution (WHO, 2015; HEI, 2020). In the past decades, similar studies in Brazil have also pointed out the role of atmospheric pollution in human diseases, mainly respiratory, such as allergies, asthma, and reduced pulmonary functions (Santana et al., 2020; Silva et al., 2020). Moreover, recently, the atmospheric occurrence of some semivolatile organic contaminants was reported to increase cancer risk in Brazilian urban areas (Guida et al., 2021a). In South America, there are few studies about atmospheric pollution compared to other global regions. Most of them usually analyze standard parameters such as particulate matter, ozone, NOx, and CO, highlighting the influences of intense traffic, wood combustion, and urbanization processes as the major sources of air pollution (UNEP, 2002; Gomez Pelaez et al., 2020).

Polycyclic aromatic hydrocarbons (PAHs) are persistent toxic substances (PTS) (Li et al., 2022), prone to long-range atmospheric transport (Meire et al., 2007; Speciale et al., 2018; Balmer et al., 2019), and able to cause damages on human health, such as respiratory diseases, skin allergies, and cancer, even at low air concentrations (Rodriguez-Aguilar et al., 2019; Låg et al., 2020; Aminiyan et al., 2021; Yang et al., 2021; Mallah et al., 2022). Therefore, PAHs are a priority class of atmospheric compounds in environmental and human health studies worldwide (Hussain et al., 2018; Yang et al., 2021). Fossil fuel combustion is usually highlighted as a major PAH source in urban and industrial areas around the world (Carratalá et al., 2017; Pokhrel et al., 2018; Aminiyan et al., 2021) and a cancer risk factor due to the inhalation of these compounds (Pokhrel et al., 2018; Fadel et al., 2022).

The main distribution routes of PAH atmospheric transport are usually associated with fine (diameter ≤ 2.5 μm) particulate matter (EPA, 2013), increasing the long-range dispersion of these compounds from their primary sources (Meire et al., 2007; Pokhrel et al., 2018). PAHs are composed of benzene rings fused in linear, clustered, or angular arrangements. There are thousands of PAH compounds in the environment, but only a selected priority group is monitored worldwide, especially to assess human health risks (EPA, 1993; WHO, 2015; 2016). PAHs are formed and released by incomplete combustion of organic materials such as fossil fuel (diesel and gas engines), coal and biomass, cigarette smoke, and industrial activities (Stogiannidis and Laane, 2015). Urbanization is usually associated with industrial development and changing society's habits, and all these factors may influence PAH concentrations in the environment.

The use of passive air sampling (PAS) methods is justified by their cost-effectiveness compared to active air samplers, as well as their ease of handling and the fact that they do not require a power supply (Harner et al., 2013; Melymuk et al., 2021; Prats et al., 2022). Polyurethane foam (PUF) disks can adsorb a wide range of semivolatile organic compounds (SVOCs) present in the atmosphere (Nguyen et al., 2020; Prats *et al.*, 2022; Strandberg et al., 2022). PUF-PAS method has been widely used as an efficient tool to determine PTS air pollution across temporal and spatial gradients, including local (Pozo et al., 2015; Meire et al., 2016; Carratalá et al., 2017), regional (Cheng et al., 2013; Meire et al., 2019), continental (Klanova et al., 2009; Yao et al., 2016), and global scales (Pozo et al., 2009). Many studies used PUF-PAS to monitor the concentration of PAHs in the atmosphere, indicating the effectiveness of the method for this purpose (Melymuk et al., 2021; Prats et al., 2022; Strandberg et al., 2022). Moreover, PUF-PAS have also been adopted to assess human health risk due to inhalation of several SVOCs in the air, including PAHs (Wang et al., 2017; Guida et al., 2021a; 2021b; Arias et al., 2022).

Macaé is a Brazilian city, located in Rio de Janeiro State, which has undergone an intense and recent process of urbanization and population growth, initiated in the 1970s. The changes in Macaé's landscape are highly associated with the installation/operation of several oil companies during the same decade. During the first years of oil industry activities, the population increased by 10,000 inhabitants (Ramires, 1991). According to the last census, 206,728 inhabitants are living in Macaé City, with 98% of them in urban areas (IBGE, 2010). Therefore, Macaé is a relevant study case regarding the sources and exposure to PAH air contamination and its effect on human health in an urban/industrial site in average-sized Brazilian coastal cities. In this context, the current study aims to investigate atmospheric PAH concentrations using PUF-PAS as a cost-effective tool to evaluate air quality in a coastal area, identify emission sources of PAHs along environmental gradients, and determine the carcinogenic potential of PAHs at sampling sites.

Materials and Methods

Study area

Macaé is a seaside city in the north of Rio de Janeiro State, Brazil (lat.: 22°22′33″S, lon.: 41°46′30″O) (Figure 1A). It has 1,215.291 km^2 and 23 km of coastline (IBGE, 2019). It is part of the Macaé River Basin, located between the *Serra do Mar* mountains and the Atlantic Ocean (Freitas et al., 2015). The city's water supply derives from the Macaé River Basin, which drains an area of 1,765 km^2 and flows for around 136 km until it reaches the Atlantic Ocean (Barroso and Molisani, 2019). Since the 1940s, this river basin has been suffering from environmental degradation because of deforestation, wood ex-

traction, and agricultural activities, especially coffee and sugar cane production (Ramires, 1991; Barros Júnior et al., 2018). These impacts increased with the intensification of oil companies' activities since the early 1970s and were worsened by unplanned urban growth (Silva, 2020; Silva and Leal, 2020).

Macaé's economy relies on oil activities, being part of the Campos Basin (Petrobras, 2019). The latter is the largest sedimentary basin and oil reserve in Brazil, operating with 44 offshore prospect fields and 591 productive wells. Additionally, 19.7 million cubic meters of natural gas from Campos Basin are processed in plants in Macaé, which categorize this city as the country's largest national gas processor. According to the Brazilian Petroleum National Agency (ANP or *Agência Nacional do Petróleo* in Portuguese), during the past 5 years, Macaé has accumulated around 600 million US dollars in royalties, with the lowest income being in 2016 at US$ 73 million and the highest in 2018 at US$ 149 million (ANP, 2019).

Passive air sampling deployment

The use of the PUF-PAS technique is a simple and cheap method to monitor atmospheric organic contaminants at several sampling sites simultaneously (Prats et al., 2022; Anh et al., 2020). Passive samplers are stainless-steel chambers consisting of two domes with diameters of 30 and 20 cm, allowing air to flow through a 2.5-cm gap between them (Figures 1B-1D). They were designed to protect PUF disks from direct meteorological conditions, such as precipitation, windy conditions, and UV radiation (Shoeib and Harner, 2002). For each passive sampler chamber, a PUF disk (dimensions: 14 cm diameter; 1.35 cm thick; surface area: of 365 cm^2; volume: 207 cm^3; density: 0.0213 $g.cm^{-3}$; TISCH Environmental, Cleves, OH, USA) was fixed inside. Previously, PUF disks were preextracted with acetone and petroleum ether (Tedia High Purity Solvents, Fairfield, OH, USA) in an automatic Soxhlet extractor (Extraction System B-811; Büchi, Switzerland) and stored in glass recipients sealed with Teflon.

The sampling campaign was conducted in Macaé city and its surroundings during the spring/summer period, from October 2018 to January 2019. PUF-PAS samplers were deployed at six sampling sites (P01–P06) along a spatial transect, including urban, industrial, and background sites. Urban areas (P01, P03, and P04), urban/industrial areas (P02), and natural preservation areas (P05 and P06) represented the main scenarios of the city. PUF disks were deployed for a period of 90 days and then stored at -20°C until analysis. Additionally, three field blanks were sampled to monitor possible transport and storage contamination. PAS procedure details for PUF samplers have been extensively reported elsewhere (Pozo et al., 2012; Harner et al., 2013; Guida et al., 2018).

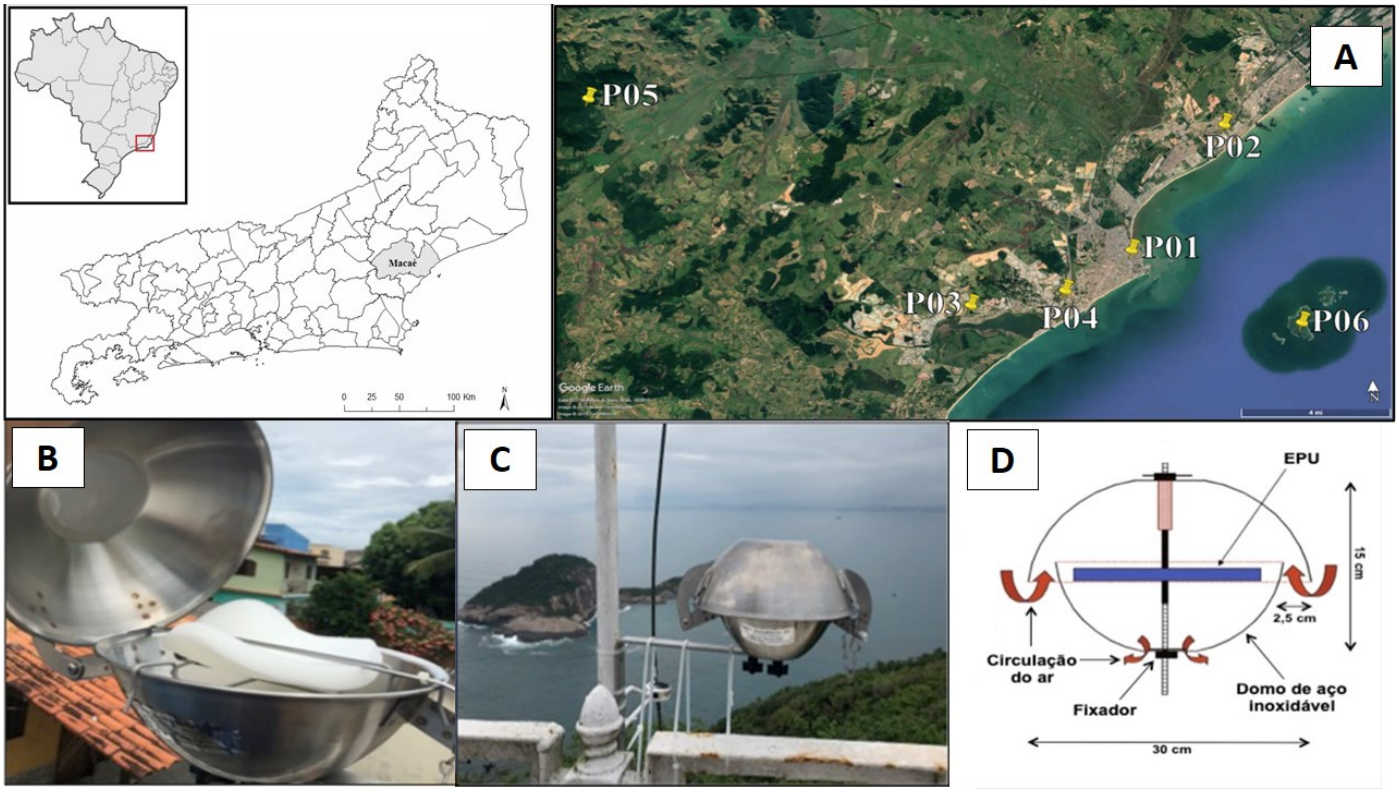

Figure 1 – (A) Details of PUF-PAS deployment at sampling sites in Macaé city and surroundings (Rio de Janeiro, Brazil). (B and C) Sampling sites of PUF-PAS (photo: the author). (D) Schematic illustration of PUF-PAS design.
P01: Downtown; P02: NUPEM/UFRJ; P03: IFF; P04: Alto da Glória; P05: Natural Municipal Atalaia Park; P06: Santana Island.

Analytical procedure

PAHs were identified by a comparison between the measured mass spectra and retention times of reference PAH standards. Target PAHs were naphthalene (Naph); 1-methylnaphthalene (1-MN); 2-methylnaphthalene (2-MN); acenaphthylene (Acy); acenaphthene (Ace); fluorene (F); dibenzothiophene (DBT); phenanthrene (Phe); anthracene (Ant); fluoranthene (Fl); pyrene (Pyr); benzo[a]anthracene (B[a]Ant); chrysene (Chr); benzo[b]fluoranthene (B[b]Fl); benzo[k]fluoranthene (B[k]Fl); benzo[e]pyrene (B[e]P); benzo[a]pyrene (B[a]P); perylene (Per); indeno[1,2,3-cd]pyrene (I[123cd]P); dibenzo[a,h]anthracene (Db[ah]Ant); and benzo[g,h,i]perylene (B[ghi]Per).

PAH quantification consisted of a linear calibration curve, regarding area versus concentration, for six different concentrations (from 10 to 250 ng mL^{-1}), using an analytic standard solution: PAH surrogates + Terphenyl D14 + Isooctane.

To monitor possible contaminations during transport and storage, three field blanks were collected at random sites during the sampling campaign. Moreover, an analytical blank was also included for each sample batch to assure analytical quality. All glassware was previously cleaned with water-soap-water, acetone, dichloromethane, and n-hexane to avoid analytical interferences. Prior to exposure, PUF disks were washed in running water, extracted with acetone, dichloromethane, and n-hexane, and finally stored in pre-cleaned glass recipients sealed with Teflon® tape.

Samples were spiked with labeled PAHs as surrogates (D8-Naphthalene, D10-Acenaphthene, D10-Phenanthrene, D12-Chrysene, and D12-Benz[a]pyrene) and then extracted by the automatic Soxhlet system (Extraction System B-811) with 150 mL of petroleum ether and 1 mL of isooctane (Tedia High Purity Solvents) in a warm extraction program, 40 min of extraction followed by 20 min of rinsing for each solvent. After extraction steps, samples were concentrated under a gentle nitrogen flow until ~5 mL. The extract was cleaned-up in a glass column with sodium sulphate and activated neutral silica. The cleaned extracts were eluted with n-hexane and blown down to 0.5 mL under a gentle N_2 flux. Terphenyl D14 (Sigma-Aldrich Corp., Bellefonte, PN, USA), at 1 µg/mL, was added as an internal standard before analysis.

The analysis was conducted on a gas chromatograph (Agilent 7890, Palo Alto, CA, USA) equipped with a capillary silica column (HP-5MS, 60 m, 250 µm, 0.25 µm) and a mass spectrometry detector (Agilent 5975), operated in electronic impact (EI) ionization and selected ionization mode (SIM).

Atmospheric PAH calculation

To calculate PAH air concentration and convert data to the most usual unit (ng m^{-3}), we assumed a PUF sampling rate (R) of 5 m^3/day, defined by Harner et al. (2013), which represents air mass sampled per day. This rate was defined by the first study to calibrate and use PUF samplers for polycyclic aromatic compounds, including PAHs, alkylated PAHs, and dibenzothiophenes, and compare the results with those from high-volume air samplers.

The calculation for each sample site was based on exposure time (in days) and the concentration of individual PAHs, using the Equation 1:

$$[\ ]\ PAH_{air} = PAH_{ind} / (R \times Days) \quad (1)$$

Where:

$[\ ]\ PAH_{air}$: the atmospheric PAH concentration (ng.m^{-3});

PAH_{ind}: the individual PAH concentration in each sample (ng/PUF);

R: the sampling rate;

Days: the exposure time.

Air mass back trajectory analysis

To investigate the influence of the atmospheric large-scale circulation on PAH air concentrations over the Macaé coastline, 5 days (120 h) back trajectories arriving at P06 (Santana Island) were calculated every 48 h at 01:00 UTC using the HYSPLIT model (Draxler and Rolph, 2012). Air mass back trajectories were calculated weekly at the P06 sampling site during all PUF sampler exposure periods.

Benzo[a]Pyrene-equivalent

PAH properties may lead to acute or chronic effects, mutations, cancer development, and pulmonary function reduction (Talaska et al., 2014; Gao et al., 2018; Mohammadi et al., 2022). In general, PAHs undergo some transformation in human organs and tissues, producing carcinogenic intermediaries by enzymatic reactions (Talaska et al., 2014; Lee et al., 2017; Stading et al., 2021). As the most carcinogenic PAH compound is benz[a]pyrene, the results are also given in benzo[a]pyrene-equivalent (BaPeq) for each sample, which is the sum of the concentrations of the seven carcinogenic compounds multiplied by their toxic equivalent factor (TEF) (IARC, 1987). The TEF points out the carcinogenic potential of each PAH when compared to benzo[a] pyrene (Azeredo et al., 2014).

Quality control

Field blanks showed relatively high concentrations of selected PAHs such as naphthalene (0.23–0.34 ng m^{-3}), 1-methylnaphthalene (0.12–0.18 ng m^{-3}), 2-methylnaphthalene (0.07–0.10 ng m^{-3}), and phenanthrene (0.03–0.05 ng m^{-3}). On the contrary, most other individual PAHs showed lower concentrations in the field blanks ranging from 0.0 to 0.34 ng m^{-3}. Analytical blanks followed the same trend as field blanks, with higher concentrations of naphthalene (0.05–0.12 ng m^{-3}), 1-methylnaphthalene (0.05–0.11 ng m^{-3}), 2-methylnaphthalene (0.03–0.07 ng m^{-3}), and phenanthrene (0.01–0.02 ng m^{-3}).

To assure data quality, recovery was calculated using tests with a surrogate concentration of a labeled standard mixture. Individual PAH concentrations were calculated based on the recoveries of those labeled surrogates, considering the number of aromatic rings. The average recovery was 70%, where 65, 66, 80, and 74% were calculated

for two-, three-, four-, and five-membered ring PAHs, respectively. The limits of quantification (LOQ) were determined as the average concentration of blank fields corrected by the analytical blanks plus three times the standard deviation (Pozo et al., 2009). The LOQ values ranged from 0.07 (dibenzo[a,h]anthracene) to 146 ng m^{-3} (naphthalene). Concentration below the LOQ was not considered for further discussion.

Results and Discussion

PAH air concentrations

In total, 21 PAHs were monitored in this study. Four of them (naphthalene, acenaphthylene, acenaphthene, and benz[a]pyrene) were below the LOQ in all samples. The total PAH air concentrations ranged from 0.3 to 3.3 ng m^{-3}, with an average of 1.7 ng m^{-3}. Basically, the PAH air concentrations observed in this study were much lower than in several urban and suburban areas around the world (Table 1). Our results were only comparable to rural and remote sites (Melymuk et al., 2012; Pozo et al., 2012; Harner et al., 2013; Peverly et al., 2015; Schuster et al., 2015; Meire et al., 2019), even though the Macaé city is considered highly urbanized. Meteorological factors are also important pieces in understanding PAH profiles, showing a seasonal trend. Usually, during winter, PAHs atmospheric concentrations are higher because of intense heating systems, which is not Macaé's situation, considering its tropical location, dry periods that lead to forest burning and less photolytic degradation (shorter daylight hours), as well as humid deposition due to drought events (Schuster et al., 2015; Pokhrel et al., 2018; Miura et al., 2019).

Regarding cities with a similar population (200,000–215,000 inhabitants), such as Pokhara, Nepal (average of 14.1 ng m^{-3}), Concepción, Chile (average of 100 ng m^{-3}), and Burgas, Bulgaria (average of 13.8 ng m^{-3}), Macaé city and surroundings (206,728 inhabitants) reveal much lower concentrations of PAH in the air (Pokhrel et al., 2018; Naydenova et al., 2022; Pozo et al., 2022). Concepción (Chile), a South American coastal city like Macaé, reported higher PAH concentrations (average of 100 ng m^{-3}, maximum of 230 ng m^{-3}) in the air than reported here. This city has ~221,000 inhabitants and intense industrial activities such as steel manufacturing plants, which probably raised PAH emissions locally (Pozo et al., 2022).

Three- to four-membered ring PAHs (low-molecular weight — LMW) were the most frequently (76%) detected in Macaé city (Figure 2). Among them, phenanthrene (0.5 ng.m^{-3}), anthracene (0.5 ng.m^{-3}), and fluoranthene (0.7 ng.m^{-3}) showed the highest air concentrations (Figure 3). This PAH profile is similar compared to other studies around the world, such as those in Concepción, Chile, Mexico City, Mexico, Tuscany Region, Italy, Manila, Philippines, Dalian, China, and Seoul, Korea, where three- and four-membered ring PAHs were the most frequently detected groups, generally above 90% contribution to the total PAH contamination (Santiago and Cayetano, 2007; Bohlin et al., 2008; Estellano et al., 2012; Pozo et al., 2012; Wang et al., 2019; Thang et al., 2020). LMW compounds are more abundant in passive sampling methods because they partition in an easier way than high-molecular weight (HMW) PAHs, which have lower volatility (Pozo et al., 2012).

The highest total PAH air concentration (3.3 ng m^{-3}) was detected in Santana Island (P06), a well-preserved island that is part of an

Table 1 – Atmospheric PAH concentrations at worldwide cities and locations.

World cities	TPAH[a]	Method[b]	Popul.[c]	References
Manila, Philippines	41-170	PUF	1,780,000	Santiago and Cayetano (2007)[1]
Mexico City, Mexico	6.1-180	PUF	8,918,653	Bohlin et al. (2008)[1]
Concepción, Chile	26-230	PUF	215,413	Pozo et al. (2012)[1]
Toronto, Canada	0.3-51	PUF/Hi-vol	2,731,571	Melymuk et al. (2012)[1]
Alberta, Canada	0.02-182	PUF	4,334,025	Harner et al. (2013)[2]
Alberta, Canada	0.03-210	PUF	4,334,025	Schuster et al. (2015)[2]
Chicago, USA	8.7-52	PUF	2,695,598	Peverly et al. (2015)[2]
Santiago de Cali, Colombia	25-66	PUF	2,754,078	Álvarez et al. (2016)[1]
Kathmandu, Nepal	6.4-29	PUF	1,442,271	Pokhrel et al. (2018)[1]
Pokhara, Nepal	6.8-29	PUF	200,000	Pokhrel et al. (2018)[1]
Hetauda, Nepal	4.1-38	PUF	84,775	Pokhrel et al. (2018)[1]
National Parks, Brazil	0.70-90	LDPE	-	Meire et al. (2019)[3]
Burgas, Bulgaria	14*	Hi-Vol	206,728	Naydenova et al. (2022)
Concepción Bay, Chile	1-2	Hi-vol	-	Pozo et al. (2022)[1]
Macaé, RJ, Brasil	**0.3-3.3**	**PUF**	**251,631**	**Present study**[3]

[a]Total PAH; [b]PAH detected method; [c]Population number; [1](13-15) PAH; [2](16-18) PAH; [3](19-21) PAH; *average value; PUF: polyurethane foam disks; Hi-vol: active high-volume air sampling; LDPE: low-density polyethylene sampling.

environmentally preserved area (*APA — Área de Preservação Ambiental*), which suggests different emission sources (Stogiannidis and Laane, 2015). Ship navigation routes, their proximity to the continent's coastline, and the lighthouse energy generator may influence the PAH profile at this site (Drotikova et al., 2021). The high concentration of 1-methylnaphthalene (0.4 ng m^{-3}) reported at Santana Island may indicate diesel combustion sources (Stogiannidis and Laane, 2015), reinforcing the probable role of ship traffic frequency in Macaé coastal waters and fuel combustion in the lighthouse generator.

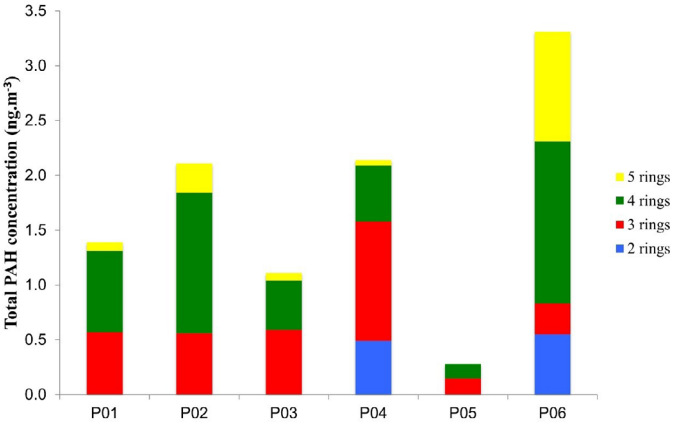

Figure 2 – Atmospheric PAH profile along spatial transects in Macaé city pointing out three- to four-membered rings compounds as the most abundant at sampling sites.
P01: Downtown area; P02: NUPEM/UFRJ; P03: IFF; P04: Alto da Glória; P05: Natural Municipal Atalaia Park; P06: Santana Island.

As an Atlantic Forest Fragment, the P05 site is protected by an exuberant vegetation canopy (235 hectares) and is relatively far away from the urban perimeter, which probably explains why it shows the lowest air concentration of total PAH (0.3 ng m^{-3}). Phenanthrene (0.15 ng.m^{-3}) and pyrene (0.13 ng.m^{-3}) were the PAHs most frequently reported at this site. Naphthalene (0.08 ng.m^{-3}) was also detected at site P05 but was below LOQ limits. The presence of these light PAHs (two and three rings) at this site could be linked to biogenic origins, associated with termite nests and plant secondary metabolites such as terpenes (Wilcke et al., 2000; Krauss et al., 2005). Wood and soil digestion by termites may produce PAHs and release these compounds into the environment (Krauss et al., 2005). The pyrene concentration in this site is comparable with the concentration of the same compound in Costa Rica, 0.003–0.64 ng m^{-3} (Daly et al., 2007), a similar environment in a tropical region. Moreover, several studies have pointed out the biogenic origins of PAHs in abiotic environmental matrices worldwide, especially in Natural Conservation Units (Wilcke et al., 2000; Wilcke et al., 2003; Meire et al., 2019).

Total PAH air concentrations between the highest and lowest values are associated with vehicle emissions (fossil combustion) in highly populated urban areas (P01, P02, P03, and P04), close to important roads, showing high levels of phenanthrene, anthracene, and fluoranthene. The highest concentration among these sites (2.1 ng m^{-3}) is not only in an urban area but close to an industrial area as well (P02). Its PAH profile indicates an emission mixture by the presence of phenanthrene (a petrogenic source), pyrene and fluoranthene (biomass burning sources) and benz[e]pyrene (a pyrolytic source) (Stogiannidis and Laane, 2015; Alani et al., 2021).

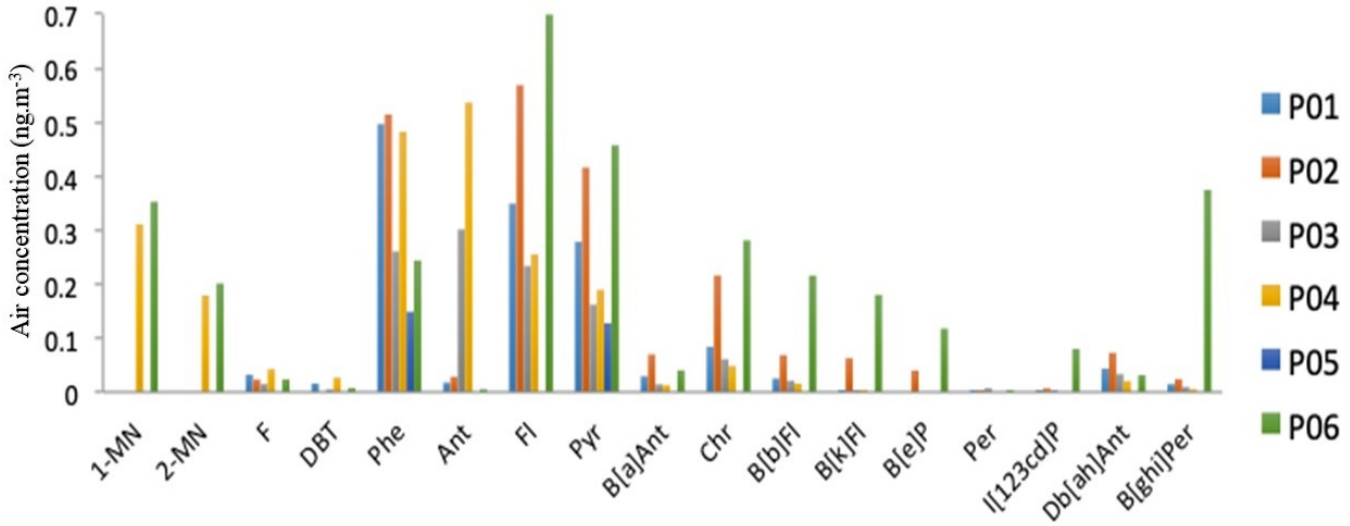

Figure 3 – PAH individual air concentration in each sample site. Compounds: 1-methylnaphthalene — 1-MN; 2-methylnaphthalene — 2-MN; fluorene — F; dibenzothiophene — DBT; phenanthrene — Phe; anthracene — Ant; fluoranthene — Fl; pyrene — Pyr, benz[a]anthracene — B[a]Ant; chrysene — Chr; benz[b]fluoranthere — B[b]Fl; benz[k]fluoranthere — B[k]Fl; benz[e]pyrene — B[e]P; perylene — Per; indeno[1,2,3-cd]pyrene — I[123cd]P; dibenzo[a,h] anthracene — Db[ah]Ant; benz[g,h,i]perylene — B[ghi]Per.
P01: Downtown area; P02: NUPEM/UFRJ; P03: IFF; P04: Alto da Glória; P05: Natural Municipal Atalaia Park; P06: Santana Island.

PAH ratio profile

Different emission sources are usually associated with variations in the composition and concentration of PAHs. To identify them, the most common method is the molecular diagnostic ratio (MDR) analysis, which is calculated using ratios of similar properties of PAHs (Tobiszewski and Namiésnik, 2012). Some pairs of PAHs were used to calculate the MDR and to infer PAH sources, though this tool is not completely accurate because many factors may influence the PAH profile (Schuster et al., 2015). Atmospheric samples usually have low concentrations of PAH compounds that have different degradation rates, which could change PAH composition (Schuster et al., 2015; Balmer et al., 2019; Gbeddy et al., 2020).

To differentiate petrogenic sources from pyrogenic sources, Anthracene (Ant)/Anthracene + Phenanthrene (Phe) (petrogenic ≤ 0.1 and pyrogenic > 0.1) and Fluoranthene (Fl)/Fluoranthene + Pyrene (Pyr) (petrogenic ≤ 0.5 and pyrogenic > 0.5) ratios were both used in this study (Khalikov et al., 2018; Ambade et al., 2022). Moreover, these LMW PAHs were the most abundant compounds in our PUF samples. In general, Ant/Ant + Phe ratios showed values lower than 0.1 (P01, P02, and P06), while Fl/Fl + Pyr ratios were around 0.5 (P01, P02, P03, and P04), indicating mainly petrogenic PAH sources. These results could be partly explained by fossil fuel combustion sources in Macaé city and its surroundings, especially downtown and at industrial sites. Indeed, petrogenic sources are the major contributor to atmospheric PAH in Macaé for most samples (P01, P02, and P06), even though pyrolytic sources were also reported for P03 and P04 sites. As PAHs are emitted as complex mixtures of compounds and may travel long distances, establishing their sources accurately is not trivial. The influence of pyrolytic sources may be justified by waste burning, which is still a common practice in communities with inappropriate waste collection. Moreover, the proximity of the city to rural areas, where biomass combustion occurs, may also drive the PAH levels towards the pyrolytic origin. The P05 site had concentrations below the LOQ and was not considered for source determination in this study.

Air mass back trajectory analysis

The air-back trajectory analysis performed on the 5-day back trajectories (Figure 4) unveiled that the trajectories arriving at the P06 site (Santana Island) basically come from the south and southwestern origins with purely Atlantic Ocean influences during the early exposure weeks (October). East and northeast airflow back trajectories also reached the Macaé coast with a major maritime influence (November). A minor contribution of west and southwest back trajectories was also identified, arriving at the P06 site as high altitudinal airflows (500–1,000 m above sea level — m.a.s.l.). Despite marine first origin (open Atlantic Ocean), the continental influences were minor, represented by north and northeast trajectories that stemmed from Espírito Santo State coastline and surroundings before reaching the sampling site (December and early January). Moreover, south trajectories were also identified coming from the Argentine coastline. The exposure of Macaé city, as a whole, to large-scale marine airflows (south and the eastern Atlantic Ocean origin), may partly explain the low atmospheric PAH concentrations at all monitored sampling sites in this study.

Benzo[a]pyrene-equivalent

Although the PAH air concentrations are considered low in Macaé, probably due to marine air mass influence, some scenarios could lead to toxicological concerns for humans. BaPeq ranged from 0.02 to 0.10 ng m^{-3} (Figure 5), indicating relatively low carcinogenic potential.

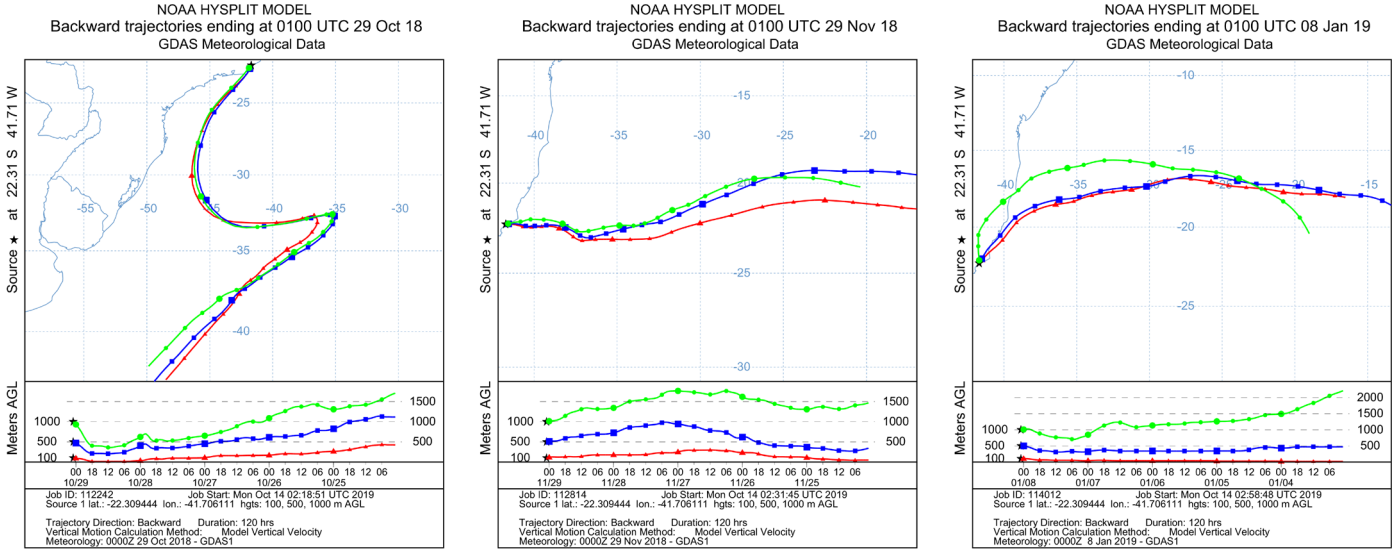

Figure 4 – The air-back trajectory analysis (HYSPLIT model) at the P06 site (Santana Island) over October 29 and November 2018, and January 8, 2019.

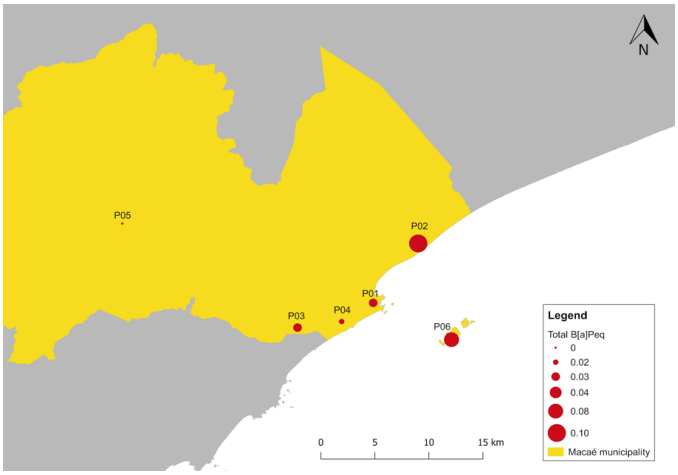

Figure 5 – Carcinogenic potential of each sample site in Macaé, RJ, regarding benzo[a]pyrene-equivalent parameter, in ng m^{-3}.
P01: Downtown area; P02: NUPEM/UFRJ; P03: IFF; P04: Alto da Glória; P05: Natural Municipal Atalaia Park; P06: Santana Island.

Site P05 did not show carcinogenic compounds above the LOQ and was not considered for results. In this case, dibenzo[a,h]anthracene was the most abundant and the only carcinogenic compound occurring in almost all field sample sites, ranging from 0.02 to 0.07 ng m^{-3}. The highest BaPeq were found at the sample site P02, in a highly populated and vulnerable community with waste burning, close to an important road and an industrial complex. P02 was the only sample site where six of the seven IARC carcinogenic compounds were found and shows a profile that indicates many emission sources (petrogenic, pyrolytic, and biomass burning). The lowest BaPeq was found in the most preserved area (Atlantic Forest — P05), showing the importance of vegetation in the control of PAH dispersion, especially for carcinogenic potential compounds.

Conclusions

In total, 17 PAHs were considered to calculate total PAH concentrations. Results show low concentrations, comparable to rural sites around the world, even though Macaé is a highly urbanized city. These results may be justified by the proximity to the ocean, where the air mass coming from the sea usually disperses air pollutants. The sampling period, during the summer, is another reason for low PAH concentrations, as it is a rainy season, decreasing forest burning and increasing scavenging from the atmosphere. Moreover, the summer season may increase photolytic PAH degradation due to longer daylight periods. Establishing a source for PAHs is not simple, because PAHs are complex compounds and may be present in samples far away from the sources. Petrogenic sources seem to be the major contributor to atmospheric emissions, especially from fossil fuel combustion, with some influence from pyrolytic sources. Background PAH concentrations do not mean that there is no carcinogenic potential, indicating no direct dependence on PAH air concentration levels. The BaPeq indicates higher concentrations of carcinogenic compounds in the most urbanized/industrialized areas. Populations living close to important roads, traffic workers, and people with waste burning habits are the most exposed and may suffer the most from atmospheric pollution consequences. The study indicates that urban/industrial areas raised human exposure to carcinogenic chemicals locally.

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