

Urban Air Quality: Occurrence, Emission Sources and Risk Assessment of Polycyclic Aromatic Hydrocarbons (PAHs) in Airborne Fine Particles

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This study evaluated the occurrence, emission sources, and health risks of polycyclic aromatic hydrocarbons (PAHs) bound to fine particulate matter (PM_{2.5}) in the urban atmosphere of Itabuna, Southern Bahia, Brazil. PM_{2.5} samples were collected at three sites with distinct anthropogenic influences: a rural area (UFSB Campus Jorge Amado), a predominantly residential area (15th Military Police Battalion), and a high-traffic commercial area (Jequitibá Shopping Mall). Thirteen of the sixteen priority PAHs were detected in all 21 samples, representing 82% of quantified PAHs. The highest total PAH concentration (3.28 ng m⁻³) occurred at the UFSB site, influenced by nearby industrial activities, freight transport, and vehicular traffic on a federal highway. Benzo(a)pyrene, an indicator of PAH pollution, was present in all samples, with concentrations below the European Union annual limit (1.0 ng m⁻³). Molecular diagnostic ratios indicated diesel and gasoline combustion as the main emission sources, with coal combustion also contributing. The incremental lifetime cancer risk (ILCR) was estimated for four population groups (infants, children, adolescents, adults), showing values within the acceptable range suggested by the U.S. EPA (10⁻⁶–10⁻⁴), but indicating potential long-term health concerns, particularly in high-traffic areas. The relevance of this study lies in the fact that Brazil still lacks regulatory limits for PAHs in ambient air, making local assessments essential to guide environmental management and public health policies. Furthermore, data on air quality in medium-sized Brazilian cities are scarce, despite rapid urbanization and increasing vehicle fleets. These findings emphasize the urgent need for continuous monitoring, improved emission control, and preventive strategies to mitigate risks to human health and environmental quality.

Keywords: PACs. PM_{2.5}. Urban Air Pollution. Vehicular Emissions. Cancer Risk.

Atmospheric particulate matter (PM) has attracted more and more attentions due to their threats to human health. Airborne particulate, especially fine particles and bound organic components are associated with health effects like cancer, but also allergic reactions, respiratory and cardiovascular diseases [1,2]. As soon, the knowledge of the composition and the concentration of chemical compounds associated with air particles is essential for risk assessment from contaminants bound on PM [3].

Polycyclic aromatic hydrocarbons (PAHs) are and mutagens human carcinogens, defined by World Health Organization through the exposure-response

function for cancer of the lung as a result of PAH exposure [4]. The PAHs are a group of harmful compounds emitted into the environment mainly through anthropogenic pyrolytic sources, such as biomass burning, fuel combustion, traffic-related emissions, industrial activities and petrogenic sources [5,6]. Gasoline and diesel vehicles emissions have been recognized as a significant source of these organic pollutants in airborne particulate matter in the urban atmosphere [7].

This study investigated the occurrence of PAHs associated with fine particulate matter (PM_{2.5}) in the urban atmosphere of Itabuna, Southern Bahia, Brazil, aiming to quantify their concentrations, identify potential emission sources and Risk assessment of PAHs based on incremental lifetime cancer risk.

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Experimental

Study Sites and Particulate Matter Collection

The study was conducted in the municipality of Itabuna, located in the southern region of the state of Bahia, Brazil. The city is situated at the geographical coordinates 14°47'21" S and 39°16'40" W, within the Cachoeira River watershed. Itabuna is the fifth most populous municipality in the state, with an estimated population of 214,123 inhabitants (IBGE, 2021).

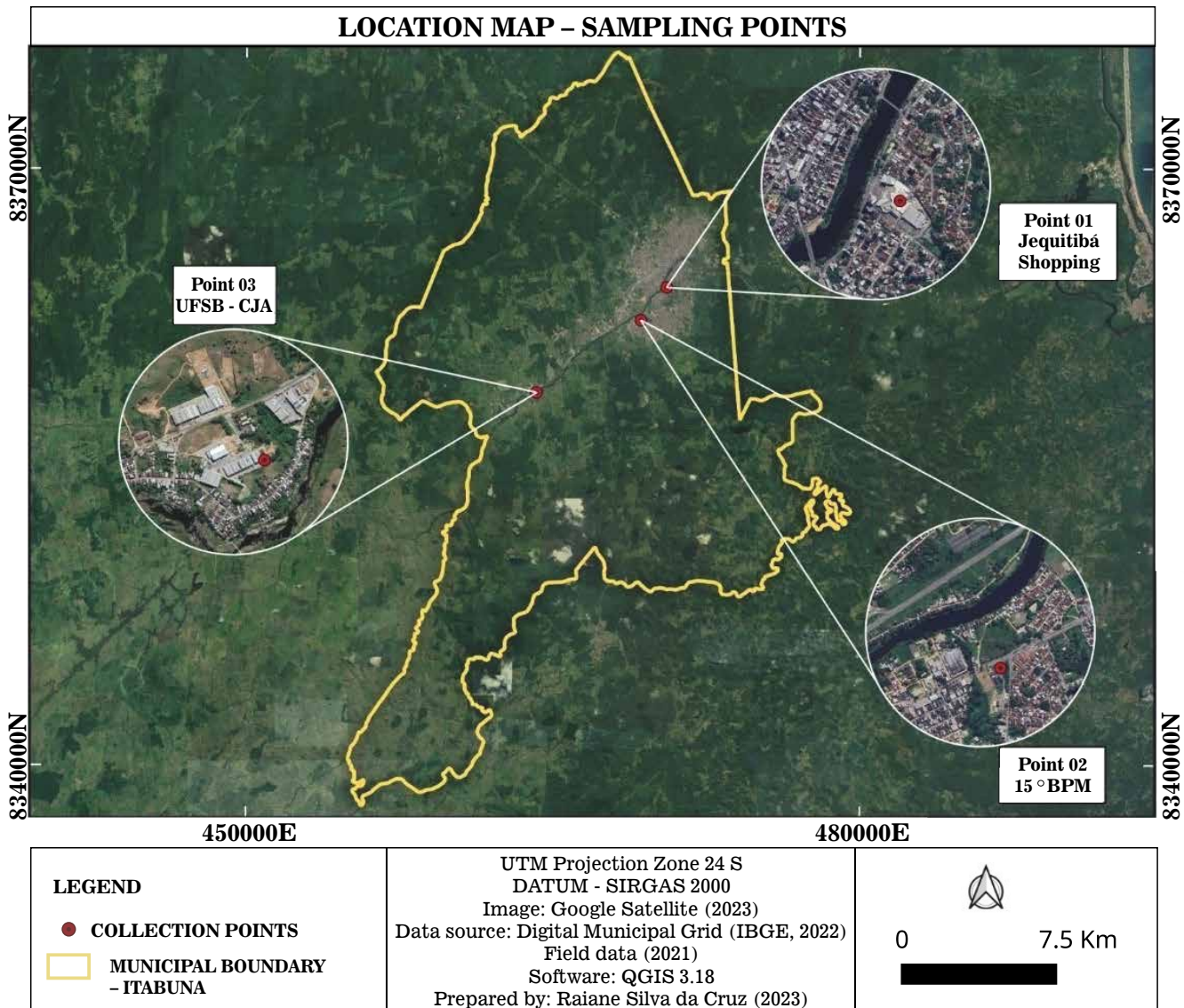
Particulate matter sampling was carried out at three distinct sites in Itabuna – BA (Figure 1):

Site 1: Federal University of Southern Bahia, Jorge Amado Campus, located in a rural area with minimal influence from anthropogenic activities.

Sites 2 and 3: located in the central region of the municipality, comprising the 15th Military Police Battalion, in a predominantly residential neighborhood, and the Jequitibá Shopping Mall, an area characterized by heavy motor vehicle traffic and high urban activity.

PM_{2.5} samples were collected using a high-volume (Hi-Vol) sampler equipped with a separator

Figure 1. Sample collection points in the municipality of Itabuna – BA.



for particles smaller than 2.5 μm aerodynamic diameter. Samples were collected on quartz fiber filters (22.8 cm \times 17.7 cm) over 24 h, at 1.13 $\text{m}^3 \text{min}^{-1}$. Each $\text{PM}_{2.5}$ sample was collected by using at least 271 m^3 of sampled air. After collection, filters were folded in half face to face, placed in a aluminum foil envelope then in a zip lock type plastic bag, transported cool to the laboratory and stored in a freezer (-4°C) until analysis by GC-MS SIM (Santos et al, 2016).

Instrumentation and Chemical Analysis

The extraction in particulate matter and Chromatographic analyses for determining PAHs were validated by Santos and colleagues (2016) [8] Sample preparation was done using approximately a filter piece of 4.15 cm^2 diameter added to a miniaturized micro-extraction device (Whatman Mini Uniprep Syringeless Filter, Cytiva, USA) with 500 μL of an acetonitrile/dichloromethane (18%:82% v:v) mixture and 23 minutes' sonication. Then, the extract was filtered in the microextraction device and placed for direct injection of a volume of 1.00 μL of the extract in the gas chromatograph coupled to a mass spectrometer GC-MS QP 2010 Ultra (Shimadzu, Japan), equipped with an AOC-20i autosampler and split/splitless injector operating in splitless mode at 310 $^\circ\text{C}$ and purge time of 0.80 min was employed for PACs analysis. The injection volume was 1.00 μL . The chromatographic separation was performed using a Rtx-5MS gas capillary column (5 % diphenyl, 95 % dimethylpolysiloxane, 30 m \times 0.250 mm ID \times 0.25 μm of film thickness) (Restek, Bellefonte, USA). High purity helium (99.9999 %) (White Martins, Brazil) was used as carrier gas under flow rate of 1.00 mL min^{-1} . Oven temperature programming initiated at 70 $^\circ\text{C}$ (2 min), then rising from 70-200 $^\circ\text{C}$ (30 $^\circ\text{C min}^{-1}$, 5 min), and 200-330 $^\circ\text{C}$ (5 $^\circ\text{C min}^{-1}$, 0.67 min). Injector temperature was set at 310 $^\circ\text{C}$ and transfer line was 280 $^\circ\text{C}$. The MS analysis was performed in electronic impact mode (EI) on positive mode with an energy of 70 eV and in selective ion monitoring mode GC-MS-SIM.

Risk Assessment of PAHs Based on Incremental Lifetime Cancer Risk

To obtain the estimates, it was necessary to convert the concentrations of PAHs into benzo(a)pyrene equivalent concentrations (BaP_{eq}) (ng m^{-3}), calculated using Equation 1, where C_i represents the concentration level of $\text{PM}_{2.5}$ for a target compound, and TEF_i corresponds to the toxic equivalency factor of the compound regarding carcinogenicity, determined for the 16 priority PAHs established by the U.S. EPA. For mutagenicity assessment, Equation 1 was applied by replacing the TEF values with the corresponding mutagenic equivalency factors (MEF).

$$\text{BaP}_{\text{eq}} = \sum C_i \times \text{TEF}_i \quad (1)$$

Daily inhalation exposure (EI) levels were calculated using Equation 2, where EI ($\text{ng person}^{-1} \text{day}^{-1}$) represents the daily exposure through inhalation, IR ($\text{m}^3 \text{day}^{-1}$) is the inhalation rate, and B(a)P_{eq} is the benzo(a)pyrene equivalent concentration (ng m^{-3}).

$$E I = \text{BaP}_{\text{eq}} \times \text{IR} \quad (2)$$

Mutagenicity-based EI values were calculated using Equation 2, but replacing the BaP_{eq} values (from Equation 1) obtained with TEF by those obtained with MEF. The incremental lifetime cancer risk (ILCR) was estimated to assess the inhalation risk for the population of Itabuna in the sampling areas defined in the present study, as described in Equation 3. In this equation, SF is the inhalation cancer slope factor for BaP, set at 3.14 ($\text{mg kg}^{-1} \text{day}^{-1}$) $^{-1}$; ED (years) corresponds to the lifetime exposure duration between the lower and upper bounds of each age range up to 70 years; EF (days year^{-1}) is the exposure frequency (365 days year^{-1}); AT (days) is the lifetime averaging time for carcinogens over 70 years ($70 \times 365 = 25,550$ days); and BW (kg) is the body weight of an individual in the target population.

$$ILCR = (EI \times SF \times ED \times cf \times EF) / (AT \times BW) \quad (3)$$

Risk assessment was performed considering four distinct target groups within the population: adults (>21 years), adolescents (11–16 years), children (1–11 years), and infants (<1 year) [9]. The inhalation rates (IR) were estimated at 16.4 m³ day⁻¹ for adults, 21.9 m³ day⁻¹ for adolescents, 13.3 m³ day⁻¹ for children, and 6.8 m³ day⁻¹ for infants. The assumed body weights were 80.0 kg for adults, 56.8 kg for adolescents, 26.5 kg for children, and 6.8 kg for infants. The exposure durations (ED) considered were 50, 6, 11, and 1 years for adults, adolescents, children, and infants, respectively.

Results and Discussion

Occurrence of PAHs in the Study Sites

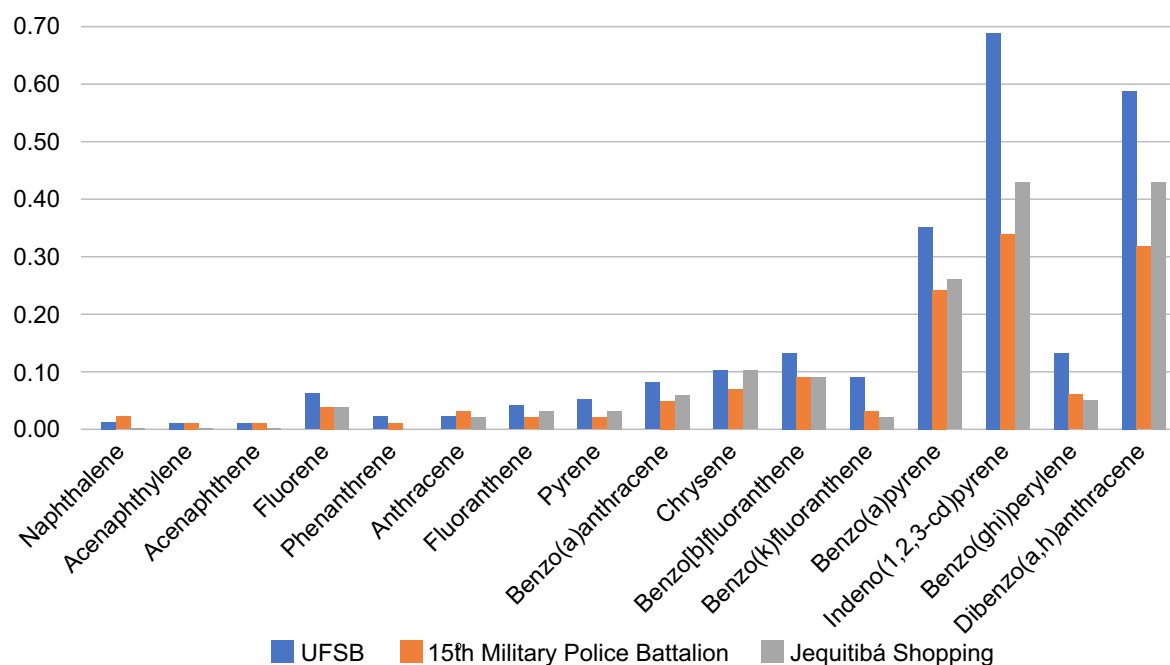
The presence of the sixteen priority PAHs was investigated. A total of thirteen PAHs were detected in all 21 samples. These compounds included fluorene, phenanthrene, fluoranthene, anthracene,

benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene, dibenzo[a,h]anthracene, and benzo[g,h,i]perylene, accounting for 82% of the PAHs quantified in the PM_{2.5} fractions of the collected samples.

The highest total PAH concentration was observed at the UFSB sampling site, with an average of 3.28 ng m⁻³. Although designated as a rural zone in the master plan of the municipality of Itabuna—where lower pollution levels would be expected due to low population density and reduced anthropogenic activity—this site is actually located in an area subject to high anthropogenic influence, including industrial activities, freight transport companies operating heavy-duty vehicles, and a federal highway with intense traffic, all contributing to increased airborne particulate matter concentrations.

The PAH distribution profiles for each sampling location are shown in Figure 2. The lowest compound concentrations were recorded at the 15th Military Police Battalion site, located in a predominantly residential neighborhood. The compound indeno[1,2,3-cd]pyrene exhibited the highest concentration at the UFSB site,

Figure 2. Average concentration (ng m⁻³) of PAHs in PM_{2.5} at each sampling location.



located in the Ferradas neighborhood, with an average of 0.69 ng m^{-3} , followed by elevated levels at the other sites (0.34 ng m^{-3} and 0.43 ng m^{-3} , respectively). This PAH has the potential to exacerbate the severity of allergic pulmonary inflammation [10,11], thereby increasing human health risks, and its presence in particulate matter underscores the contribution of vehicular emissions [12]. In contrast, acenaphthylene showed the lowest recorded concentration, with the average across all sampling sites totaling 0.02 ng m^{-3} .

Benzo(a)pyrene, a key indicator compound representing the PAH class, was detected in 100% of the samples, with mean concentrations of 0.35 ng m^{-3} , 0.24 ng m^{-3} , and 0.26 ng m^{-3} , respectively. These values were below the annual limit established by the European Union for atmospheric concentrations (1.0 ng m^{-3}). In Brazil, no regulatory limits have been established for benzo(a)pyrene in ambient air; therefore, international standards are used as reference.

Molecular Diagnostic Ratios and Identification Sources

Molecular diagnostic ratios among PAHs are commonly used to identify potential sources of atmospheric emissions. The ratios of selected PAHs were obtained following the approaches of Yu and colleagues (2014) and Kamal and colleagues (2015) [13,14]. The BbF/BkF ratios (1.44, 3.0, and 4.5) at the three sampling sites were >0.50 , indicating diesel exhaust as the likely source. The BaP/BgP ratios (2.69, 4.0, and 5.20) were >1.25 , suggesting coal combustion as a probable source. The BaP/(BaP+CRY) ratio, with a value of 0.73, indicated gasoline combustion as the main source in the Jequitibá Shopping Mall area, a finding further supported for the other sites by the FLT/(FLT+PYR) ratio, which ranged from 0.35 to 0.51.

Overall, the results demonstrate a predominance of emissions originating from the combustion of fuels such as diesel and gasoline, primarily from

vehicular sources in the municipality. This aligns with local characteristics, as the sampling sites are located in areas with constant vehicle traffic, contributing to increased PAH emissions into the atmosphere.

Cancer Risk from Inhalation Exposure

The total incremental lifetime cancer risk (ILCR) for the UFSB site was 8.31×10^{-8} (infants), 4.58×10^{-7} (children), 1.92×10^{-7} (adolescents), and 8.51×10^{-7} (adults). These ILCR estimates indicate a probability ranging from approximately 8.31 infants per one hundred million to 8.51 adults per ten million living in the UFSB area developing cancer over their lifetime.

At the 15th Military Police Battalion site, the estimated ILCR values were 4.90×10^{-8} (infants), 2.71×10^{-7} (children), 1.13×10^{-7} (adolescents), and 5.02×10^{-7} (adults). For the Jequitibá Shopping Mall site, the total ILCR values were 5.88×10^{-8} (infants), 3.25×10^{-7} (children), 1.36×10^{-7} (adolescents), and 6.03×10^{-7} (adults).

Across all three sampling locations, the ILCR values fell within the acceptable risk range of 10^{-6} to 10^{-4} , as suggested by the U.S. EPA (2005), in which ILCR values greater than 10^{-4} are considered indicative of high potential health risks.

Conclusion

The results demonstrated the presence of polycyclic aromatic hydrocarbons (PAHs), identified emission sources, and estimated the daily health risk to the population exposed to mutagenic and carcinogenic compounds associated with fine particulate matter ($\text{PM}_{2.5}$) in the urban atmosphere of Itabuna, southern Bahia, Brazil. The results highlighted the significant contribution of vehicle emissions to PAH levels in urban air. This study provides the first published data on air quality in Itabuna, highlighting the need for continuous monitoring and mitigation measures to assess the risks to public health and environmental quality in the region.

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