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Tijuca forest contribution to the improvement of air quality and wellbeing of citizens in the city of Rio de Janeiro, Brazil

Graciela Arbilla [a,*], Guilherme Dantas [a], Cleyton M. da Silva [a,b]

[a] Universidade Federal do Rio de Janeiro, Instituto de Química, Rio de Janeiro, RJ, 21941-909, Brazil
[b] Universidade Veiga de Almeida, Campus Tijuca, Rio de Janeiro, RJ, 20271-020, Brazil

HIGHLIGHTS

- The Tijuca Forest is one of the largest urban forests in the world.
- Hydrocarbons were analyzed with the aid of heart-cutting multidimensional gas chromatography.
- Total HC concentrations within the forest were clearly lower than in the urbanized area.
- The forest contributes to the reduction of air pollution.

GRAPHICAL ABSTRACT

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ABSTRACT

The Tijuca Forest, one of the largest urban forests in the world, is a protected area of the Brazilian Atlantic Forest, one of the world's biodiversity hotspots. The forest and the Metropolitan Region of Rio de Janeiro coexist and interact, but their mutual influence regarding air quality is still not well known and a more detailed study is needed. Here, air samples were collected inside the forest, in Tijuca National Park (TNP) and Grajaú State Park (GSP) and in two representative urban areas (Tijuca and Del Castilho Districts). Sampling was performed using stainless steel canisters, and ozone precursor hydrocarbons (HCs) were analyzed with the aid of heart-cutting multidimensional gas chromatography. The sampling points within the forest are currently visited by hundreds of people. Total HC concentrations within the green area were clearly lower than in the urbanized districts, in spite of the anthropogenic impact of visitors and the proximity of the urban area. Median values were 21.5, 35.5, 57.9 and 148.6 μg m^{-3} at TNP, GSP, Tijuca and Del Castilho, respectively. Total HC concentrations were Del Castilho > Tijuca > GSP > TNP. The kinetic reactivity and ozone-forming potential of individual HCs were evaluated, as well as the intrinsic reactivity of air masses. The air masses in the urbanized area showed a higher average reactivity in all scales. In fact, in spite of the forest's contribution to isoprene emissions, its net contribution to ozone formation was lower than that of urbanized air masses, owing to a reduction in HC concentration, particularly for alkenes and monoaromatic compounds. It is not clear if the forest plays a role in the adsorption of pollutants or if it acts as a physical natural barrier to air masses carrying pollutants. Nonetheless, improving air quality within Tijuca Forest is essential to the welfare of citizens.

* Corresponding author.
E-mail addresses: gracielaiq@gmail.com, graciela@iq.ufrj.br (G. Arbilla).

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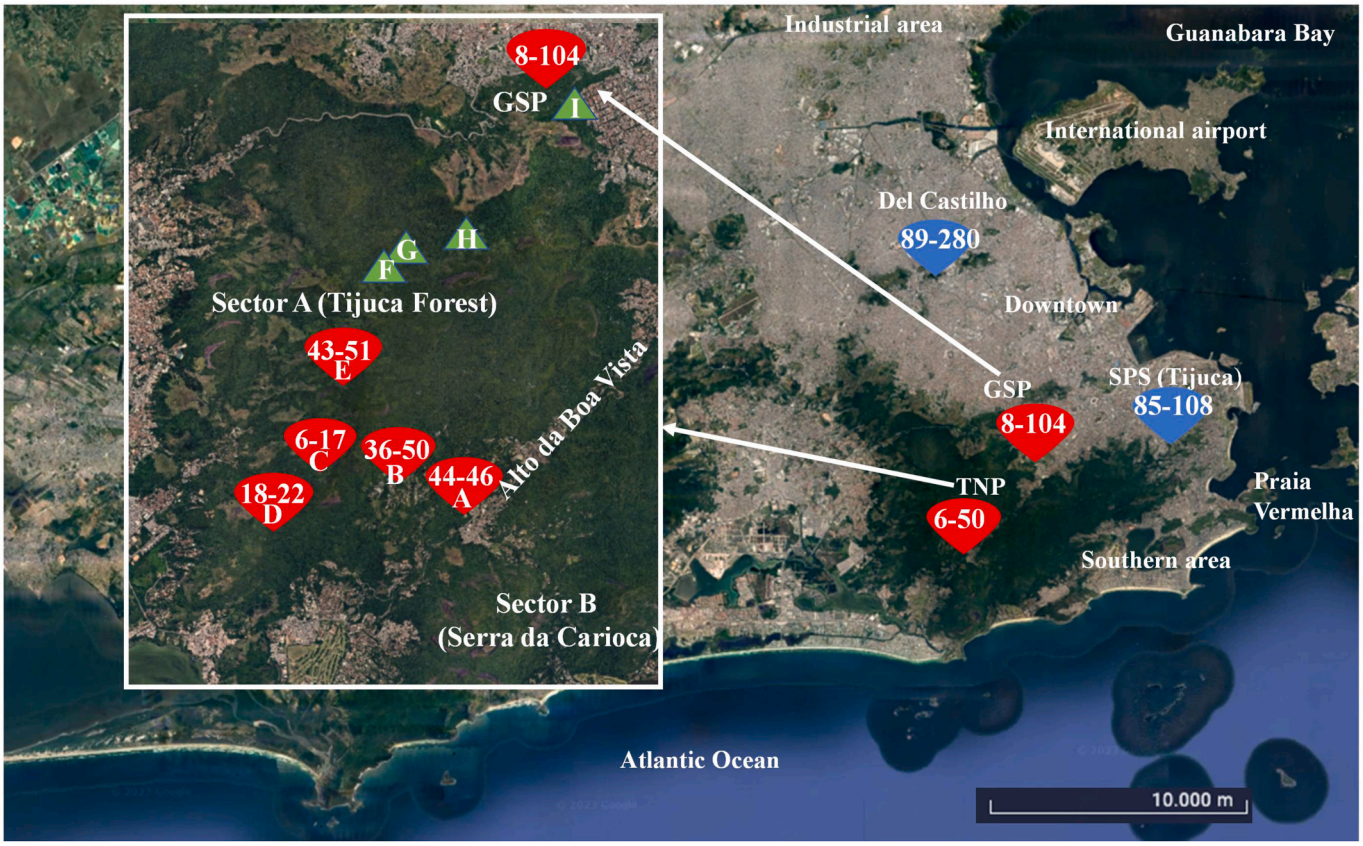

Fig. 1. Minimum and maximum total C_2–C_{12} HC concentrations. Key to acronyms: TNP: Tijuca National Park; SPS: Saens Peña Square; GSP: Grajaú State Park; A: Taunay Waterfall (altitude 384 m); B: Mayrink Chapel (altitude 461 m); C: Manacas Garden; D: Ponte Pensil; E: Restaurant The Forest (altitude 596 m); F: Tijuca Peak (altitude 1021 m); G: Tijuca Mirim Peak (altitude 920 m); H: Andaraí Maior Peak (altitude 860 m); I: Perdido Peak (altitude 445 m). Forested and urbanized areas are indicated in red and blue, respectively.
Source: Adapted from Google Earth.

1. Introduction

Tropospheric ozone, fine particulate matter ($PM_{2.5}$) and nitrogen oxide (NO_2) are the criteria pollutants of major concern regarding human health effects (Dantas et al., 2021; Sicard et al., 2023a; WHO, 2023). Trends in urban air pollution over the last two decades (covering 13,160 urban areas) have been recently published (Sicard et al., 2023a), and showed that $PM_{2.5}$ and ozone exposure of urban population has increased at 65% and 89% of the studied stations, respectively. In particular, mean concentrations and means of the daily maximum 8 h values have increased in some parts of South America, as Brazil. Clearly, actions are needed to improve air quality and mitigate the effects to exposure to air pollution (Dantas et al., 2021; Sicard et al., 2023a). As discussed by Sicard et al. (2023b), urban trees are key elements to reduce urban air pollution and noise, increase carbon stock, reduce temperature and regulate water runoff and, also, to improve the well-being of citizens. Recent initiatives, as the EU's biodiversity strategy for 2030 to protect and recover nature for the benefit of people, climate and planet, provide guidelines on afforestation, reforestation, mapping and monitoring of forests (EU, 2023).

The Brazilian Atlantic Forest once covered most of the country's Atlantic coast, in an area of approximately 1,290,000 km^2. The massive deforestation began after 1500, with the increase of agriculture and spread of urbanization in the 19th and 20th Centuries. In the 21st Century more than 60% of Brazilian population lives in this biome domain, with 21 and 12 million inhabitants in the metropolitan regions of São Paulo and Rio de Janeiro, respectively. The remaining original forest (approximately 7.5–11.5%) is highly fragmented and 83.5% of the fragments are <0.5 km^2 (Scarano and Ceotto, 2015). In 2000, this biome was identified as one of the biodiversity hotspots, and harbor approximately 2.7% and 2.1% of global endemic plants and vertebrates, respectively (Myers et al., 2000).

The Tijuca National Park (TNP), with 29.52 km^2, is an important protected area of the Brazilian Atlantic Forest, situated in the Metropolitan Region of Rio de Janeiro (MRRJ) in the Tijuca Massif mountains. The park is divided into four sub-units: Tijuca Forest (Sector A), Serra da Carioca (Sector B), Pedra da Gávea/Pedra Bonita (Sector C) and Covanca Pretos Forros (Sector D). The Tijuca Forest is the largest secondary urban forest in the world and divides the city of Rio de Janeiro into its southern and northern zones (Custódio et al., 2010; Freitas et al., 2006). A rather small area (0.55 km^2), located in the north of Tijuca Forest sector was not included within the TNP limits, but has been preserved as a State park, known as Grajaú State Park (GSP).

The MRRJ coexists with the Atlantic Forest and, in spite of human devastation and centuries of transformation and destruction, the city is an inseparable part of the rainforest and other ecosystems of this biome (like the *restinga*, sandbanks and mangroves). The Tijuca Forest and other areas of the Atlantic Forest (in particular, the Pedra Branca and Gericinó-Mendanha Massifs), form a green belt around the city, host several endemic and threatened species and include several natural, architectural and cultural landmarks of Rio de Janeiro, such as the Corcovado with Christ the Redeemer and the Sugar Loaf (Arbilla and Silva, 2018; Escobar, 2016; Scarano, 2014; Vieira et al., 2010). In spite of the importance of the Tijuca Forest to the life and climate of the city, there have been few published studies related to the air quality and the role of the forest in mitigating air pollutant concentrations.

The first study about Tijuca Forest was published in 1999 by Azevedo et al. (1999). The authors collected total particulate matter from three

locations within the urbanized area of the city and in Taunay Waterfall, at approximately 500 m from the entry to TNP. Samples collected in the park showed the lowest levels of vehicular pollutants, a greater percentage of n-alkanes (attributed to plant wax), an absence of steranes, and hopanes and polycyclic aromatic hydrocarbons (PAHs) in trace quantities. In another study, conducted in 2015–2016, fine particulate matter was collected in Tijuca District (near the Maracanã stadium) and at approximately 1.5 km from the entry to TNP. Total PAHs levels were 0.46 ± 0.61 ng m^{-3} and 1.12 ± 0.71 ng m^{-3} in the forest and the urbanized area, respectively, and the compound distribution indicated that they originated from vehicular sources (Oliveira et al., 2018).

In 2008, Custódio et al. (2010) determined the atmospheric concentrations of aldehydes and monoaromatic hydrocarbons (BTEX) in four locations within the TNP and at Saens Peña Square, a commercial-residential area about 10 km from the entrance to the park (for comparison). The authors concluded that formaldehyde and acetaldehyde might have a contribution from biogenic sources and that aldehydes, benzene and toluene concentrations were approximately 2–7, 2–3 and 3–5 higher in the urbanized area, respectively, which suggests that the vehicular contribution (especially for BTEX) was very low and that the forest was an important sink for many anthropogenic pollutants. A new environmental pollutant determination, using the same method, was carried out in 2017, at about 4 km from the entrance to the park. Mean levels were 1.02 ± 1.00 μg m^{-3} and 0.93 ± 1.05 μg m^{-3} for formaldehyde and acetaldehyde, respectively. These values were approximately three times lower than the concentrations determined at Saens Peña Square in the same period (Braga et al., 2019).

Recently, a new method for the determination of C_2–C_{12} hydrocarbons (HCs) in atmospheric samples was implemented (da Silva et al., 2022), which involved employing an improvement of Method TO-15A (US EPA, 2019), aided by heart-cutting multidimensional gas chromatography. A few samples were collected from different locations within the Atlantic Forest (Pedra Branca State Park; Grajaú State Park, Tijuca National Park and Chacrinha State Park). Isoprene concentrations were approximately 2.7 times lower than levels found in a public square (with grass, trees and flower shops) in Irajá, a typical urban area in the city of Rio de Janeiro (with mixed emissions sources) while the other compounds were >3 times lower. Clearly, a more detailed study is needed to characterize the relationship between the city and the forest regarding air quality. Furthermore, the effect of dense forests (both with primary and secondary vegetation) with regard to CO2 absorption, has been shown in a previous study conducted in Rio de Janeiro and other Brazilian cities (Moreira Junior et al., 2017).

It is well known that HCs play a key role in the chemical processes leading to tropospheric ozone and fine particulate matter (da Silva et al., 2022; Finlayson-Pitts and Pitts, 2000). Considering the lack of information and the importance of this biome, the main goal of this study is to highlight the importance of the Atlantic Forest and the Tijuca Forest in improving living standards, restoring species, mitigating the effects of climate change, and make new determinations of HC levels as an indication of the crucial role of vegetation in the reduction of pollutants.

2. Materials and methods

2.1. Sampling locations

Air samples were collected at two areas of the forest: a) in Sector A (Tijuca Forest) and b) at Grajaú State Park located in the northern boundary of PNT (Figures S1a and S1b in the Supplementary Material section). In spite of being a part of Tijuca Forest, the Grajaú area was not included in the PNT, but was declared a protected conservation area (by the State of Rio de Janeiro) and a State park. The sampling points in Sector A were between 500 and 4000 m from the entrance of the PNT and at an altitude of between 384 and 596 m above sea level. The sampling locations within TNP are also shown in Fig. 1. The sampling location in GSP, at an altitude of 250 m above sea level, was approximately 400 m from the entrance to the park and 400 m from Perdido Peak (445 m high). A more detailed description of GSP and PNT is given in Table S1 (Supplementary Material).

Samples were also collected in two representative urban areas: a) Saens Peña Square (Tijuca District), at approximately 10 km and 5 km from the entrance to TNP and GSP, respectively and b) near the entrance of a shopping center in Del Castilho District, at approximately 9.5 km and 15 km from the entrance to GSP and TNP, respectively. Saens Peña Square is a residential and commercial area, characterized by vehicular emission sources (both light and heavy-duty vehicles, mainly buses), with a heavy flow of traffic and pedestrians, three bus stops, a subway station and in close proximity to the Sumaré mountain range (with Atlantic Forest vegetation) (Custódio et al., 2010). Del Castilho District is also a commercial and residential area, with mixed emission sources: local emissions of light and heavy-duty vehicles (mainly from Avenue Dom Helder Câmara and the Linha Amarela highway) and industrial emissions transported from the northern area of the MRRJ (mainly from chemical and petrochemical companies).

The climate in the MRRJ is Atlantic tropical, with dry winters, rainy summers and rainfall of more than 1200 mm $year^{-1}$ (mainly in the period from November to April). The thermal amplitude is low (approximately 6 °C), and the mean annual temperature is 29 °C (Dantas et al., 2021). According to Freitas et al. (2006), temperature falls in accordance with altitude (approximately 0.4 °C/100 m in the regions between 80 and 1021 m, which is the highest point in PNT).

Samples were collected in the period between October 15, 2022 and March 3, 2023 during the morning.

2.2. Experimental method

Sampling and analytical procedures have recently been described in detail (da Silva et al., 2022). Briefly, an improvement of the EPA Method TO-15A (US EPA, 2019) was used to determine C_2–C_{12} HCs with the aid of heart-cutting multidimensional gas chromatography.

A total of 40 air samples were collected by means of previously cleaned and evacuated Entech Silonite™ and Restek SilcoCan™ stainless steel canisters (6.0 L). A final pressure of 1 atm was reached, for a total sampling time of 1 h, with the aid of restrictors (Entech Flow Controller CS1200E with a Silonite®filter).

The samples were analyzed in duplicate using a preconcentrator/thermal desorption unit (Markes CIA Advantage-HL and Markes Unity 2™, OH, USA) coupled with a gas chromatograph (Agilent, model GC 7890A, CA, USA) equipped with a capillary flow technology (CFT) Deans Switch. The C_4–C_{12} fraction was resolved using the primary column a DB-624 (60 m × 0.32 mm × 1.8 μm) while the C_2–C_3 fraction was analyzed with the aid of the primary and a PoraPlot Q-HT (25 m × 0.32 mm × 10 μm) secondary column. The initial temperature of the oven was set at 27 °C (10 min) and then the temperature was raised (5 °C min^{-1}) to 250 °C. The carrier gas was He (99.999%, ultra-high purity grade) with a constant flow of 1.5 mL min^{-1} and 2.5 mL min^{-1} for primary and secondary columns, respectively. The primary column was coupled to a mass spectrometer (MS Agilent 5975C), and the secondary column to a flame ionization detector.

All the analytical details have been described by da Silva et al. (2022), including the determination of the limits of detection (LOD) and quantification (LOQ), linearity, precision, and linear range. LOD and LOQ were calculated for all the compounds from the noise standard deviation, as 0.1 ng and 0.3 ng, respectively. When the injected sample volumes (500 mL) are taken into account, these values correspond to approximately 0.2 μg m^{-3} and 0.6 μg m^{-3}, respectively. A standard reference mixture (57 compounds, Restek, 20–60 ppbC, PO#P43615, Certificate 22–91962, PA, USA) was used for quantification and also for confirming the identity of each of the HCs.

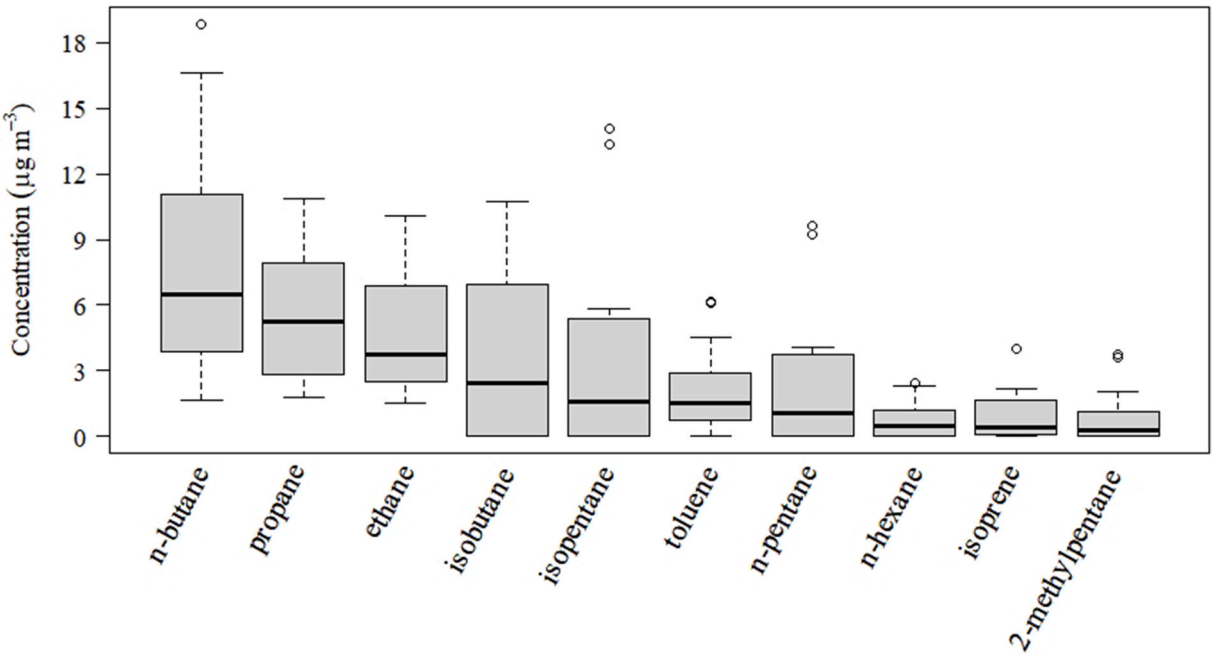

Fig. 2. Boxplots of the 10 most abundant HCs determined in the TNP and GSP (urban forest). Compounds with median concentrations in the range of 6.5–0.2 μg m^{-3}.

2.3. Calculation of hydrocarbon reactivity and ozone-forming potential

Ozone chemistry and the fundamental role played by HCs in ozone formation and consumption processes in urban atmospheres has been discussed in several books and research articles (Atkinson, 2000; Finlayson-Pitts and Pitts, 2000; Mo et al., 2018; Kumar and Sinha, 2021). In this study, the kinetic reactivity and ozone forming potential (OFP) of each individual HC was evaluated, as outlined in detail by Dantas et al. (2020).

The contribution of individual HCs to kinetic reactivity (Carter, 2010; Zou et al., 2015; Dantas et al., 2020) was evaluated by means of Equation (1):

$$\text{kinetic reactivity}_i = k_{i,OH} * [HC_i] \quad (1)$$

where:

$[HC_i]$ are the individual HC concentrations

$k_{i,OH}$ are the specific rate coefficient for the reaction of each HC with hydroxyl radicals (•OH).

The ozone forming potential of each individual hydrocarbon (OFP_i) was evaluated by means of the reactivity scales developed by Carter (2010): Maximum Incremental Reactivity (MIR), Maximum Ozone Incremental Reactivity (MOIR) and Equal Benefits Incremental Reactivity (EBIR). The limitations and applicability of these scales to Rio de Janeiro were discussed by Dantas et al. (2020) for an urban environment. Calculations were made as follow (Equation (2)):

$$OFP_i = IR_i * [HC_i] \quad (2)$$

where:

$[HC_i]$ are the individual HC concentrations.

IR_i, are the dimensionless incremental reactivity (IR) coefficients for each compound: MIR_i, $MOIR_i$ and $EBIR_i$ as estimated by Carter (2010).

After calculating the individual OFP_i values, the average reactivity (average IR) or average OFP, in each scale, for each individual sample was evaluated using Equation (3):

$$\text{Average OFP} = \text{Average IR} = \left[\sum (IR_i \text{ x } HC_i)\right] \Big/ \text{ total HC concentration} \quad (3)$$

where:

IR_i = IR coefficient for each compound (for each scale: MIR, MOIR, and EBIR).

[HC]i = concentration of each HC in μg m.$^{-3}$

3. Results and discussion

3.1. Hydrocarbon concentrations

A total of 25 and 15 samples was collected in the forested and urbanized areas, respectively. Total C_2–C_{12} HC concentrations (minimum and maximum values) are shown in Fig. 1.

As previously described, and also shown in the Supplementary Material (Table S1 and Figures S1a and S1b), Tijuca Forest is the only Brazilian national park located at the heart of a metropolis. The sampling points in TNP are currently visited by hundreds of people, especially at weekends, and are between 500 and 4000 m away from the entrance to the park. Moreover, vehicles are authorized to circulate within TNP (up to 300 vehicles per day). Points A, B and E (Fig. 1) are alongside the main road leading to the most visited peaks (called Estrada dos Picos). Points C and D are near a smaller road. GSP is surrounded by the Grajaú District, with a moderate traffic flow of cars and buses, and the sampling point is approximately 400 m from the entrance, by a hikers'path used to reach Perdido Peak. In spite of these facts, total HC concentrations within the green area are clearly lower than in the urbanized districts (Tijuca and Del Castilho). The median values were 21.5, 35.5, 57.9 and 148.6 μg m^{-3} at TNP, GSP, Saens Peña Square (Tijuca) and Del Castilho, respectively. Total HC concentrations were Del Castilho > Saens Peña Square > GSP > TNP.

Owing to the influence of the mountains and Guanabara Bay, the northern area of the city (including Del Castilho and Grajaú districts), are often affected by air masses from the north and north-east, carrying industrial and vehicular pollutants at night and in the morning. On these days, higher total HC concentrations are found in both the urbanized area of Del Castilho and the GSP (see Figure S2, Supplementary Material). Anyway, and in spite of its reduced area, in the GSP all the concentrations are lower than in the urbanized area. The effect of the native forest is also shown by the fact that the total concentrations for two samples collected by the entrance (not shown in Fig. 1), were

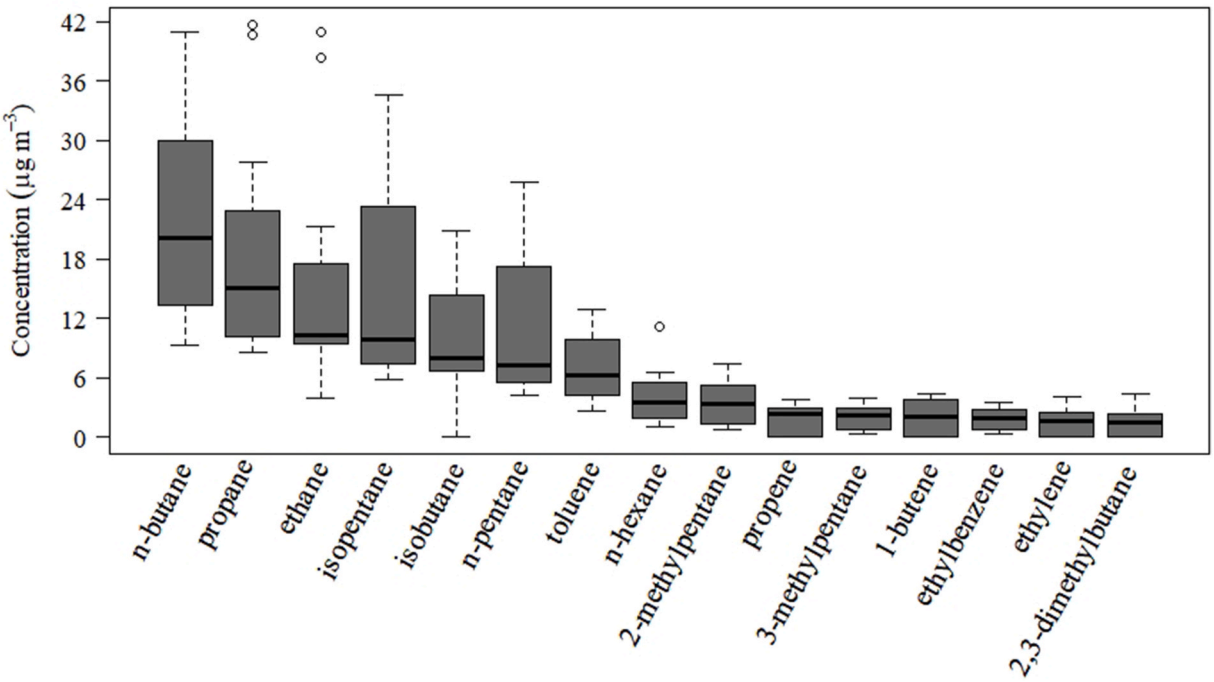

Fig. 3. Boxplots of the 15 most abundant HCs determined in Del Castilho and Saens Peña Square (urbanized areas). Compounds with median concentrations in the range of 20.2–1.6 μg m^{-3}.

approximately 120 μg m^{-3} (compared with 8–104 μg m^{-3} inside the park).

Due to its close proximity to the mountains, Tijuca District (including the sampling point at Saens Peña Square), predominantly receives winds from the south (mountain breezes) and also experiences local vehicular pollutants (Dantas et al., 2021). The sampling locations within Tijuca National Park are less affected by air masses from the north and north-east because the main peaks (at the north of Sector A, see Fig. 1) form a natural barrier to air masses. The vehicular emissions are caused by buses and light vehicles in Alto da Boa Vista Street and the urbanized areas in the vicinity (Tijuca, Usina, Alto da Boa Vista) and also local traffic (visitors and park maintenance). Lower concentrations within the forest suggest that trees, especially those that form dense forests, assist in the adsorption of pollutants and/or form a natural barrier to the air masses carrying pollutants, as previously found in other studies (Azevedo et al., 1999; Braga et al., 2019; Custódio et al., 2010; da Silva et al., 2022; Moreira Junior et al., 2017; Oliveira et al., 2018). Local emissions, originating from the vehicles of visitors could also have an impact on the forest, as suggested by the higher values obtained in points A, B, and E. In one sample (not included in Fig. 1), all the concentrations collected near the top of Tijuca Peak were < LOQ.

The most abundant compounds found in all the samples obtained from the forested areas (PNT and GSP), were as follows: n-butane, propane, ethane, isobutane, isopentane, toluene, n-pentane, n-hexane, isoprene, 2-methylpentane and 3-methylpentane (in the case of these compounds, the median concentrations were > LOD). With regard to all the other HCs, the median values were < LOD. Individual values are represented as boxplots in Fig. 2. Isoprene, the most abundant biogenic compound was determined in the interval < LOQ - 4.0 μg m^{-3}, and had a median concentration of 0.4 μg m^{-3} which represents 1.8% of the total HC mass. Alkanes and monoaromatic compounds represented approximately 90.6 and 7.6% of the total mass, respectively, and the concentration of alkenes was < LOD in most of the samples, which suggests that all these compounds were of anthropogenic origin and mainly transported from the urbanized area. Moreover, the most reactive compounds (mainly alkenes) reacted during the movement of air masses.

The concentrations at Del Castilho and Tijuca (Saens Peña Square) locations were higher, as shown in Fig. 3, where the 15 most abundant compounds were represented as boxplots. The compounds, in decreasing order of abundance, were: n-butane, propane, ethane, isopentane, isobutane, n-pentane, toluene, n-hexane, 2-methylpentane, propene, 3-methylpentane, 1-butene, ethylbenzene, ethene and 2,3-dimethylbutane, and these represented 89.3% of the total HC mass. 26 compounds showed median concentrations > LOD. Alkanes, alkenes and monoaromatic compounds represented 82.8, 5.7 and 11.0% of the total mass of HCs.

All the compounds in Fig. 3, were recently determined in an underground parking lot; they are emitted by vehicles (da Silva et al., 2022) and can be transported from the industrial area in the north and north-east. Propane and n-butane may be attributed to domestic and commercial activities (such as restaurants and bars which use bottled gas, so-called cooking gas). Monoaromatic compounds were determined in lower concentrations than those published for four monitoring campaigns carried out in several locations of the MRRJ (12–27% of total mass) in 2015 (da Silva et al., 2018). This was an expected result because light flex-fuel vehicles manufactured in Brazil since 2013, have to comply with new and more stringent emission legislation. Dynamometer measurements showed that the new vehicles (corresponding to PROCONVE L6, Tier 2 equivalent) emit approximately 40–50% less monoaromatic compounds and higher amounts of alkanes (Siciliano et al., 2022). The fleet modernization and the transition to more restricted standards has led to a reduction in pollutants (Holnicki et al., 2021).

Within the urbanized area, levels of isoprene (the unique biogenic compound found in this study) were relatively low and was not among the 15 most abundant HCs. This was determined in the range of <LOD - 6.6 μg m^{-3}, with a median concentration of 0.6 μg m^{-3}, which represents 0.5% of total HC mass, and suggests the contribution of non-forested green areas in the city (grass, shady trees, and leisure spots) and other sources to isoprene emissions. The levels were higher at Saens Peña Square (median value 0.7 μg m^{-3}, compared with 0.5 μg m^{-3} in Del Castilho). This was an expected result because the vegetation cover is higher in Tijuca District and the mountainous area of Sumaré is at approximately 300 m from the sampling location. Anyway, isoprene concentrations were higher in the urbanized area than in the forest.

Table 1
Individual contribution made by HCs to kinetic and ozone-forming potential, in decreasing order, for the compounds determined in this study.

Kinetic reactivity	Ozone-forming potential (OFP_i)		
(k_{OH})	(MIR)	(MOIR)	(EBIR)
PNT and GSP samples			
isoprene	n-butane	n-butane	n-butane
n-butane	Toluene	Toluene	Propane
propane	Isoprene	propane	Isobutane
toluene	Isobutane	isobutane	Isopentane
isobutane	Propane	isoprene	Isoprene
isopentane	Isopentane	isopentane	Toluene
n-pentane	n-pentane	n-pentane	n-pentane
ethane	Ethane	ethane	Ethane
n-hexane	n-hexane	n-hexane	n-hexane
2-methylpentane	3-methylpentane	3-methylpentane	3-methylpentane
Accumulated reactivity = 98.8% of kinetic reactivity (k_{OH})	Accumulated reactivity = 98.3% of mechanistic reactivity (MIR)	Accumulated reactivity = 98.3% of mechanistic reactivity (MOIR)	Accumulated reactivity = 98.6% of mechanistic reactivity (EBIR)
Del Castilho and Saens Peña Square samples			
propene	propene	n-butane	n-butane
1-butene	toluene	propene	propene
isoprene	n-butane	isopentane	isopentane
n-butane	1-butene	toluene	1-butene
isopentane	ethylene	1-butene	n-pentane
ethylene	isopentane	n-pentane	isobutane
n-pentane	isobutane	ethylene	propane
toluene	n-pentane	isobutane	ethylene
propane	(m + p)-xylene	propane	toluene
(m + p)-xylene	propane	2-methylpentane	2-methylpentane
isobutane	isoprene	n-hexane	n-hexane
n-hexane	ethylbenzene	(m + p)-xylene	3-methylpentane
2-methylpentane	o-xylene	3-methylpentane	ethane
3-methylpentane	2-methylpentane	ethylbenzene	(m + p)-xylene
ethylbenzene	n-hexane	isoprene	Isoprene
Accumulated reactivity = 92.3% of kinetic reactivity (k_{OH})	Accumulated reactivity = 91.8% of mechanistic reactivity (MIR)	Accumulated reactivity = 90.7% of mechanistic reactivity (MOIR)	Accumulated reactivity = 92.4% of mechanistic reactivity (EBIR)

Since isoprene emissions are in general of biogenic origin (85–90%), this might seem an unexpected result (Guenther et al., 2012; Khan et al., 2021). In fact, isoprene emissions from vegetation are related to photosynthesis, and depend on several factors, such as plant species, temperature, radiation, and stress (plant damage and air pollution) (Gu et al., 2022; Khan et al., 2021). It has been argued that isoprene emissions protect the photosynthetic system of plants against non-biotic stress factors (in particular, light damage and heat stress, and even harmful oxidants) (Kesselmeier and Staudt, 1999). These facts could explain why trees inside the Atlantic forest, and in an environment with lower temperatures than in the city (by at least 5–6 °C), natural shade and a lower anthropogenic effect, emit lower levels of isoprene (and even other isoprenoids) than vegetation in squares, streets and small parks. The experimental results of this study, suggest that Tijuca Forest acts as a sink and/or a barrier of pollutants with minor contribution to isoprene emissions.

3.2. *Hydrocarbon reactivity and ozone-forming potential in both scenarios*

Hydrocarbon reactivity and ozone-forming potential were evaluated using Equations (1) and (2). HCs were arranged in decreasing order of reactivity (kinetic reactivity and OFP_i), as shown in Table 1. All the compounds with median concentrations >0.2 μg m^{-3} were included in the calculations.

Currently, volatile organic compounds (VOCs) and nitrogen oxides (NO_x) concentrations in the urbanized area of Rio de Janeiro are typical of a MOIR/EBIR scenario (da Silva et al., 2018). As shown in Table 1, isoprene was the most important compound with regard to kinetic reactivity (within the forest), but owing to its relatively low concentration, it makes a relatively low contribution to ozone formation, in the urbanized area, particularly when computed in the MOIR and EBIR scales. In the forested locations, the main alkanes (n-butane, propane and isobutane) also showed higher OFP_i (in the MOIR and EBIR scales).

The average reactivity, in each scale, for each individual sample was evaluated using Equation (3). The results, calculated on the basis of the three scales, are shown in Fig. 4.

Incremental reactivity coefficients depend on the chemical mechanism and environmental conditions and, then, the scales adopted here

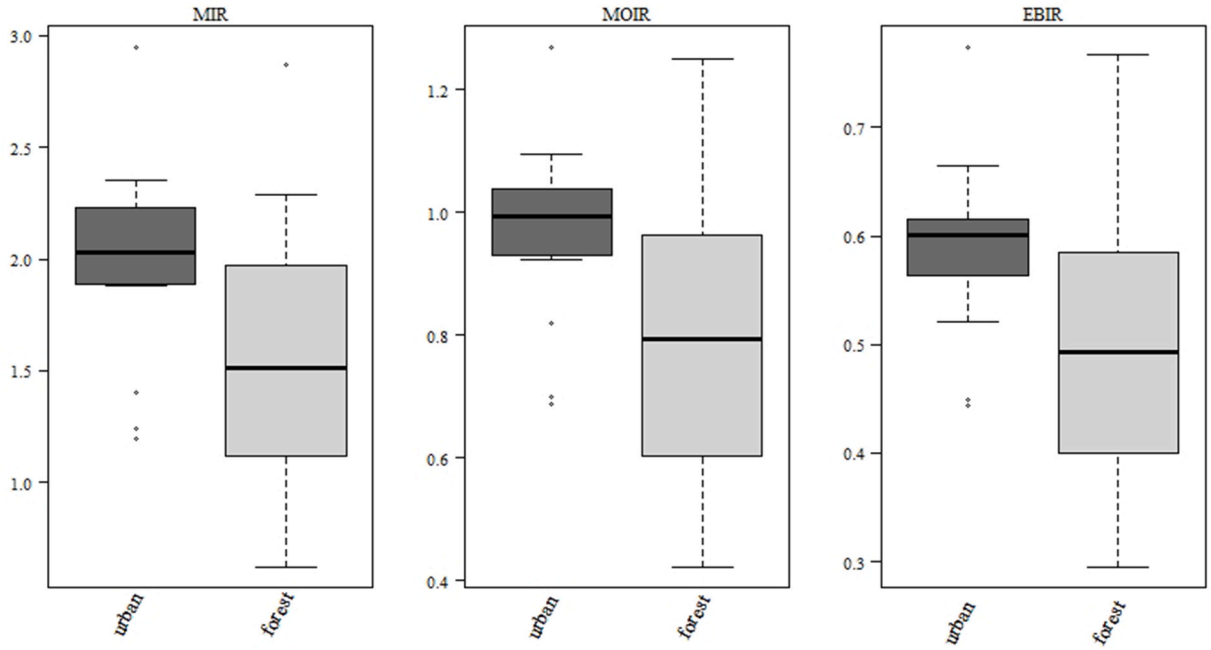

Fig. 4. Average reactivity of each individual sample, in each reactivity scale, calculated for the air mixtures collected in this study. Units: $gO_3/gHCs$.

are approximated values (Zhang et al., 2021). However, results in Fig. 4 suggest that the air masses in the urbanized area show a higher average reactivity in all the scales. In fact, although the forest is a source of isoprene emissions, its net contribution to ozone formation is lower than that of urbanized air masses, owing to the reduction in the concentration of HCs, particularly for alkenes and monoaromatic compounds (which are the most reactive).

4. Conclusions

Tijuca Forest is one of the main public recreational facilities in the MRRJ, because its natural features, hiking trails, climbing areas, lakes, waterfalls and picnic sites, as well as its cultural treasures (like Christ the Redeemer and the Chinese Belvedere). The forest is a contributory factor in temperature reduction, and its rivers, and waterfalls are key water sources for the formation of the city's hydrological system. Vegetation helps to protect the slopes and reduce pollution. The results obtained in this study showed that concentrations of HCs are lower within the forest, in spite of the anthropogenic impact of visitors and the proximity of the urbanized area. It is not clear if the role of the forest is in assisting the adsorption of pollutants or if it acts as a natural physical barrier to air masses carrying pollutants. Whatever the case, the better air quality within Tijuca Forest is essential to the welfare of citizens. In a metropolitan area, with 12 million inhabitants, and several sources of pollution (of vehicular and industrial origin), this conservation area, in the heart of the city, provides a free opportunity for the public to carry out a wide range of activities to improve both their physical and mental health. Finally, attention should be drawn to the role of the forest as the home of endangered species, and characterized by a high degree of endemism, and its potential value as a means of mitigating the effects of climate change through the reduction of pollutants.

Author contributions

Graciela Arbilla: conceptualization; methodology; validation; investigation; data curation; writing original draft; writing-review & editing; funding acquisition; supervision, **Guilherme Dantas:** software; formal analysis; writing-review & editing, **Cleyton Martins da Silva**: conceptualization; methodology; writing original draft; writing-review & editing; funding acquisition; supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix B. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2023.139017.

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