

## Black Carbon Associated to PM<sub>1,0</sub> and PM<sub>2,5</sub>: Mass Variation due to Combustion of Biodiesel/Diesel Blends (B5, B6, B7 and B8)

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The present study aims to quantify black carbon (BC), particulate matter (PM<sub>1,0</sub> and PM<sub>2,5</sub>, particles with diameter  $\leq 1.0$  and  $2.5 \mu\text{m}$ , respectively) levels and their variability during the combustion of biodiesel/diesel blends used in heavy-duty vehicles. The samplings were conducted in the years 2014, 2016 and 2017 inside a semi closed bus station, a direct source of emission from engines burning blends of B5 to B8 biodiesel/diesel. Diesel engines using B5 and B6 presented a high contribution of BC in PM<sub>1,0</sub> fraction representing 95 and 98% in mass, respectively. Results obtained from engines fueled with B7 and B8 diesel blends showed about 47% BC mass contribution in fine PM. The ratio PM<sub>1,0</sub>/PM<sub>2,5</sub> remained relatively constant showing that the fine PM mass did not change significantly. Those measurements are important to follow the behavior of the addition of biodiesel in the diesel fuel as well as to help indicate a fingerprint of BC and PM<sub>2,5</sub> concentrations in biodiesel increase.

**Keywords:** diesel emissions, diesel blends, particulate matter, bus station, black carbon equivalent

### Introduction

Black carbon (BC) pollution has become a crucial issue due to its multiple effects on urban air quality, global climate change and public health.<sup>1</sup> Liu *et al.*<sup>2</sup> pointed an increasing number of air pollution source apportionment studies worldwide that have focused on the BC fraction of ambient particulate matter (PM) given its correlation with adverse public health and climate impacts. BC is mainly associated to fine PM and is one of the most harmful air pollutants. It can remain in the air for a long time and due to its small size, BC in fine particles can penetrate deeply into the human respiratory system.<sup>3</sup>

Janssen *et al.*<sup>4</sup> showed that BC is a valuable additional air quality indicator. Moreover, BC could be particularly useful to evaluate not only the health risks of air pollution dominated by primary combustion emissions, but also the benefits of traffic abatement measures. The International Agency for Research on Cancer (IARC) re-evaluated the carcinogenicity of diesel exhaust and gasoline engine exhaust in June 2012, upgrading diesel exhaust from a

Group 2A probable human carcinogen to a Group 1 known human carcinogen.<sup>5</sup>

Vehicular emissions contribute significantly to air pollution in urban areas and heavy-duty vehicles using diesel/biodiesel blends are responsible for fine particle and nitrogen oxides (NO<sub>x</sub>) emissions, among other pollutants.<sup>6</sup> In order to reduce the impact of some pollutants from vehicular emissions, the use of alternative fuel blends have been employed. To have a better understanding of such emissions, real life condition studies have been carried out.<sup>6-8</sup>

Results obtained from measurements at bus stations represent a bulk of the emissions from a large number of vehicles under operational conditions.<sup>6,7,9</sup> In this way, studies have been conducted inside the Central Bus Station in Londrina since 2002. Along these years, toxic species such as polycyclic aromatic hydrocarbons (PAH) and their nitro-derivatives,<sup>7,10</sup> carbonyl compounds and major ions,<sup>11-13</sup> among others were determined following the increase in the amount of biodiesel in diesel fuel blend according to Brazilian Legislation for 3% of biodiesel added to fossil diesel (B3) up to B8.

The present study aims, for the first time, to quantify BC, PM<sub>1,0</sub> and PM<sub>2,5</sub> (particles with diameter  $\leq 1.0$  and

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2.5  $\mu\text{m}$ , respectively) levels and their variability during combustion of biodiesel/diesel blends used in heavy-duty vehicles under real operational conditions. The samplings were conducted in the years 2014, 2016 and 2017 inside a semi closed bus station, which is a direct source of emission from engines burning blends of B5 up to B8 biodiesel/diesel. The results can be useful as reference values in future studies on emission inventories and mainly in vehicular emission control strategies considering the expanded share of biodiesel in the diesel mixtures.

## Experimental

### Sampling site description

Field measurements were carried out inside the Central Bus Station in downtown Londrina (23.308°S and 51.161°W). The station is a two-story building and the samples were collected on the ground floor. This place is semi-closed with low air circulation where the average speed of the buses circulating is 20 km h<sup>-1</sup>. The sampling site selection took into consideration the place where urban heavy-duty diesel buses frequently enter and exit the terminal and where several passengers wait for them. No other activity takes place on the ground floor, except the traffic of buses arriving and departing. Parked vehicles in the area remain with their engines off. The specifications of biodiesel/diesel blend (B3/B4/B5/B6/B7/B8) and biodiesel (B100) used in Brazil in 2008, 2014, 2016 and 2017 account Brazilian resolutions (ANP resolutions No. 15/2006, No. 07/2008, No. 45/2014 and No. 30/2016)<sup>14</sup> are presented in Table 1.

### Sampling and analysis

Measurements were made over a period of four years (2014–2018) inside Londrina Central Bus Station, following the increase of biodiesel in diesel blends (B5,

B6, B7, B8). A number of 150 samples were collected along five campaigns. The first campaign occurred from April 22 to 29, 2014; the second, from August 24 to 31, 2014; the third, from October 16 to 31, 2016; the fourth, from December 02 to 31, 2016 and the fifth campaign, from June 13 to 30, 2017. The samples were collected for 14 h a day including the periods of increased circulation of buses. The metropolitan bus fleet had not changed from 2014 to 2017.

Samples of PM<sub>1.0</sub> and PM<sub>2.5</sub> were collected using cyclones (PM<sub>1.0</sub> URG-2000-30EH and PM<sub>2.5</sub> URG-2000-30EH, URG® Corporation, USA) operated at flow rate of 16.7 L min<sup>-1</sup> using glass fiber filters of 47 mm (Sartorius, Germany). Collectors were connected to a diaphragm pump and the flow rates were controlled by critical orifices. The flow rates were measured daily by rotameters. Temperature and relative humidity were obtained with Data Logger HOBO (USA).

The glass filters were treated at 90 °C (Biopar-S150ST, Brazil) for 12 h, placed individually in a Petri dish in a desiccator containing silica for 24 h and put in a room with controlled temperature and humidity (22 ± 3 °C and 50 ± 2%). Before sampling, filters were kept in the same room for 24 h and then, they were weighed. Along with the samples, 10% filter blanks were selected.<sup>15</sup> After sampling, filters were stored in Petri dishes and transported to the laboratory. The PM mass was obtained based on the difference between the mass of the filter before and after each collection by using the ultra-analytical balance (Mettler Toledo, AX26, Switzerland) with accuracy of 1.0  $\mu\text{g}$ .

After gravimetric measurements, the concentration of BC was determined through the light reflectance method, using the EEL 43D Smoke Stain Reflectometer (Diffusion Systems Ltd., London, UK).<sup>16</sup> BC concentration was obtained from reflectance value, filter area and sample volume.<sup>17</sup> The conversion of the reflected light is inversely proportional to the light absorbed, which is a function of

**Table 1.** Biodiesel/diesel blend (B3/B4/B5/B6/B7/B8) and biodiesel (B100) specification used in Brazil in 2008, 2014, 2016 and 2017<sup>14</sup>

Characteristic	Biodiesel/diesel blend (B3-B5)	Biodiesel/diesel blend (B6-B8)	Biodiesel <sup>a</sup> (B100)	Biodiesel <sup>b</sup> (B100)
Density at 20 °C / (kg m <sup>-3</sup> )	820.0-880.0	817.8-865.0	850.0-900.0	850.0-900.0
Viscosity at 40 °C / cSt	2.0-5.0	1.9-4.1	3.0-6.0	3.0-6.0
Water / (mg kg <sup>-1</sup> )	–	200	500	200
Carbon residue / wt.%	0.25	0.25	0.050	–
Cetane index	42	48	–	–
Sulfur / (mg kg <sup>-1</sup> )	500	10	50	10
Corrosiveness (copper, 3 h at 50 °C)	1	1	1	1
Flashpoint / °C	38	38	100	100
Total glycerol / wt.%	–	–	0.25	0.25

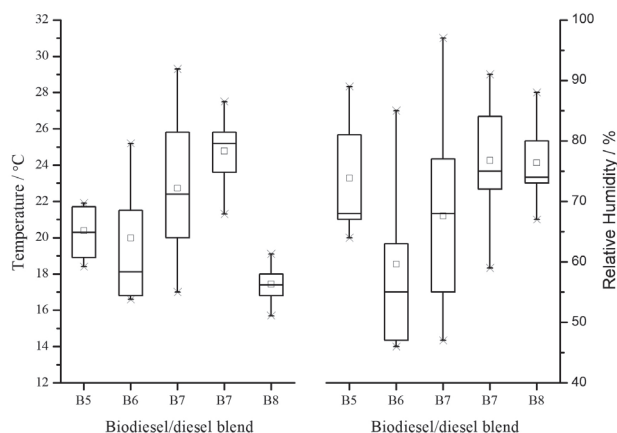
<sup>a</sup>From 2005 to 2014; <sup>b</sup>from 2014 until nowadays.

the quantity of absorbent material present in the sample. BC concentration is given in  $\mu\text{g m}^{-3}$ .

## Results and Discussion

### PM<sub>1.0</sub> and PM<sub>2.5</sub> mass concentration

One hundred and fifty samples were collected along five campaigns carried out in Londrina Central Bus Station. Within those periods the average ambient temperature ranged from 9.4 to 37 °C and the relative humidity varied from 46 to 97% (Figure 1).

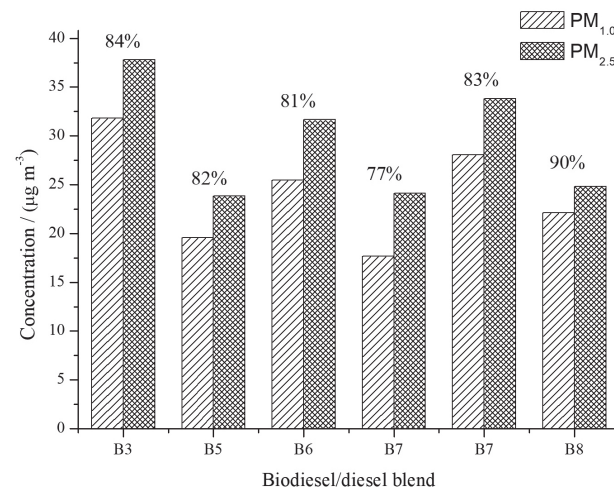


**Figure 1.** Minimal, maximal and mean temperatures (°C), average relative humidity with associated standard deviation (SD) in the campaign periods, Londrina, Brazil.<sup>18</sup>

Mass concentrations of fine particle fraction were obtained and compared with results from measurements carried out in 2008, in the same place and diesel engine fueled with B3 biodiesel/diesel blend.<sup>6</sup> Table 2 shows average concentrations of PM<sub>1.0</sub>, PM<sub>2.5</sub> and the ratio PM<sub>1.0</sub>/PM<sub>2.5</sub>, which were calculated for each campaign with different blends of biodiesel/diesel (B3, B5, B6, B7 and B8).

While B3 blend was used, the levels of PM<sub>1.0</sub> and PM<sub>2.5</sub> were higher than the other biodiesel/diesel blends. Results from samples collected inside the central bus

station suggest that in real condition, slow moving buses that run with the addition of biodiesel to diesel may cause a decrease in the fine PM concentration. The ratio PM<sub>1.0</sub>/PM<sub>2.5</sub> remains relatively constant with a mean of 0.83 and a variation of 0.04 (4.8%). Figure 2 shows the comparison and the percentage of PM<sub>1.0</sub> in PM<sub>2.5</sub>. The high contribution of PM<sub>1.0</sub> (average of 83%) in the fine particle fraction is evident and is worrying due to the environmental and health implications.



**Figure 2.** Comparison between PM<sub>1.0</sub> and PM<sub>2.5</sub> concentration and the relative contribution of PM<sub>1.0</sub> in PM<sub>2.5</sub> in dependence of biodiesel/diesel blends.

Metropolitan diesel/biodiesel sulfur content is showed in Table 1. Sulfur content decreased from 500 (B3) to 10 mg kg<sup>-1</sup> (B5-B8). To compare, PM<sub>1.0</sub> mean concentrations decrease from 31.8 (B3) to 21.6  $\mu\text{g m}^{-3}$  (B8) and for PM<sub>2.5</sub> the variation was from 38.8 to 24.9  $\mu\text{g m}^{-3}$ . These results show a reduction of about 30% in the fine PM concentration. For the others blends (B5 to B8) sulfur content was the same (10 mg kg<sup>-1</sup>) and indicate no effect on PM and BC concentration.

As can be seen in Figure 1, the variation in temperature and relative humidity inside the urban station during the campaigns have not significant changes that justify

**Table 2.** Range of concentrations of PM<sub>1.0</sub> and PM<sub>2.5</sub> and the ratio PM<sub>1.0</sub>/PM<sub>2.5</sub> inside Londrina Central Bus Station with the use of B3, B5, B6, B7 and B8 biodiesel/diesel blends

Biodiesel/diesel	No. of samples	PM <sub>1.0</sub> / ( $\mu\text{g m}^{-3}$ )	PM <sub>2.5</sub> / ( $\mu\text{g m}^{-3}$ )	Ratio PM <sub>1.0</sub> /PM <sub>2.5</sub>	Reference
B3	24	20.6-42.7	24.8-48.2	0.84	6
B5	16	12.8-26.7	15.2-33.4	0.82	this work
B6	12	17.0-31.6	21.2-37.4	0.81	this work
B7	30	6.7-21.1	12.1-35.5	0.77	this work
B7	60	16.0-39.6	22.1-47.6	0.83	this work
B8	26	12.2-30.9	15.7-32.7	0.90	this work

PM<sub>1.0</sub> and PM<sub>2.5</sub>: particles with diameter less than 1.0 and 2.5  $\mu\text{m}$ , respectively.

influencing the results of the concentrations of the PM and BC.

#### BC levels in PM<sub>1.0</sub> and PM<sub>2.5</sub> samples (BC<sub>1.0</sub> and BC<sub>2.5</sub>)

Table 3 presents the results for BC mass concentration associated to PM<sub>1.0</sub> and PM<sub>2.5</sub> at the bus station with engines in real operation using B5, B6, B7 and B8 biodiesel/diesel fuels. Mass concentration of BC was found and ranged from 8.7 to 24.9 µg m<sup>-3</sup>. The highest average of BC concentrations was measured at B6 campaigns with concentration ranges of 24.8 ± 7.3 and 24.9 ± 7.1 µg m<sup>-3</sup> in PM<sub>1.0</sub> and PM<sub>2.5</sub>, respectively, indicating that on average, about 98% of BC mass was contained in the finer fraction of the particulate matter. Slightly lower BC values were observed for B7 first campaign with values of 8.7 ± 5.6 and 10.8 ± 7.5 µg m<sup>-3</sup> in PM<sub>1.0</sub> and PM<sub>2.5</sub>, respectively. It should be noted that in the second B7 measurements, the elevation of BC and PM mass influenced the number of buses whose results increased despite the fact that it was Christmas time. In these periods in Brazil, shops have extended opening hours, increasing four hours daily and consequently the availability of public transport also increases.

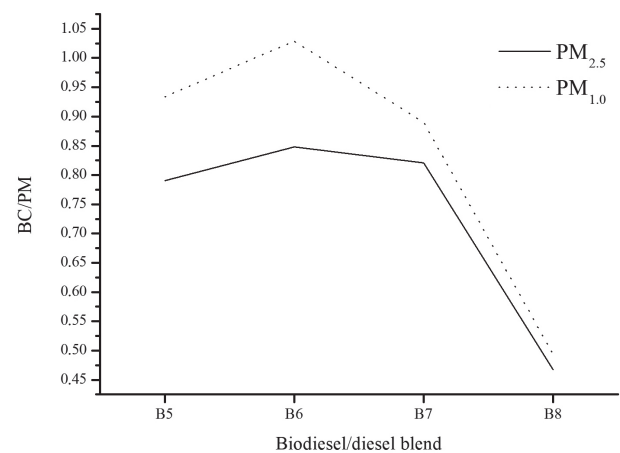
Diesel engines using B5 and B6 showed high contribution of BC in PM<sub>1.0</sub> fraction representing 95 and 98% in mass, respectively. Results for engines using B7 and B8 diesel blends showed about 47% BC mass contribution in fine PM.

The BC contribution to PM<sub>1.0</sub> fine particles is an important factor which determines the toxicity of aerosol particles.<sup>4</sup> Our measurements show the decrease of BC amount in fine PM emitted from buses in real operation. This is a positive result that indicates a significant contribution of the biodiesel addition in diesel blends.

#### Ratio of BC<sub>2.5</sub>/PM<sub>2.5</sub> and BC<sub>1.0</sub>/PM<sub>1.0</sub>

For traffic source emissions, Chow *et al.*<sup>19</sup> reported the ratio BC<sub>2.5</sub>/PM<sub>2.5</sub> higher than that from other sources. The

highest BC<sub>2.5</sub>/PM<sub>2.5</sub> ratio was 0.77, observed in heavy-duty diesel source testing. Figure 3 shows the ratios BC<sub>2.5</sub>/PM<sub>2.5</sub> and BC<sub>1.0</sub>/PM<sub>1.0</sub> for the four biodiesel/diesel blends used in the buses over the years of sampling. Some differences of the two ratios could be observed mainly for the B6 measurements when the relative humidity was lower than that in the other periods. The relative humidity inside the station ranged from 46 to 71% (60 ± 14%) collaborating for particles resuspension. According to Liu *et al.*<sup>2</sup> ambient air, low BC<sub>2.5</sub>/PM<sub>2.5</sub> suggested mainly the influence of solid fuel sources (e.g., coal and biomass burning), while high BC<sub>2.5</sub>/PM<sub>2.5</sub> indicated predominant influence by liquid fuel (traffic) sources. We investigated the profile originating from a primary source of mobile traffic (liquid fuel) collected at a place exclusively affected by bus traffic and different fuel blends. These results are very important as they allow us to recognize a fingerprint and therefore help identify other sources of air pollution. Figure 3 shows the profile of BC/PM with significant rate decrease depending on the biodiesel/diesel blends. Certainly, this information can be used to assess real world situation, where the contribution of BC is considered a result of several complex sources.



**Figure 3.** Ratio BC<sub>1.0</sub>/PM<sub>1.0</sub> and BC<sub>2.5</sub>/PM<sub>2.5</sub> for biodiesel/diesel blends collected in Londrina Central Bus Station, Brazil.

**Table 3.** BC, PM<sub>1.0</sub> and PM<sub>2.5</sub> mean concentrations and associated standard deviation, and the percentage contribution of BC (values within parentheses) to PM<sub>1.0</sub> and PM<sub>2.5</sub> inside Londrina Central Bus station with combustion of B5, B6, B7 and B8 biodiesel/diesel fuel

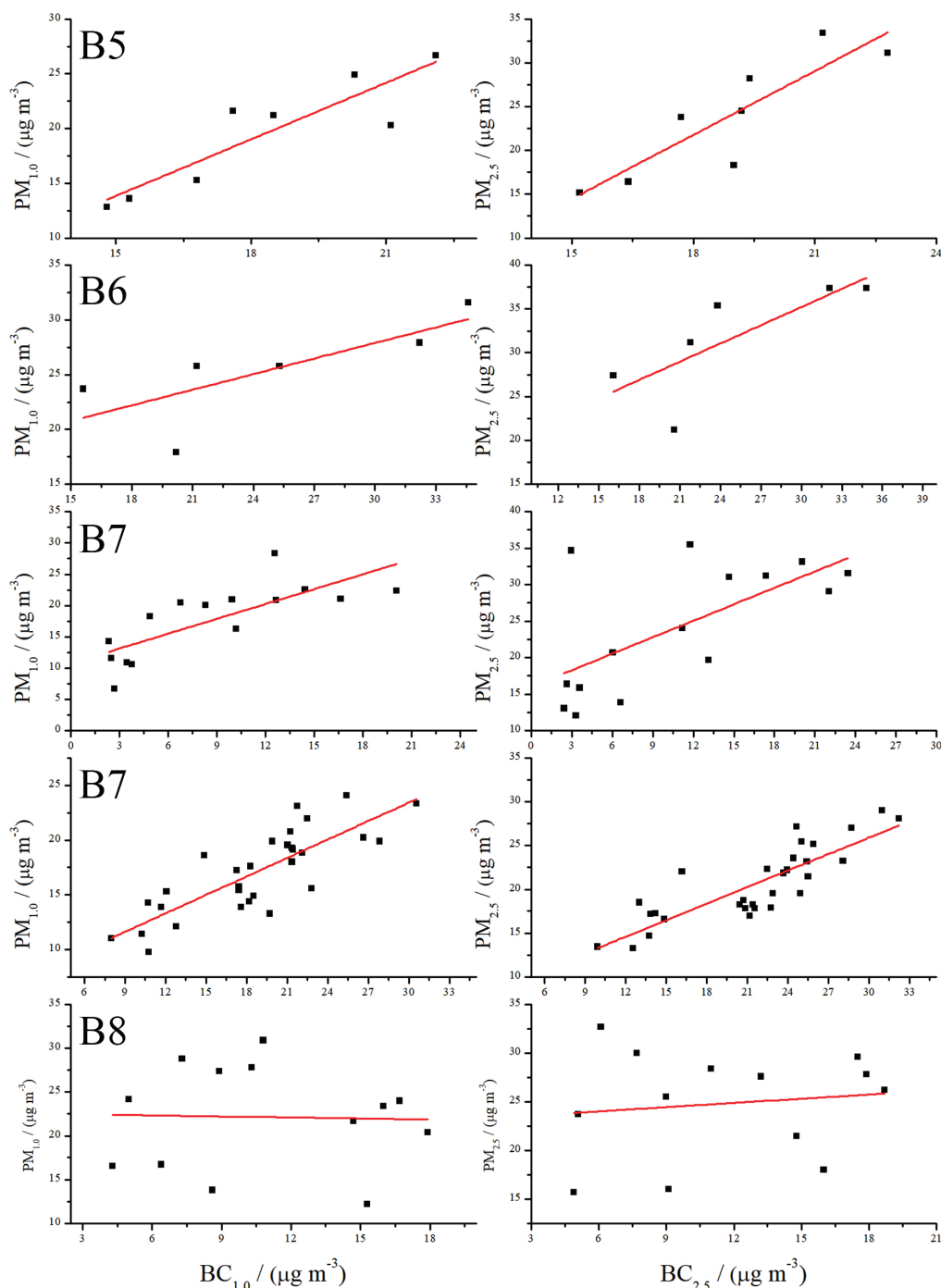
Biodiesel/diesel	BC <sub>1.0</sub>	PM <sub>1.0</sub>	BC <sub>2.5</sub>	PM <sub>2.5</sub>
	Mean ± SD / (µg m <sup>-3</sup> )			
B5	18.3 ± 2.7	19.2 ± 5.2 (95%)	18.9 ± 2.4	23.9 ± 6.8 (79%)
B6	24.8 ± 7.3	25.4 ± 4.6 (98%)	24.9 ± 7.1	31.7 ± 6.4 (78%)
B7	8.7 ± 5.6	17.7 ± 5.8 (49%)	10.8 ± 7.5	24.1 ± 8.6 (45%)
B7	18.7 ± 5.5	28.0 ± 6.2 (67%)	21.5 ± 5.7	33.8 ± 7.0 (64%)
B8	10.9 ± 4.7	22.1 ± 5.9 (49%)	11.6 ± 5.0	24.8 ± 5.5 (47%)

BC: black carbon; PM<sub>1.0</sub> and PM<sub>2.5</sub>: particles with diameter less than 1.0 and 2.5 µm, respectively; SD: standard deviation.

Figure 4 shows the correlations between BC and  $PM_{1.0}$  and  $PM_{2.5}$ . By comparing the variables of interest in the five campaigns, was found a reduction of the correlation coefficient  $R^2 = 0.77$  (B5) to  $-0.09$  (B8) for  $BC_{1.0}$ , while for  $BC_{2.5}$  the correlation decreases from  $R^2 = 0.73$  to  $-0.07$ . Those values show the clear alteration in the emission of BC with the decrease of diesel content and a possible independence with the particulate formation.

## Conclusions

BC is a pollutant primarily emitted from different combustion sources (fossil fuel, indoor biofuel combustion, open biomass burning) and it is very important to observe the real-time emission differences as new fuels and new mixtures are introduced into the supply of a country's fleet and what can be inferred about their impact on



**Figure 4.** Correlations between BC and fine PM concentrations ( $\mu\text{g m}^{-3}$ ) at Londrina Central Bus Station, with B5, B6, B7 and B8 biodiesel/diesel blends (2014-2017).

the environment and region. In our case, the increase of biodiesel in the diesel blend showed a considerable reduction of 41 and 44% of BC<sub>1.0</sub> and BC<sub>2.5</sub>, respectively. However, the fine PM concentration did not change significantly. The BC mass in PM<sub>1.0</sub> and PM<sub>2.5</sub> decreased for B5 to B8 biodiesel/diesel blends.

Interest in BC research has increased in the past years. There are no specific standard measuring methods developed for different types of combustion sources. The measurement of BC emissions is still inaccurate as it is very difficult to be assessed. Different measuring methods might lead to various errors, causing even greater problems to compare data obtained from measurements conducted by different research groups.<sup>20</sup> The same instrument was used to measure BC along all campaigns; the bus fleet was reasonably constant except during the second B7 campaign when there is a small increase in the number of buses circulating; the samplers were placed in the same positions and the sampling duration was also the same. Therefore, the comparison of the data collected throughout this study, with variation of diesel blends, can be considered accurate.

Currently, there are few measurements of BC in PM<sub>1.0</sub> in internal or external environments in Brazil and in other countries. Furthermore, there is no monitoring by national or international government agencies.<sup>21</sup>

BC is a marker of vehicular traffic that can have high environmental concentrations that prove to be harmful to health. It becomes useful and necessary the use of BC as an additional indicator for evaluation of local actions that aim to reduce the population's exposure to PM generated by combustion, mainly from vehicles, a predominant source of air pollution in cities.

Under the Paris Agreement,<sup>22</sup> Brazilian government is committed to increasing the share of sustainable bioenergy in the Brazilian energy matrix to approximately 18% by 2030, thus expanding biofuel consumption, increasing the supply of ethanol and expanding the share of biodiesel in the diesel mix.

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