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# Black Carbon and Particulate Matter Concentrations: Air Pollution Levels in Rio de Janeiro, Brazil

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This research explores the concentration of black carbon (BC) in particulate matter (PM<sub>10</sub> and PM<sub>2.5</sub>) from ten monitoring stations in the Metropolitan Region of Rio de Janeiro (MRRJ), Bonsucesso (BS), Botafogo (BOT), Copacabana (COP), Gavea (GAV), Gericino (GER), Lagoa (LAG), Recreio dos Bandeirantes (REC), Santa Cruz (SC), Castelo (CAS) and Urca (URC), covering a range of pollution sources (vehicular, industrial, and residential). PM samples were collected using filter units every week from January 2018 to December 2019. Results revealed high concentrations of PM<sub>10</sub> in BS ( $86 \pm 22 \ \mu g \ m^{-3}$ ) and PM<sub>2.5</sub> in REC ( $30 \pm 11 \ \mu g \ m^{-3}$ ). Likewise, both monitoring stations exceeded the international limits. In 2019, BC in PM<sub>10</sub> decreased in the following order: BS > CAS > GER > BOT > SC > GAV. For 2018, BC in PM<sub>2.5</sub> decreased as follows REC > LAG > SC, while 2019 REC > GAV > LAG > COP > URC. REC and BS have industrial and commercial activities and intense vehicular traffic. During the period of study, average BC concentrations in PM<sub>10</sub> and PM<sub>2.5</sub> were  $3.3 \pm 1.5$  and  $1.9 \pm 0.70 \ \mu g \ m^{-3}$ , respectively. These findings indicate that BC concentrations should be monitored and regulated in locations with high levels of traffic-related air pollution for offering new insights and guiding efforts to minimize emissions and enhance public health.

Keywords: black carbon, PM2.5, PM10, Rio de Janeiro, South America

### Introduction

Air pollution, characterized by the emission and release of pollutants into the atmosphere, poses significant risks to public health, ecosystems, and the overall well-being of our planet.<sup>1</sup> Among pollutants, particulate matter (PM), nitrogen dioxide (NO<sub>2</sub>), ozone (O<sub>3</sub>), sulfur dioxide (SO<sub>2</sub>), and carbon monoxide (CO) are of major health concern because they cause cardiorespiratory diseases and are sources of mortality and morbidity.<sup>1</sup> PM encompasses a complex mixture of organic and inorganic particles, originating from both natural sources such as volcanic dust and anthropogenic sources including transportation, industry, and agriculture.<sup>2</sup> In order to evaluate air quality, PM is categorized into two groups:  $PM_{10}$ -particles < 10 µm in diameter and  $PM_{2.5}$ -particles < 2.5 µm in diameter).<sup>2</sup> The health effects and risks of exposure to  $PM_{10}$  and  $PM_{2.5}$  are well documented.<sup>3-6</sup> Likewise,  $PM_{10}$  and  $PM_{2.5}$  are related to visibility reduction and affect adversely climate change, ecosystems, and materials.<sup>7.8</sup>

High PM mass concentrations are common in areas densely populated and with heavy vehicular traffic.<sup>9,10</sup> A significant portion, and one of the most toxic species present in both  $PM_{2.5}$  and  $PM_{10}$  is the black carbon (BC), a carbonaceous species.<sup>11,12</sup>

Black carbon pollution has become a global environmental problem that negatively impacts public health, urban air quality, agriculture, reduces visibility, and causes global climate change.<sup>13,14</sup> Epidemiological studies

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revealed the association of mortality and cardiopulmonary morbidity with exposure to BC because it acts as a universal carrier of a wide variety of chemicals (of different toxicity) to the human body.<sup>15</sup> Likewise, it is responsible for producing a positive radiative forcing, that absorbs solar radiation, leading to the warming of the atmosphere.<sup>16</sup> BC is a primary aerosol produced and emitted mainly by incomplete combustion of fossil fuels related to traffic, wood, petrol, agricultural waste, stubble, biomass burning, biofuel, and industrial processes.<sup>17,18</sup> In urban and industrial areas, the main sources of BC emissions are related to vehicular traffic, industrial activities, residential heating activities and wood combustion.<sup>19,20</sup>

Thus, knowledge of BC concentration and its sources in the atmosphere of metropolitan regions is important to establish strategies for reducing their emission. The Metropolitan region of Rio de Janeiro (MRRJ), with its 22 municipalities and 13.4 million inhabitants, has a road fleet of more than 3 million vehicles. There is limited information on BC levels in particulate matter (PM<sub>10</sub> and PM<sub>2.5</sub>) in the MRRJ. Only three studies have been reported by Soluri *et al.*,<sup>21</sup> Godoy *et al.*,<sup>22</sup> and de Miranda *et al.*,<sup>23</sup> Prior research has explored the concentrations of BC in Rio de Janeiro, but by focusing on spatial and temporal variation, new information can be gleaned on the sources and impacts of BC pollution in the MRRJ.

Examining the variation in BC levels between various neighborhoods or at different times of the day, for instance, can help identify locations where initiatives would have the most impact. Therefore, the aim of this study is to measure  $PM_{2.5}$ ,  $PM_{10}$ , and BC levels at ten sites in the MRRJ during 2018 and 2019. The groundbreaking findings of this study hold immense potential to shape policy decisions, establish robust air quality standards, implement effective emission controls, and guide sustainable urban development. By shedding light on the interplay between air pollution, public health, and the urgent need for pollution reduction, this research serves as a catalyst for improving public wellbeing and safeguarding our environment.

# Experimental

### Study area

The study was conducted in the Metropolitan Region of Rio de Janeiro (MRRJ), Brazil, which is the second largest industrial center in Brazil and the third largest region in South America, as reported by the Brazilian Institute of Geography and Statistics (IBGE).<sup>24</sup> The MRRJ has a vehicular fleet of 3 million, including buses, trucks, and passenger cars, that run on gasoline, diesel,

ethanol, and natural gas (GNV), as reported by IBGE in 2021. Likewise, this region is also home to oil refineries, power plants, metallurgical and petrochemical industries.<sup>23</sup> The samples of PM<sub>10</sub> and PM<sub>25</sub> were collected at ten monitoring stations located at Bonsucesso (BS, 22°52'53"S and 43°15'17"W), Botafogo (BOT, 22°57'18" S and 43°10'57"W), Copacabana (COP, 22°57'47"S and 43°10'40"W), Gávea (GAV, 22°58'50"S and 43°13'58"W), Gericinó (GER, 22°50'42" S and 43°28'20" W), Lagoa (LAG, 22°58'33"S and 43°12'14"W), Recreio dos Bandeirantes (REC, 23°00'54"S and 43°28'55"W), Santa Cruz (SC, 22°54'14"S and 43°43'01"W), Castelo (CAS, 22°54'14"S and 43°43'01"W), and Urca (URC, 22°54'14"S and 43°43'01"W) (Figure 1). These monitoring stations were selected because some have similar urban/ residential areas with intense and light vehicular traffic and commerce, and industrial areas that encompass a diversity of industries and port.

Table 1 shows a brief description of the monitoring stations.

#### Measurements of PM<sub>2.5</sub> and PM<sub>10</sub> mass concentration

PM<sub>10</sub> and PM<sub>25</sub> samples were collected using glass fiber filters of 1.6 µm pore size (Whatman, Fisher Scientific, Maidstone, United Kingdom), for 24 h, once a week (usually weekdays), by the State Environmental Institute (INEA) (BS, BOT, COP, GER, LAG, REC, SC, CAS, and URC) and by the Atmospheric Chemistry Laboratory (LAQ) at GAV using monitoring systems following the Brazilian standards (ABNT-NBR 9547/86)<sup>25</sup> and the United States Environmental Protection Agency (US EPA) methods (Method IO-2.1).<sup>26</sup> For this, a High-Volume air sampler (Hi-Vol 3000, Energética, São Paulo, Brazil) with a mean air flow rate of 1.07 m<sup>3</sup> min<sup>-1</sup> were used. Filters were conditioned in a desiccator for 24 h and submitted to gravimetric analysis before and after samplings using an analytical balance (Gehaka AG200 ± 0.0001, Marte Científica, São Paulo, Brazil) to guarantee the correct particulate mass.

Relative humidity's were between 20 and 30% and temperatures between 20 and 25 °C were maintained during the weighing of the filters. For this work, all available  $PM_{2.5}$  and  $PM_{10}$  samples were analyzed to determine their particulate mass.

Measurement of BC concentration in  $\text{PM}_{\scriptscriptstyle 2.5}$  and  $\text{PM}_{\scriptscriptstyle 10}$  mass concentration

Black carbon (BC) determination in  $PM_{10}$  and  $PM_{2.5}$  selected were carried out using an optical transmissometer



**Figure 1.** PM<sub>2.5</sub> and PM<sub>10</sub> monitoring stations: BS: Bonsucesso, BOT: Botafogo, COP: Copacabana, GAV: Gávea, GER: Gericinó, LAG; Lagoa, REC: Recreio dos Bandeirantes, SC: Santa Cruz, CAS: Castelo, and URC: Urca. QGIS 3.26.3.

(SootScan, OT-21, Berkeley, Florida, USA) portable with an infrared beam ( $\lambda = 880$  nm), for non-destructive and rapid BC determination (analysis time is less than 1 min) on different types of filters. This equipment has a movable tray with two filter holder slots (inside and outside). The outside holder is used to measure light attenuation through the sample filter, while the inside holder maintains the reference (blank) which is measured simultaneously.<sup>27</sup> The equipment measures and compares the transmission intensity of light at 370 and 880 nm to determine the attenuation ATN (ATN =  $-\ln (T/T_0)$ ), where T is the transmission intensities of loaded filter and to the blank filter. It is assumed by the researchers that the ATN of the filter is proportional to the BC loading on the filter paper. The BC density is calculated by dividing the relative ATN by the specific attenuation coefficient  $\sigma$ ATN in units of  $m^2 g^{-1}$ , using the formula BC = ATN/ $\sigma$ ATN. This value is then converted into a BC concentration (µg m<sup>-3</sup>) using a conversion factor.28

Table 1. Brief description of monitoring stations of  $PM_{10}$  and  $PM_{2.5}$  in Rio de Janeiro's metropolitan region (MRRJ)

Station	Surrounding characteristics	Surface / km <sup>2</sup>	Population	PM fraction	Period and months of sampling
BS	area with intense industrial and commercial activities	2.19	18,711	PM <sub>10</sub>	2019 (February, April-July, September-December)
вот	a residential site with an intense flow of both light and heavy vehicles, mainly buses likewise intense commerce	4.80	82,890	PM <sub>10</sub>	2018 (January-April, July- December); 2019 (January, February, April, May, November, December)
СОР	a residential coastal neighborhood characterized by intense vehicular traffic and the presence of commercial enterprises	4.10	14,6392	PM <sub>2.5</sub>	2019 (January-August, October, December)
GAV	residential area, located a few meters from subway line and 8.5 km from a tunnel	2.58	16,003	PM <sub>2.5</sub> , PM <sub>10</sub>	2019 (January-December)
GER	urban area located near urban roads with heavy traffic	2.53	13,564	PM <sub>10</sub>	2019 (January-December)
LAG	a residential neighborhood in the southern zone of the city, with heavy vehicular traffic and commerce	5.11	21,198	PM <sub>2.5</sub> , PM <sub>10</sub>	2018 (January-July, October-December); 2019 (January, July, October- December)
CAS	a neighborhood, part of the center of Rio de Janeiro, covering the Rio Branco Avenue, airport Santos Dumont with heavy traffic, and commercial areas	5.42	29,555	PM <sub>10</sub>	2019 (February, March, May- December)
REC	urban area located in the west zone with light and heavy vehicle traffic	30.66	84,224	PM <sub>2.5</sub>	2018 (January-November); 2019 (January-June)
SC	located 5 km from the Santa Cruz Industrial District, has an intense flow of light and heavy vehicles	125	217,333	PM <sub>2.5</sub> , PM <sub>10</sub>	2018 for PM <sub>2.5</sub> (January- December), 2019 for PM <sub>10</sub> (July-November)
URC	a residential neighborhood in the southern zone of the city, with light traffic and near Guanabara Bay	2.32	7,061	PM <sub>2.5</sub>	2019 (July-December)

BS: Bonsucesso, BOT: Botafogo, COP: Copacabana, GAV: Gavea, GER: Gericino, LAG: Lagoa, CAS: Castelo, REC: Recreio, SC: Santa Cruz, URC: Urca;  $PM_{10}$ : particles < 10  $\mu$ m in diameter;  $PM_{2,5}$ : particles < 2.5  $\mu$ m in diameter.

#### Data analysis

The Wilcoxon non-parametric test was applied to compare  $PM_{2.5}$ ,  $PM_{10}$ , and BC concentrations among the monitoring stations. A value of p < 0.05 was considered significant. All statistical analyses were performed using CRAN R free software, version 4.0.2., and the package ggplot2.<sup>29</sup>

### **Results and Discussion**

### $PM_{10}$ and $PM_{2.5}$ concentrations

The annual average (period 2018 and 2019) of PM<sub>10</sub> (n = 103) and PM<sub>25</sub> (n = 139) concentrations MRRJ were  $38 \pm 18 \ \mu g \ m^{-3}$  (values between 6 to 109  $\ \mu g \ m^{-3}$ ) and  $10 \pm 7 \ \mu g \ m^{-3}$  (varying from 1 to 41  $\mu g \ m^{-3}$ ), respectively. Previous works were carried out in the same city and other cities inside the MRRJ between December 2003-February 2004<sup>22</sup> and January 2013-December 2015<sup>30</sup> and reported similar values of PM<sub>10</sub> (37 ± 12  $\mu$ g m<sup>-3</sup>; 28 ± 5  $\mu$ g m<sup>-3</sup>) and  $PM_{25}$  (12 ± 4 µg m<sup>-3</sup>; 10 ± 2 µg m<sup>-3</sup>), respectively. Here, the values found of PM<sub>10</sub> and PM<sub>25</sub> measured during 2018-2019 are very close to those reported in earlier research. This means that despite implementing numerous initiatives to reduce emissions such as encouraging the use of newer vehicles, and introducing alternative fuels such as biodiesel, natural gas, and hydrated alcohol, as well as increasing the use of renewable fuels, the aim is still not reached.

Figure 2 depicts the monthly variations of PM<sub>10</sub> and BC concentrations for six monitoring stations: (BOT, n = 11), (BS, n = 16), (CAS, n = 15), (GAV, n = 24), (GER, n = 25), and (SC, n = 9) during 2019. For 2018, there is only information from the monitoring site of BOT (n = 18), which is why no other figure was made, but that reported an average of  $PM_{10}$  and BC of 25 ± 11 and  $2.9 \pm 1.0 \ \mu g \ m^{-3}$ , respectively. From Figure 2, the BS monitoring station recorded higher PM<sub>10</sub> concentrations for most of the year (excluding November) compared to the other stations, with the highest concentration occurring in July (86  $\pm$  22 µg m<sup>-3</sup>). Higher PM<sub>10</sub> concentrations in BS may be related because this area contains intensive commercial (sixteen communities spread over about 800 km<sup>2</sup>) and industrial activities and a large circulation of motor vehicles (three main avenues as Brazil, Red line, and Yellow line). Measurements taken during the dry season (May to November) showed that PM<sub>10</sub> concentrations were higher at all monitoring locations than during the wet season (December to April). The minor PM concentration in the wet season may be explained by the fact that when a raindrop falls through the atmosphere, it attracts tens to

hundreds of small suspended particles through the clotting process, causing these particles to hit the ground.<sup>31</sup> This tendency is consistent with earlier findings reported by other study.32 Although none of the monitoring stations exceeded the Conselho Nacional do Meio Ambiente (CONAMA)33 limit of 120 µg m<sup>-3</sup> for 24-h averages, the BS (for most months), CAS (for some months), and SC (for some months) monitoring stations exceeded the World Health Organization (WHO)<sup>34</sup> limit of 45 µg m<sup>-3</sup> (Figure 2). The BS monitoring station recorded an annual mean concentration of PM<sub>10</sub> that exceeded 50 µg m<sup>-3</sup>, as reported by previous research.<sup>22</sup> Previous work<sup>30</sup> reported annual average PM<sub>10</sub> concentration for 2013 (23 µg m<sup>-3</sup>), 2014 (35 µg m<sup>-3</sup>), and 2015 (31 µg m<sup>-3</sup>) in GER,<sup>30</sup> which results are similar to the results of the present study  $(36 \pm 10 \,\mu\text{g m}^3)$  (Table 2). Gioda et al.<sup>35</sup> reported PM<sub>10</sub> concentrations from 1998 to 2013 in CAS with an annual average ranging from 35 to 45  $\mu$ g m<sup>-3</sup>, which is similar to those found in the present study  $(42 \pm 14 \ \mu g \ m^{-3})$ . CAS is a site located in the downtown area of Rio de Janeiro influenced by heavy vehicular traffic, large avenues, and urban characteristics. In contrast, the lowest PM<sub>10</sub> values  $(30 \pm 14 \,\mu\text{g m}^{-3})$  for the period 2003 to 2005 in SC were reported by Godoy et al.,<sup>22</sup> compared to this one  $(57 \pm 20 \ \mu g \ m^{-3})$ . This increase in PM<sub>10</sub> levels in the air in SC may be related to the increase in urban areas, vehicular traffic, and the presence of industrial activities. No significant differences were found between monitoring stations and months (p > 0.05).

Figures 3 and 4 present the monthly variation of  $PM_{25}$ and BC concentrations at three monitoring stations (LAG, n = 16); (REC, n = 18), and (SC, n = 21) during 2018, and at five monitoring stations ((COP, n = 19), (GAV, n = 22), (LAG, n = 20), (REC, n = 12) and (URC, n = 11)) during 2019. The REC site for both years registered the highest PM<sub>2.5</sub> concentrations for most of the months excluding the unmeasured months. May  $(30 \pm 11 \ \mu g \ m^{-3})$  and February  $(25 \pm 17 \ \mu g \ m^{-3})$  were the months with the highest PM<sub>2.5</sub> concentration for 2018 and 2019, respectively. The increase of PM<sub>2.5</sub> concentration and other pollutants in REC may be ascribed to the major influence of heavy traffic, which started in 2008 due to the implementation of an expressway for bus circulation (Bus Rapid Transit (BRT)-TransOeste) and the construction of new buildings, sports parks, and Village's Athletics for the 2016 Olympic games. No significant differences were observed in concentration between the monitoring stations LAG and SC for most months (except January and July). This similar behavior is likely due to the fact that LAG is influenced by heavy traffic, while SC is influenced by commercial, residential, and industrial areas.<sup>30</sup> Likewise, PM<sub>2.5</sub> concentration was found to be relatively higher during the dry season (May



**Figure 2.** Monthly concentration ( $\mu$ g m<sup>-3</sup>) of PM<sub>10</sub> and BC at six and seven monitoring stations during 2019, respectively. Same letter on each month indicates no significant differences (p > 0.05) between monitoring sites. Blank space is because it was not measured. BS: Bonsucesso, BOT: Botafogo, COP: Copacabana, GAV: Gavea, GER: Gericino, LAG: Lagoa, CAS: Castelo, REC: Recreio, SC: Santa Cruz, URC: Urca.



**Figure 3.** Monthly concentration ( $\mu$ g m<sup>-3</sup>) of PM<sub>2.5</sub> and BC at three monitoring stations during 2018. The same letter on each month indicates no significant differences (p > 0.05) between monitoring sites. Blank space is because it was not measured. BS: Bonsucesso, BOT: Botafogo, COP: Copacabana, GAV: Gavea, GER: Gericino, LAG: Lagoa, CAS: Castelo, REC: Recreio, SC: Santa Cruz, URC: Urca.

to November) compared to the wet season (December to April). This behavior has already been reported in several previously published works.<sup>32,36,37</sup> Most authors attribute the phenomenon to the cleaning effect of rain, which traps, and sediment suspended particles in the atmosphere.<sup>32,36,37</sup> PM<sub>2.5</sub> concentrations measured in REC exceed the 24-h average WHO limits for most months (except August and November) (Figure 2). In contrast, no violation of the CONAMA limits was observed in all monitoring stations

for PM<sub>2.5</sub>. One reason why the limits may not be exceeded is because the CONAMA values are more permissive and not all monitoring stations are installed directly over heavy traffic avenues or commercial centers, which have influence of PM<sub>2.5</sub>.

Previous studies performed in 2007 and 2009 in REC reported lower concentrations of  $PM_{2.5}$  (8 µg m<sup>-3</sup>).<sup>21,22</sup> On the other hand, Ventura *et al.*,<sup>30</sup> reported similar  $PM_{2.5}$  (11 to 16 µg m<sup>-3</sup> from 2013 to 2015) concentrations at this one



**Figure 4.** Monthly concentration ( $\mu$ g m<sup>-3</sup>) of PM<sub>2.5</sub> and BC at six and seven monitoring stations during 2019, respectively. Same letter on each month indicates no significant differences (p > 0.05) between monitoring sites. Blank space is because it was not measured. BS: Bonsucesso, BOT: Botafogo, COP: Copacabana, GAV: Gavea, GER: Gericino, LAG: Lagoa, CAS: Castelo, REC: Recreio, SC: Santa Cruz, URC: Urca.

 $(15 \pm 8 \,\mu\text{g m}^{-3})$ . Likewise, significant differences (p < 0.05) were found between REC and the other monitoring stations (LAG and SC) for all months.

Black carbon in PM<sub>10</sub> and PM<sub>2.5</sub>

Table 2 present the annual average ( $\pm$  standard deviation) of BC concentration in PM<sub>10</sub>, and PM<sub>2.5</sub> on the different monitoring stations installed in the MRRJ. The annual averages (period 2018 and 2019) of BC concentrations were  $3.3 \pm 1.5 \ \mu g \ m^{-3}$  (ranging from 0.9 to 7.3  $\mu g \ m^{-3}$ ) and  $1.9 \pm 0.7 \ \mu g \ m^{-3}$  (ranging from 0.8 to 3.9  $\mu g \ m^{-3}$ ) for PM<sub>10</sub> and PM25, respectively. A decrease in BC mass concentration from 2.4  $\pm$  1.3 to 1.9  $\pm$  0.7 µg m<sup>-3</sup> is observed compared to the previous work reported by Godoy et al.22 Similarly, the BC concentration in PM<sub>2.5</sub> had an average of  $1.8 \pm 0.9 \,\mu g \,m^{-3}$ (varying from 0.3 to 6.9 µg m<sup>-3</sup>) in Londrina (Paraná) for the period May 2017 to July 2018.38 Zhang et al.,39 in Beijing (China), observed a gradual decrease in BC and PM<sub>2.5</sub> concentrations after the application of a series of stringent measurements. Peláez et al.40 revealed a decrease in the levels of PM2.5 in some cities of South America including São Paulo and Bogota.

The reduction in the MRRJ may be ascribed to a variety of programs launched in Brazil and in the state of Rio de Janeiro such as the Alcohol National Program (PROALCOHOL-provided combustible fuel for light-duty vehicles),<sup>41</sup> program for controlling air pollution from motorcycles and similar vehicles (PROMOT-aimed to control the emissions of these vehicles) implemented in

2002, the National Biodiesel Production Program (PNPB) aims to promote domestic biodiesel production and lower emissions are released.<sup>42</sup> In the same perspective, the Vehicle Emission Control Program (PROCONVE) established by the Brazilian National Council (CONAMA) Resolution No. 18, regulates the control of air pollution generated by motor vehicles and establishes emission limits during vehicle manufacture.43 For this, new rules and guidelines were instituted, being mandatory the use of Arla-32 for every vehicle with the Selective Catalytic Reduction (SCR) system,<sup>44</sup> which considerably reduces (> 90%) the emission of pollutants by heavy vehicles powered by fossil fuels (diesel). Likewise, an analysis of the BRIC countries (Brazil, Russia, India, and China) indicated that despite Brazil having a comparatively high rate of renewable energy, it is necessary to increase preventive actions and major investment in renewable technology for reduce air pollution.45

For PM<sub>10</sub> in 2018, BC concentration was only measured in BOT with an annual average of 2.8 ± 0.9 µg m<sup>-3</sup> (ranging from 1.2 to 4.1 µg m<sup>-3</sup>). In 2019, the annual average in the MRRJ, BC concentration was recorded at 3.3 ± 1.5 µg m<sup>-3</sup> (ranging from 0.9 to 7.3 µg m<sup>-3</sup>) (Table 2). BC concentration in PM<sub>10</sub> decreased in the following order based on monitoring stations: BS > CAS > GER > BOT (2.9 ± 0.7 µg m<sup>-3</sup>) > SC > GAV. Besides, concentrations were noted to be relatively higher during the dry season compared to the wet season. July showed the highest values (Figure 2). Black carbon is not soluble in water; thus, a minor concentration of BC may be related to the

Monitoring stations <i>per</i> year	$PM_{10} / (\mu g m^{-3})$	$PM_{2.5} / (\mu g m^{-3})$	BC in $PM_{10} / (\mu g m^{-3})$	BC in $PM_{2.5}$ / (µg m <sup>-3</sup> )	
		2018			
BOT	25 ± 11 (3-52)	-	$2.9 \pm 1.0 (1.2-4.1)$	-	
LAG	—	$8 \pm 5^{a} (1-10)$	-	$1.9 \pm 0.8^{a} (0.2-3.6)$	
REC	—	$15 \pm 7^{\rm b} (2-32)$	-	$2.0 \pm 0.8^{a} (0.6-3.7)$	
SC	—	$8 \pm 6^{a} (2-33)$	-	$1.5 \pm 0.7^{\rm b} (0.1-2.9)$	
Average	$25 \pm 11$	$10.6 \pm 7.2$	$2.8 \pm 1.0^{\text{A}}$	$1.8 \pm 0.8^{\text{A}}$	
(Min-max)	(3-52)	(1.0-32.0)	(1.2-4.1)	(0.1-3.7)	
		2019			
BS	52 ± 20 (25-109)	-	$5.6 \pm 1.3^{a} (2.3-7.3)$	_	
BOT	33 ± 8 (20-48)	-	$2.9 \pm 0.7^{\rm b} (2.0-4.1)$	-	
CAS	$42 \pm 14$ (26-78)	-	$4.3 \pm 1.0^{\circ} (2.7-6.5)$	-	
COP	_	$7 \pm 3$ (3-12)	_	$1.7 \pm 0.7^{a} (0.2-2.5)$	
GAV	$23 \pm 12 (6-45)$	10 ± 8 (1-29)	$2.2 \pm 1.0^{d} (0.9-4.2)$	$2.1 \pm 0.9^{\text{b}} (0.9-3.9)$	
GER	36 ± 10 (20-53)	-	$3.6 \pm 1.1^{e} (2.1-5.9)$	-	
LAG	_	9 ± 5 (1-21)	-	$1.8 \pm 0.7^{\circ} (0.8-3.4)$	
REC	_	$14 \pm 11 (5-41)$	_	$2.2 \pm 0.6^{\text{b}} (1.3-3.1)$	
SC	$57 \pm 20$ (28-105)	-	$2.3 \pm 1.2^{d} (1.3-5.2)$	-	
URC	—	$10 \pm 7 (2-24)$	-	$1.1 \pm 0.7 \ (0.3-2.7)$	
Average	$38 \pm 18$	$10 \pm 7$	$3.3 \pm 1.5^{\text{A}}$	$1.8 \pm 0.8^{\text{A}}$	
(Min-max)	(6-108)	(1-41)	(0.92-7.3)	(0.2-3.9)	

**Table 2.** Annual average of particulate matter ( $PM_{10}$  and  $PM_{2.5}$ ) and black carbon (BC) concentrations (min-max) at different monitoring stations from the Metropolitan Region of Rio de Janeiro for 2018 and 2019

Each vertical column followed by the same letter does not differ significantly (p > 0.05). (–) data was not measured. BOT: Botafogo, LAG: Lagoa, REC: Recreio dos Bandeirantes, SC: Santa Cruz, BS: Bonsucesso, CAS: Castelo, COP: Copacabana, GAV: Gavea, GER: Gericino, and URC: Urca; PM<sub>10</sub>: particles < 10 µm in diameter; PM<sub>25</sub>: particles ≤ 2.5 µm in diameter.

wet deposition (process removing atmospheric particles containing BC). BC concentrations in PM<sub>2.5</sub> for 2018 and 2019 were reported as  $1.9 \pm 0.7 \ \mu g \ m^{-3}$  (ranging from 0.8 to 3.7  $\ \mu g \ m^{-3}$ ) and  $1.9 \pm 0.7 \ \mu g \ m^{-3}$  (ranging from 0.8 to 3.9  $\ \mu g \ m^{-3}$ ), respectively. BC concentration in PM<sub>2.5</sub> decreased in the following order in 2018 REC > LAG > SC, while in 2019 showed the following order REC > GAV > LAG > COP > URC. In terms of order, a similar behavior between the years was observed, with REC showing higher BC concentrations for both 2018 (1.9 ± 0.8  $\ \mu g \ m^{-3}$ ) and 2019 (2.2 ± 0.6  $\ \mu g \ m^{-3}$ ). Here, a slightly increased BC concentration in 2019 compared to 2018 is also observed. However, no significant differences (*p* > 0.05) were found.

Likewise, as shown previously (Figures 3 and 4), BC concentrations for both years were higher in the dry season than wet season. Similar findings were reported by Santanna *et al.*,<sup>36</sup> and de Miranda *et al.*,<sup>23</sup> in other cities of Brazil.

Particulate matter in metropolitan areas is mainly composed of organic (BC, polycyclic aromatic hydrocarbons (PAHs)) and inorganic compounds.<sup>46</sup> In addition, carbonaceous species, BC, and organic carbon constitute a major and sometimes dominant fraction of PM<sub>2.5</sub> whereas PM<sub>10</sub> is composed of aerosol from street dust, nitrated and

chlorides of sodium, and suspended soil.<sup>47</sup> Black carbon contribution in this study was quite variable, accounting for 11 to 24% of the fine particle fraction ( $PM_{2.5}$ ) and 9-11% of the coarse particle fraction ( $PM_{10}$ ). Previously, Soluri *et al.*,<sup>21</sup> Godoy *et al.*,<sup>22</sup> and de Miranda *et al.*,<sup>23</sup> reported a proportion of BC in  $PM_{2.5}$  ranging from 17-29, 18-31; and 20%, respectively, which are consistent with our findings. For  $PM_{10}$ , BC accounted for 4-14% in Makassar, Indonesia, which is similar to what was found in this study (4 to 11%). As BC is considered as a marker of vehicular traffic and chemically is main associated to the fine particulate matter.<sup>13</sup> These BC fractions in  $PM_{10}$  and  $PM_{2.5}$  indicate that probably traffic emissions are the main responsible for a significant fraction of both aerosol mass, since trucks and automobile emissions are the largest contributors of BC in urban areas.

A comparison of the average BC mass concentration measured in  $PM_{10}$  and  $PM_{2.5}$  reported at different locations in Brazil and other countries is shown in Table 3. The average BC mass concentration in  $PM_{2.5}$  at MRRJ (1.9 ± 0.7 µg m<sup>-3</sup>) was lower than those reported in other cities' measurements, such as 7.6 µg m<sup>-3</sup> in São Paulo, Brazil,<sup>48</sup> 5.4 µg m<sup>-3</sup> in Beijing, China,<sup>39</sup> 3.2 µg m<sup>-3</sup> in Buenos Aires, Argentina,<sup>49</sup> and 2.2 µg m<sup>-3</sup> in Curitiba, Brazil.<sup>50</sup> Our lowest BC concentrations compared to other cities may be

due to the fact that São Paulo, Beijing and Buenos Aires have a larger population, territorial extension, vehicular fleet and industries. For instance, de Miranda *et al.*<sup>51</sup> argue that the main source of BC in São Paulo is traffic, which is a good tracer of heavy vehicles. It also indicates that BC concentrations are influenced by the wind direction (windward and leeward of the sampling site) due to the transport of burned biomass from the interior.

In the case of Curitiba, it may be attributed to the fact that around 54% of the population concentrates in the metropolitan region, and because a largest regional extension of the city houses industries as chemical and petrochemical, pharmaceutical, steel, civil construction, furniture and others.<sup>52</sup> Higher values compared to other cities include 1.1 µg m<sup>-3</sup> at Cuiabá, Brazil,<sup>36</sup> 1.7 µg m<sup>-3</sup> in Londrina Brazil,38 1.8 µg m-3 at Caracas, Venezuela,11 1.2 µg m<sup>-3</sup> in Helsinki, Finland,<sup>47</sup> and 1.7 µg m<sup>-3</sup> at Chungcheong, Korea.<sup>53</sup> Higher concentrations of BC found in this study may be due to the fact that MRRJ has a larger population, territorial extension, industries, and vehicular fleet. The lowest BC values reported in Helsinki (Finlandia) may be due to the fact that this city is known as clean and with great air quality. Among the actions carried out are the phase-out of personal vehicle ownership by 2025, government investment in renewable energy, protection of lakes and forests, promotion of the adoption of electric vehicles, reduced population, limitations on the practice of coal-fired power plants, waste burning, deforestation, and transportation.54,55 Similarly, the average BC mass concentration in  $PM_{10}$  (3.3 ± 1.5 µg m<sup>-3</sup>) was higher compared to the other cities, i.e., 1.3 µg m<sup>-3</sup> at Cuiabá, Brazil,<sup>36</sup> 1.2 µg m<sup>-3</sup> in Helsinki, Finland,<sup>44</sup> and

2.0 µg m<sup>-3</sup> at Makassar, Indonesia.<sup>56</sup> Likewise, previous works<sup>21-23</sup> reported higher BC concentrations in PM<sub>2.5</sub> for the MRRJ. The differences among BC concentration found in the different monitoring stations are probably related to local pollutants, as that is highly dependent on the sources that are very close to the sampling. Furthermore, as most monitoring stations are located near residential and commercial areas, another source of BC may be associated to cooking. Typically, at almost all cities, the BC mass concentration values were higher in the dry season compared to the wet season. It is worth mentioning that the MRRJ presents distinct characteristics of topography, socioeconomic development, and traffic, which contribute to different levels of air quality. Studies on BC and PM in Rio de Janeiro can inform policy decisions concerning air quality standards, emission controls, and urban development. This information can assist policymakers in prioritizing initiatives with the greatest impact on reducing pollution levels and enhancing public health. No studies were found measuring BC during the same period (2018-2019), which is why only works related to other cities from Brazil, and some of other countries were selected.

Figure 5 shows the spearman correlation between BC and  $PM_{10}$  ((BS), (BOT), (CAS), (GER), and (SC)) and BC and  $PM_{2.5}$  ((COP), (GAV), (LAG), (REC), and (URC)). Correlation coefficient (r<sup>2</sup>) ranged from 0.46 to 0.77 for BC<sub>PM10</sub>, while for BC<sub>PM2.5</sub> varied from 0.34 to 0.75. Likewise, it was observed different correlation on all sites, with higher correlation found in BS (r<sup>2</sup> = 0.77) and URC (r<sup>2</sup> = 0.75) and lower in BOT (r<sup>2</sup> = 0.46) and GAV (r<sup>2</sup> = 0.0.33) for PM<sub>10</sub> and PM<sub>2.5</sub>, respectively. Theses finding indicates differences in sources on each

Table 3. Comparison of BC mass concentration measured in PM10 and PM25 at various locations of Brazil and other countries

Place	Location	Period	BC in PM <sub>2.5</sub> / (µg m <sup>-3</sup> )	BC in PM <sub>10</sub> / (μg m <sup>-3</sup> )	Reference
Caracas, Venezuela	urban	June 2008 and October 2019	$1.8 \pm 0.9$		11
Londrina, Brazil	urban	May 2017 to July 2018	$1.7 \pm 0.60$		13
Rio de Janeiro, Brazil	urban	September 2003 to August 2004	$2.3 \pm 0.7$		21
Rio de Janeiro, Brazil	urban	September 2003 to December 2005	$2.4 \pm 1.3$		22
Rio de Janeiro, Brazil	urban	June 2007 to August 2008	$3.4 \pm 2.5$		23
Cuiabá, Brazil	forest	June 2004 to April 2005	$1.1 \pm 0.6$	$1.3 \pm 0.7$	36
Beijing, China	urban	December 2012 to January 2020	$5.4 \pm 3.2$		39
Helsinki, Finland	urban	July 2000 to July 2001	$1.2 \pm 0.5$	$1.2 \pm 0.6$	47
São Paulo, Brazil	urban	July to September 1997	7.6	-	48
Buenos Aires, Argentina	sub urban	November 2014 to March 2016	3.2		49
Curitiba, Brazil	urban	June 2004 to April 2005	2.2		50
Chungcheong, Korea	urban	September 2015 to April 2016	$1.7 \pm 0.5$		53
Makassar, Indonesia	urban	February 2012 to January 2013		$2.0 \pm 0.9$	56
Rio de Janeiro, Brazil	urban	January 2018 to December 2019	$1.9 \pm 0.7$	$3.3 \pm 1.5$	this study

BC: black carbon;  $PM_{10}$ : particles < 10 µm in diameter;  $PM_{2.5}$ : particles ≤ 2.5 µm in diameter.



Figure 5. Correlations between BC and PM<sub>10</sub> and PM<sub>2.5</sub> concentrations (µg m<sup>-3</sup>) at all monitoring stations.

site. Choi *et al.*<sup>57</sup> indicated that all motorized transport using diesel fuel releasing great quantities of BC. Thus, a higher correlation probably is related a high diesel engine exhaust emission. BS is recognized as a place with intense vehicular traffic where huge cars circulate that use diesel as the main source of combustion, while URC has the "Bondinho" cable car which is quite visited by tourists who arrive daily through their own cars or taxi. Also close to this place is Botafogo beach, which serves as a depot or port area for diesel-powered ships. Besides, currently, there are few measurements of BC in  $PM_{10}$  and  $PM_{2.5}$  in internal or external environments from Brazil.

# Conclusions

Analyzing the levels of black carbon (BC) and particulate matter (PM) in the Metropolitan Region of Rio de Janeiro (MRRJ) is essential for comprehending the effects of air pollution on public health and climate change in this area. The main conclusion is that there was a decrease in the concentrations of PM<sub>10</sub> and PM<sub>2.5</sub> in the MRRJ between the periods of 2018-2019 and previous research, which may be attributed to the implementation of measures to reduce emissions from industry and cars, promote the use of newer vehicles and introduce alternative fuels. However, some monitoring stations still exceeded the WHO limit of 45  $\mu$ g m<sup>-3</sup> for PM<sub>10</sub> concentrations, and the BS monitoring station recorded an average annual PM<sub>10</sub> concentration that exceeded 50 µg m<sup>-3</sup>. The text also discusses the monthly and annual variations of PM10 and BC concentrations in different monitoring stations in MRRJ and their possible causes.

For BC, it was observed a decrease in the concentration in recent years. Annual BC concentration averages were  $3.3 \pm 1.5 \ \mu g \ m^{-3}$  for PM<sub>10</sub> and  $1.9 \pm 0.7 \ \mu g \ m^{-3}$  for PM<sub>2.5</sub> in 2018, and  $1.9 \pm 0.7 \ \mu g \ m^{-3}$  for PM<sub>10</sub> and PM<sub>2.5</sub> in 2019. This slight reduction in the concentration of BC may is attributed to the attempt to reduce PM<sub>2.5</sub> and PM<sub>10</sub> through several programs launched in Brazil and the state of Rio de Janeiro, such as the National Alcohol Program, the Air Pollution Control Program by Motorcycles and Similar Vehicles and the National Biodiesel Production Program, however, more data is needed to corroborate this information. The study also found that BC concentrations were higher in the dry season than in the rainy season and that BC concentration in PM<sub>2.5</sub> decreased at some monitoring stations between 2018 and 2019.

To further advance the research on BC in Rio de Janeiro, it is necessary to explore the varying spatial and temporal distribution of this pollutant. By examining the concentrations of particulate matter and BC in different neighborhoods and at different times of the day, we can gain fresh insights into where people are at a higher risk of exposure, and thus inform public health measures. Additionally, understanding the origins and concentrations of these pollutants can help mitigate their environmental impact on climate change and ecosystems. Ultimately, this research can inform policy decisions on air quality standards, emission controls, and urban development, leading to initiatives with the greatest impact on reducing pollution levels and improving public health.

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### **Author Contributions**

Alex Huaman De La Cruz was responsible for data curation, writingoriginal draft preparation; Luis Fhernando M. da Silva for visualization, methodology; Felipe Luiz M. Silva for conceptualization; Vanessa A. dos Anjos for methodology, formal analysis; Ricardo Henrique M. Godoi for writing-reviewing and editing; Adriana Gioda for supervision, writing-reviewing, and editing.

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