Public health implications of particulate matter inside bus terminals in Sao Paulo, Brazil

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Abstract

Good quality ambient air is recognized as an important factor of social justice. In addition, providing access to high-capacity public transportation in big cities is known to be a good practice of social equity, as well as economic and environmental sustainability. However, the health risks associated with air pollution are not distributed equally across cities; the most vulnerable people are more exposed to ambient air as they commute to work and wait for buses or trains at the stations. The overall goal of this work was to assess the determinants of human exposure to particulate matter (PM) during commuting time spent inside bus terminals in the Metropolitan Area of Sao Paulo (MASP), in Brazil. Fine and coarse particles were collected at four bus terminals in the MASP. The concentrations of PM and its harmful constituents (black carbon and metals) were used in order to estimate potential doses and the associated health risk during the time spent at bus terminals in the MASP. Our findings show that bus commuters travelling through the bus terminal in the MASP on weekdays inhaled up to 128% higher doses of coarse particles than did those travelling outside the terminal; even on weekends, that difference was as high as 56%. Our risk assessment indicated that time spent inside a bus terminal can result in an intolerable health risk for commuters, mainly because of the Cr present in fine particles. Although bus commuters are exposed to fine particle concentrations up to 2 times lower than the worldwide average, we can affirm that inhalable particles in the MASP bus terminals pose a high carcinogenic risk to the daily users of those terminals, mainly those in the most susceptible groups, which include people with heart or lung disease, older adults and children.

Keywords:

Bus commuters

Black carbon

Potential dose

Risk assessment

Toxic metals

1. Introduction

Particles in the atmosphere determine air quality because they can adversely affect human health (Apte, Brauer, Cohen, Ezzati, and Pope, 2018; Burnett, Chen, Szyszkowicz, Fann, Hubbell, et al., 2018; Heal, Kumar, and Harrison, 2012), climate (United Nations, 2011) and visibility (Finlayson-Pitts and Pitts Jr., 2000). Particles are classified by their aerodynamic diameter. Those with a diameter ≤ 2.5 µm ($PM_{2.5}$) are classified as fine particles and include the most harmful fraction—those < 1 µm. Particles between 2.5 µm and 10 µm in diameter ($PM_{2.5–10}$) are classified as coarse particles. The sum of fine and coarse particles (i.e., all those ≤ 10 µm in diameter) is referred to as PM_{10}. The fine particle fraction ($PM_{2.5}$) primarily comprises elemental carbon—commonly known as black carbon (BC)—organic carbon, sulphate, nitrate, ammonium, and other inorganic constituents such as metals (Donahue, Robinson, and Pandis, 2009). Studies show that the fine particle fraction is more strongly linked with health effects. In 2018, the Brazilian government, following a guideline applied in the USA, established a $PM_{2.5}$ standard, setting a yearly average limit of 20 µg/m^{-3} (CONAMA, 2018). Although information on the determinants of human exposure to PM in transport environments is currently available for cities in Asia, Europe and the USA, the same is not true for cities in Brazil (Kumar, Patton, Durant, et al., 2018). Pollutants such as $PM_{2.5}$ and BC have a well-known association with vehicle emissions and have not been extensively addressed in studies conducted in Brazil. In 2012, the International Agency for Research on Cancer, which is part of the World Health Organization (WHO), classified diesel engine exhaust as a Group 1 carcinogen (carcinogenic to humans), based on sufficient evidence that exposure to diesel exhaust is associated with an increased risk of lung cancer (IARC, 2012).

The Metropolitan Area of Sao Paulo (MASP), the fifth most populous urban region in the world, like many other megacities, faces challenges in improving air quality. There have been several studies evaluating the improvements in air quality achieved after the implementation of national and state agency programs in Brazil (Andrade, Kumar, Freitas, Ynoue, Martins, et al., 2017; Kumar, Andrade, Ynoue, Fornaro, Freitas, et al., 2016). Such studies suggest that up to 10,000 deaths each year are linked to air pollution in the country (Bravo, Son, De Freitas, Gouveia, and Bell, 2016; Miranda, Andrade, Fornaro, Astolfo, de Andre, et al., 2012). Although short- and long-term exposure to fine particles has been significantly associated with health effects (Fajersztajn, Saldiva, Pereira, Leite, and Buehler, 2017; Feng, Li, Sun, Zhang, and Wang, 2016; HEI, 2010), there have been no epidemiological studies of human exposure to $PM_{2.5}$ in the MASP. That is due to the limited number of monitoring stations across the region. However, recent studies using biomarkers have shown significant health effects of such exposure. In a 3-month study of mice exposed daily to $PM_{2.5}$ concentrations similar to those in the ambient air, de Oliveira et al. (2018) observed increased levels of DNA damage related to cancer development. Vilas Boas et al. (2018) evaluated the genotoxic effects of air pollutants ($PM_{2.5}$

and NO_2) in individuals working daily outdoor shifts in the city of Sao Paulo. The authors observed a direct correlation between the individual dose of $PM_{2.5}$ and micronucleus frequency in the buccal mucosa, indicating that workers in the most urbanised areas of Sao Paulo were exposed to higher concentrations of $PM_{2.5}$, as well as showing higher micronucleus frequencies in the buccal mucosa and in lymphocytes.

Commuters, especially those commuting in big cities, spend considerable time in the transport environment. When the time spent inside bus or underground stations is added to that spent on buses, in trains, in cars, biking or walking, the total commute time can be several hours (Kumar and Goel, 2016; Rivas, Kumar, and Hagen-Zanker, 2017). Providing access to high-capacity public transportation in big cities is recognised as a good practice of social equity, as well as economic and environmental sustainability (Gómez-Perales, Colvile, Fernández-Bremauntz, Gutiérrez-Avedoy, Páramo-Figueroa, et al., 2007). In the MASP, which is the most economically developed region in Brazil and has more than 21 million inhabitants, most of whom are concentrated in 2000 km^2 of its total area of 8000 km^2 (IBGE, 2017), there were approximately 41 million trips (to or from work) per day in 2017. Approximately 15.3 million (37.0%) of those trips were made on public transportation, whereas approximately 12.9 million (31.2%) were made by private car, 12.8 million (31.1%) were made by walking and 370,000 (0.9%) were made by bicycle (Metro, 2018). In 2017, users of public transportation in the MASP spent an average of 60 min on their trip, compared with 26 min for commuters in private cars (Metro, 2018). Therefore, a large portion of the urban population in the MASP is exposed to traffic-related air pollutants. In the MASP, bus emissions of pollutants such as PM tend to exceed those of passenger vehicles by 10 times (CETESB, 2017a). Nevertheless, there are few data on the determinants of the individual level of exposure to PM in cities in developing countries, especially those in Latin America.

In Brazil, studies assessing the pollutants inside bus terminals are scarce. At a bus terminal in the city of Salvador, the average values for PM_{10} and $PM_{2.5}$ were found to be 309 ± 56 µg m^{-3} and 201 ± 56 µg m^{-3}, respectively (Mkoma, Da Rocha, Regis, Domingos, Santos, et al., 2014). At another bus terminal, in the city of Londrina, the PM_{10} and $PM_{2.5}$ mass concentrations were found to be 49.8 ± 10 µg m^{-3} and 38.0 ± 8.6 µg m^{-3}, respectively (Martins, Silva Junior, Solci, Pinto, Souza, et al., 2012). Brazil also provides a unique example of the long-term use of a biodiesel–diesel blend containing a significant percentage of biodiesel (Nogueira, Cordeiro, Muñoz, Fornaro, Miguel, et al., 2015). Another study carried out at a bus terminal in Londrina showed that the BC contribution to the fine fraction decreased from 79% when buses ran on a biodiesel–diesel blend containing 5% biodiesel to 47% when they ran on one containing 8% biodiesel (Silva Junior, Lemos, Pinto, Amador, and Solci, 2018). Targino et al. (2018) evaluated exposure to BC among individuals commuting by bus, by bicycle or on foot in

Londrina. The authors found that the BC concentrations inside buses were up to 6 times higher than those that commuters were exposed to when walking or bicycling. In yet another study conducted in Londrina, car and bus commuters were found to be exposed to similar $PM_{2.5}$ concentrations during their commutes, although the bus commuters were found to be exposed to higher concentrations of BC (Moreira, Squizzato, Beal, Almeida, Rudke, et al., 2018). Some studies have suggested that BC is a better indicator of harmful exposure than are $PM_{2.5}$ and PM_{10} (UNEP/WHO, 2012). Janssen et al. (2011) estimated that a one-unit reduction in BC concentration resulted in an increase in life expectancy 4–9 times greater than that resulting from a one-unit reduction in the concentration of $PM_{2.5}$. In addition, in cases of long-term exposure, it has been estimated that a 1.0 $\mu g\ m^{-3}$ reduction in the concentration of BC could reduce the premature mortality rate by 6% (Hoek, Krishnan, Beelen, Peters, Ostro, et al., 2013).

To bridge the gap in the literature regarding commuter exposure to pollutants from buses in Brazil, we carried out four intensive campaigns at bus terminals in the MASP in 2016. The effects of engine type and changes in fuel composition, as well as the implications that such changes have for pollutant emissions, have previously been discussed (Nogueira, Dominutti, Vieira-Filho, Fornaro, and Andrade, 2019). Here, we assessed the determinants of human exposure to BC, $PM_{2.5}$ and PM_{10} during commuting time spent inside four different bus terminals in the MASP. Unlike previous studies conducted in Brazil, this work assesses, for the first time, the inhalation doses of PM and its harmful constituents (e.g., BC and toxic metals), steering the discussion toward the enhanced uptake during commuting on weekdays (as opposed to weekends). We also compare the inhalation doses between bus commuters and active commuters (pedestrians).

2. Methods

2.1. Bus terminal characteristics

Commuter exposure to pollutants was measured at three sites in the MASP—the Santo Andre, Guarulhos and Diadema bus terminals (SA, GRU and DIA, respectively)—and at one site in the city of Campinas, which is 90 km west of the MASP—the Campinas bus terminal (CAM). With the exception of CAM, all of the terminals have roofs covering their entire area of operation. At CAM, only the walkways are covered. All of the buses serving CAM and GRU were running on a blend of 7% biodiesel and 93% diesel, whereas SA and DIA were served by a mix of diesel-powered buses and electric buses. Most of the diesel-powered buses circulating at the four terminals were powered by EURO 3-class engines. Additional details regarding the bus fleet and daily circulation can be found in Nogueira et al. (2019). The four terminals collectively serve more than 300,000 passengers day^{-1}, each passenger spending approximately 20 min inside the respective terminal. Approximately 44% of commuters are female, and approximately 59% are between 22 and 48 years of age.

2.2. Instrumentation

Samples of PM were collected in two fractions: fine ($PM_{2.5}$) and coarse ($PM_{2.5–10}$). The sampler consisted of ten stacked filter units (NILU, Norwegian Institute for Air Research, Oslo, Norway) coupled to an inlet that provided a 50% cut-off diameter of 10 µm. Each sampler was loaded with a 47-mm diameter polycarbonate filter, with pore sizes of 8 µm and 0.4 µm, for collecting the fine and coarse fractions, respectively, due to the effect of a combination of surface and depth filtration. A small container, placed at a height of 2 m from the ground, was employed to house the instruments during all bus terminal fieldwork. More details of the system set-up are provided in Nogueira et al. (2019).

The *Companhia Ambiental do Estado de São Paulo* (CETESB, Sao Paulo State Environmental Protection Agency) provided the external PM concentration data (CETESB-QUALAR, 2017). Measurements of PM_{10} and $PM_{2.5}$ mass concentrations were taken with a continuous ambient particulate monitor (5014i Beta; Thermo Fisher Scientific, Waltham, MA, USA).

2.3. Data collection and analysis

The fieldwork was performed over a total of 59 days in 2016: 19 days at SA (May 12–30); 14 days at GRU (June 3–16); 11 days at CAM (September 26 through October 6); and 15 days at DIA (December 5–19). At all of the bus terminals, PM was sampled from 4:00 h to 22:00 h local time. The weekday PM samplings accounted for 75% of the samples. The external PM concentrations were obtained from the CETESB air quality monitoring stations closest to each terminal: Sao Bernardo–Centro and Santo Andre–Paco Municipal for SA; Guarulhos–Pimentas for GRU; Campinas–Taquaral and Campinas–Vila Uniao for CAM; and Sao Bernardo–Centro and Diadema for DIA.

Filters used in order to collect PM were conditioned in a weighing room at ~22°C and ~45% relative humidity for 24 h before and after each sampling. PM mass concentrations were measured with an electronic microbalance (MX5; Mettler-Toledo, Columbus, OH, USA).

Concentrations of BC in the filter samples were determined with a digital smoke stain reflectometer (model 43D; Diffusion Systems Ltd., London, UK). An empirical calibration curve was employed to convert the reflected light into the concentration of BC (Hetem and Andrade, 2016).

Elemental composition analysis was performed by energy dispersive X-ray fluorescence (EDX-700HS; Shimadzu Corporation, Analytical Instruments Division, Tokyo, Japan). In the present study, we discuss concentrations of the following toxic metals: Al, V, Cr, Mn, Ni and Zn. Details of the concentrations of other elements can be found in Nogueira et al. (2019).

2.4. Meteorological parameters

The experimental campaigns were conducted in different seasons. Table S1 presents the average meteorological conditions during each campaign. Inside the bus terminals, the direction and velocity of the wind are strongly influenced by vehicular movement near the sampling system. Outside the terminals, the wind velocity varied (1.4–2.3 m s^{-1}). In the winter (June–August), the temperature ranged from (a low of) 2°C (at GRU) to (a high of) 27°C (at SA). In spring and summer (September–February), the temperature ranged from (a low of) 14°C (at DIA) to (a high of) 31°C (at CAM). In the state of Sao Paulo, wide variations between the minimum and maximum temperatures are common. Even during winter, it is possible to have clear skies and radiation that promotes the formation of ozone. Precipitation was the most important factor in the reduction of pollutant concentrations, due to wet scavenging and the inhibition of resuspension caused by humidification of the soil. In the state of Sao Paulo, precipitation is expected to be greater in the spring and summer. However, during our campaigns, precipitation was greatest in May and June.

2.5. Respiratory deposition doses

The inhalation potential dose (D_{pot}) for the coarse and fine particles fractions was estimated according to Eq. (1), devised by the US Environmental Protection Agency (1992):

$$D_{pot}[\mu g\ kg^{-1}\ h^{-1}] = \frac{C_a \times IR}{BW} \tag{1}$$

where C_a is the pollutant concentration (μg m^{-3}), *IR* is the inhalation ratio ($m^3\ h^{-1}$), stated as 0.875 $m^3\ h^{-1}$ and 0.690 $m^3\ h^{-1}$ for adult males and females, respectively, and *BW* is body weight (in kg) for individuals 30–44 years of age, stated as 75.4 kg and 63.8 kg for males and females, respectively (IBGE, 2010). The IR values were taken as the 95th Percentile Inhalation Rate Values for Free-Living Normal-Weight Males and Females aged 31 to 41 years, as described in Chapter 6 of the Inhalation Rates of Exposure Factors Handbook (US Environmental Protection Agency, 2011). The D_{pot} gradient, expressed as ΔD_{pot}, was estimated by subtracting the D_{pot} estimated for commuters outside terminals ($Dpot_{out}$) from the D_{pot} obtained for commuters inside terminals ($Dpot_{in}$), as shown in Eq. (2):

$$\Delta D_{pot}[\mu g\ kg^{-1}\ h^{-1}] = Dpot_{in} - Dpot_{out} \tag{2}$$

The increase in the inhalation dose was estimated as a percentage increase in the inhaled dose, as shown in Eq. (3):

$$Inhalation\ dose\ increase\ [\%] = \frac{\Delta D_{pot}}{Dpot_{out}} * 100 \tag{3}$$

2.6. Risk assessment

Exposure to toxic metals is associated with non-carcinogenic and carcinogenic effects on human health. The risk of non-carcinogenic effects was estimated based on the hazard quotient (HQ), calculated as in Eq. (4):

$$HQ = \frac{C_a}{RfC} \tag{4}$$

where C_a is the concentration (in mg m^{-3}) of a toxic metal (V, Cr, Mn, Ni or Pb) in air and *RfC* is the reference concentration for chronic inhalation exposure, in mg m^{-3}, obtained from the US Environmental Protection Agency (EPA) Integrated Risk Information System (IRIS, 2019). The HQ gives an estimate of continuous inhalation exposure to the human population, including susceptible groups, that is likely to have no appreciable risk of deleterious effects during a lifetime. If the HQ is ≤ 1.0, significant health effects are not expected. When the HQ is > 1.0, the exposure is considered intolerable and a reduction in the level of exposure is recommended. The carcinogenic risk of the exposure to each toxic metal was estimated by Eq. (5):

$$Cancer\ Risk = C_a \times IUR \tag{5}$$

where *IUR* is the inhalation unit risk, which is an estimate of the increased cancer risk from lifetime inhalation exposure to a concentration of 1 µg m^{-3}. The IUR values were obtained from the EPA Integrated Risk Information System (IRIS, 2019). The total cancer risk was given by the sum of the cancer risk for each toxic element. A cancer risk ≤ 1×10^{-6} is used as a tolerability criterion adopted by many countries and recommended by the WHO. However, risks up to 1×10^{-4} can be considered acceptable in specific situations. In the remediation of soil contamination in Brazil, the CETESB considers 1×10^{-5} to be a tolerable level of cancer risk (CETESB, 2017b).

2.7. Statistical analysis

The average value, maximun and minimun, standard deviation, 5th – 95th percentiles were conducted with Igor Pro 6.7 (Wavemetrics, Portland, US). The Student t-test was used to compare the concentrations inside and outside the terminals, and the results were reported as significant as $p \leq 0.05$. Additionally, we compared our results with those of other studies conducted around the world.

3. Results

3.1. Weekday and weekend PM concentrations in MASP bus terminals

Fig. 1a shows the PM concentrations, by size fraction, in the four MASP bus terminals on weekdays and weekends. The widest variability in PM_{10} mass concentrations was observed on weekdays at GRU (24.5–76.4 μg m^{-3}), followed by SA (19.5–48.3 μg m^{-3}), DIA (29.5–65.9 μg m^{-3}) and CAM (31.4–67.9 μg m^{-3}). The average PM_{10} concentrations were higher on weekdays than on weekends at all of the terminals except SA. The weekday/weekend ratio for the PM_{10} concentration was approximately 1.5 at CAM, DIA and GRU, whereas it was close to 1.0 at SA (Fig. 1b).

The average coarse and fine particle fractions showed different trends (Fig. 1a). For the coarse particles, concentrations were higher on weekdays than on weekends at all of the bus terminals: GRU (34.0 vs. 13.3 μg m^{-3}); CAM (23.2 vs. 13.0 μg m^{-3}); DIA (22.7 vs. 11.7 μg m^{-3}); and SA (19.6 vs. 15.0 μg m^{-3}). The weekday/weekend ratio for the coarse particle concentrations was 2.56, 1.94, 1.78 and 1.31 at GRU, DIA, CAM and SA, respectively (Fig. 1c). However, for the fine particles, the concentrations were higher on weekdays only at CAM and DIA, with weekday/weekend ratios of 1.37 and 1.12, respectively, compared with 0.83 and 0.79 for GRU and SA, respectively (Fig. 1d).

The PM concentrations recorded outside the terminals were also higher on weekdays than on weekends, except at SA. Fig. 1e shows the concentrations of PM_{10} and $PM_{2.5}$ outside the terminals. On weekdays, the average PM_{10} concentrations were 37.8 μg m^{-3}, 24.3 μg m^{-3}, 29.0 μg m^{-3} and 23.7 μg m^{-3}, at GRU, DIA, CAM and SA, respectively. On weekends, the average PM_{10} concentrations were lower at GRU, DIA and CAM (29.1 μg m^{-3}, 21.2 μg m^{-3} and 19.2 μg m^{-3}, respectively), whereas a slightly higher concentration (25.5 μg m^{-3}) was observed at SA. The weekday/weekend PM_{10} concentration ratio was 1.5, 1.3, 1.2 and 0.96 at GRU, CAM, DIA and SA, respectively (Fig. 1f).

Outside the bus terminals, the average concentration of coarse particles was highest (17.3 μg m^{-3}) on weekdays at GRU and lowest (~10.4 μg m^{-3}) on weekends at CAM. Unlike the concentrations observed inside the terminals, the coarse fractions presented values that were only slightly higher on weekdays than on weekends. The weekday/weekend ratio for the coarse fraction was highest (1.5) at GRU and lowest (close to 1.0) at SA and DIA (Fig. 1g). The average concentration of fine particles was also highest (20.5 μg m^{-3}) on weekdays at GRU and lowest (8.8 μg m^{-3}) on weekends at CAM. The out-of-terminal weekday/weekend $PM_{2.5}$ concentration ratio was 1.2, 1.6 and 1.2 at GRU, CAM and DIA, respectively, whereas it was 0.82 at SA (Fig. 1h).

3.2. Fractional contributions of fine and coarse particles

Fig. 2 shows the fractional contributions of the fine and coarse particles to the total PM. On weekdays, the in-terminal PM concentrations were typically dominated by the coarse fraction, which accounted for 63.1%, 57.8%, 56.7% and 49.6% of the PM_{10} at GRU, DIA, SA and CAM, respectively (Fig.

2a). On weekends, PM concentrations showed an opposite trend, the fine fraction accounting for 64.2%, 55.8%, 55.8% and 56.8% of the PM_{10} at GRU, DIA, SA and CAM, respectively, although the differences were not statistically significant for DIA and CAM ($p = 0.07$ and $p = 0.34$, respectively).

The contribution of fine particles to the total PM was slightly higher on weekends at GRU and SA—61% and 54%, respectively. However, there was no statistical difference between the weekday and weekend contributions of fine particles at SA, CAM or DIA (Fig. 2b).

3.3. Weekday and weekend BC concentrations inside MASP bus terminals

As can be seen in Fig. 3a, the average in-terminal BC concentrations in PM_{10} were higher on weekdays than on weekends at all four MASP bus terminals: SA (9.0 vs. 7.7 $\mu g\ m^{-3}$); DIA (8.6 vs. 6.7 $\mu g\ m^{-3}$); GRU (8.5 vs. 6.8 $\mu g\ m^{-3}$); and CAM (5.8 vs. 2.2 $\mu g\ m^{-3}$). In addition, BC is predominantly found in the fine fraction, 91.8%, 84.4%, 85.2% and 85.0% being found in the $PM_{2.5}$ on weekdays at CAM, GRU, DIA and SA, respectively. On weekends, the proportion of BC in the fine fraction was even higher, being approximately 92% at all terminals. The weekday/weekend ratio ranged from 1.1 to 2.6 for PM_{10}, from 1.3 to 2.6 for coarse particles, and from 1.1 to 2.6 for fine particles (Fig. 3b-c).

3.4. Toxic metal elements

Metal elements were measured in the coarse and fine fraction only for SA, GRU and CAM, and we evaluated the combined (weekday and weekend) data for selected toxic metals, as shown in Fig. 4. Among toxic metals, Cr showed the highest concentrations, which were, at GRU and SA, 430 ng m^{-3} and 77 ng m^{-3}, respectively, in PM_{10}, compared with 299 ng m^{-3} and 74 ng m^{-3}, respectively, in $PM_{2.5}$. As can also be seen in Fig. 4, most of the Cr concentration was in the fine fraction—96% and 69% at SA and GRU, respectively. In addition, Ni was found in the PM_{10}, at concentrations of 28 ng m^{-3}, 1.2 ng m^{-3} and 0.6 ng m^{-3} at GRU, SA and CAM, respectively. Particles containing Pb were also found in the PM_{10}, at concentrations of 9.9 ng m^{-3} and 34.0 ng m^{-3} at SA and GRU, respectively. It was found that 68% of the Pb was in the fine fraction at GRU, compared with 28% at SA. Concentrations of Mn and V are also shown in Fig. 4. Whereas most (~80%) of Mn was found in the coarse fraction at all terminals, V was more or less equally distributed between the two fractions at GRU and CAM, although 87% of the V was in the coarse fraction at SA.

3.5. Weekday and weekend D_{pot} of particle fractions

We estimated the D_{pot} of PM_{10}, as well as that of the fine and coarse particle fractions, using the inhalation rates for males and females (Fig. 5 and Fig. S1, respectively). The D_{pot} of PM_{10} was higher on weekdays than on weekends, as well as being higher inside than outside the bus terminals. On weekdays, the median D_{pot} of PM_{10} was highest (0.70 µg kg^{-1} h^{-1}) at GRU and lowest (0.23 µg kg^{-1} h^{-1}) at DIA.

The median D_{pot} of the coarse fraction showed the widest variability on weekdays, ranging from 0.10 µg kg^{-1} h^{-1} (at DIA) to 0.38 µg kg^{-1} h^{-1} (at GRU), whereas on weekends it ranged from 0.09 µg kg^{-1} h^{-1} (at DIA) to 0.17 µg kg^{-1} h^{-1} (at SA). There was no such trend for the median D_{pot} of the fine fraction, which ranged from 0.11 µg kg^{-1} h^{-1} (at DIA) to 0.26 µg kg^{-1} h^{-1} (at CAM) on weekdays, ranging from 0.07 µg kg^{-1} h^{-1} (at CAM) to 0.27 µg kg^{-1} h^{-1} (at GRU) on weekends.

3.6. In-terminal and out-of-terminal D_{pot} of particle fractions

The dataset provided by the D_{pot} calculations is particularly interesting because it allowed us to estimate the difference between the dose inhaled by commuters travelling outside bus terminals in the MASP and that inhaled by commuters travelling inside those same terminals. We present those results in terms of a percentage increase in the inhaled dose, for both genders combined. On weekdays, the increase (from outside to inside) in the D_{pot} of PM_{10} ranged from 58% (at GRU) to 94% (at CAM) and was greater on weekdays than on weekends at three of the four bus terminals under study, the exception being GRU (Fig. 6). On weekends, that increase ranged from 43% (at SA) to 88% (at CAM). As shown in Fig. 6b, the greater increases on weekdays are mainly attributable to coarse particle inhalation. At all of the terminals studied, the increase in the D_{pot} of coarse particles was higher on weekdays than on weekends, ranging from 81% (at CAM) to 128% (at DIA) on weekdays and from 30% (at CAM) to 56% (at GRU) on weekends. However, as can be seen in Fig. 6c, the increase in the D_{pot} of fine particles ranged from 37% (at SA) to 186% (at CAM) on weekends and from 11% (at GRU) to 110% (at CAM) on weekdays, being higher on weekends at three of the four bus terminals, the exception being SA.

3.7. Weekday and weekend D_{pot} of BC

We estimated the D_{pot} of BC in PM_{10} (BC-PM_{10} D_{pot}), as well as in the fine and coarse particle fractions, using the inhalation rates for males and females (Fig. 7 and Fig. S2, respectively). The BC-PM_{10} D_{pot} values were higher on weekdays than on weekends at all of the terminals, that difference being greatest at CAM. The median BC-PM_{10} D_{pot} values for the various terminals (weekdays vs weekends; Fig. 7a) were as follows: CAM (6.9×10^{-2} vs 2.5×10^{-2} µg kg h^{-1}); SA (10.8×10^{-2} vs 7.8×10^{-2} vs µg kg h^{-1}); GRU (9.2×10^{-2} vs 8.2×10^{-2} µg kg^{-1}); and DIA (9.4×10^{-2} vs 6.9×10^{-2} µg kg h^{-1}). As can be seen in Fig. 7b, the D_{pot} of BC in the coarse fraction was also higher on weekdays, on which it ranged from 5.6×10^{-3} µg kg h^{-1} (at CAM) to 16.2×10^{-3} µg kg h^{-1} (at SA), whereas on weekends it ranged from 2.1×10^{-3} µg kg h^{-1} (at CAM) to 10.7×10^{-3} µg kg h^{-1} (at SA). The contribution of BC was greatest in the most harmful fraction (the fine fraction). The estimated D_{pot} of BC in the fine fraction was highest on weekdays, on which it ranged from 6.3×10^{-2} µg kg h^{-1} (at CAM) to 9.2×10^{-2} µg kg h^{-1} (at SA), whereas on weekends it ranged from 2.3×10^{-2} µg kg h^{-1} (at CAM) to 7.8×10^{-2} µg kg h^{-1} (at GRU), as shown in Fig. 7c.

3.8. Health impacts of exposure to toxic metals

The estimated HQ values for exposure to toxic metals are shown in Table 1. The estimated HQs were highest for Cr, for which they ranged from 0.77 (at SA) to 4.3 (at GRU). For the other toxic metals (V, Mn, Ni and Pb), the HQ values were all less than 1.0. The HQ values for exposure to $PM_{2.5}$ and $PM_{2.5–10}$ are shown in Fig. 8.

3.9. Comparative analysis

In Fig. 9 and Table S2, fine particle concentrations in bus terminals are compared, between the present study and studies conducted in other countries, as well as between studies conducted in Brazil in general and studies conducted elsewhere. In addition, Fig. 10 and Table S3 compare the BC concentrations at the bus terminals in the MASP and in Londrina with the concentrations observed at the respective background sites.

4. Discussion

The close proximity of bus commuters to exhaust emissions and the resuspension of particles leads to PM concentrations that are higher inside than outside bus terminals. In the present study, bus commuter exposure to coarse particles was found to be higher on weekdays than on weekends at all of the bus terminals in the MASP. The fact that the in-terminal concentrations of coarse particles were higher on weekdays is presumably because there was relatively greater resuspension of paved road dust at the terminals, due to the higher density of bus traffic. That pattern was more pronounced inside the terminals. For coarse particles, the in-terminal concentrations were 1.3–2.6 times higher on weekdays than on weekends, whereas the out-of-terminal concentrations were only 1–1.5 times higher. In contrast, the concentrations of fine particles did not differ dramatically between weekdays and weekends, either inside or outside the terminals.

The results obtained in this study provide a useful dataset for comparison with other studies conducted around the world. The fine particle concentrations found inside MASP bus terminals in the present study were lower than those reported for bus terminals in other countries. For example, the reported $PM_{2.5}$ concentrations at bus terminals in Taiwan range from 35.4 µg m^{-3} in the city of Chiayi

(Lee, Lin, Aniza, et al., 2017) to 51.7 μg m^{-3} in Taipei (Cheng, Chang, and Yan, 2012), which were approximately 1.2 and 1.7 times higher, respectively, than the overall average of all of the studies we identified in the literature (30 μg m^{-3}). In the city of Brisbane, Australia, the average $PM_{2.5}$ concentration inside bus terminals was reported to be 25.3 μg m^{-3} (Wang, Morawska, Jayaratne, Mengersen, and Heuff, 2011), approximately 1.3 times lower than the overall average. In the town of Jurong West, Singapore, bus commuters are reportedly exposed to a $PM_{2.5}$ concentration of 47.8 μg m^{-3} (See, Balasubramanian, Yang, et al., 2006), approximately 1.6 times higher than the overall average. In a study conducted at a bus terminal in the city of Londrina, Brazil, the $PM_{2.5}$ concentration was found to be 38 μg m^{-3}, approximately 1.3 times higher than the overall average. Comparing our data for the $PM_{2.5}$ concentration at bus terminals in the MASP with the overall average, we found that our values were 2 times lower at SA, 1.5 times lower at GRU, 1.3 times lower at CAM, and 1.9 times lower at DIA. The average concentration calculated for bus terminals in Brazil (22.6 μg m^{-3}, including those in the MASP and in Londrina) was 1.8 times lower than the overall average. Unlike other bus terminals around the world, the MASP bus terminals presented average 24-h concentrations of fine particles lower than the WHO guideline value of 25 μg m^{-3}.

Commuters inside the MASP bus terminals were exposed to higher concentrations of BC in particles than were commuters outside those terminals. In addition, commuters were exposed to higher BC concentrations on weekdays, which was mainly due to a higher number of vehicles circulating through the terminals on weekdays. Miranda et al. (2017) reported BC concentrations at background sites in the MASP. The average BC concentration observed inside the MASP terminals in the present study is approximately 3.3 times higher than that reported for the background sites. However, the average BC concentration at the MASP terminals was 1.6 times lower than the average of those reported for the bus terminals in the mid-size city of Londrina (Silva Junior, Lemos, Pinto, Amador, and Solci, 2018; Targino, Rodrigues, Krecl, Cipoli, and Ribeiro, 2018). In Londrina, the average BC concentrations were approximately 6.9 times higher at the bus terminals than at the background sites. That can be attributed to factors such as the age of the vehicles in the fleet, which are replaced more frequently in the MASP than in other Brazilian cities (CETESB, 2017c; Nogueira, Dominutti, Vieira-Filho, Fornaro, and Andrade, 2019).

In the present study, we found that commuters whose commute took them through bus terminals in the MASP were exposed to a higher D_{pot} of fine and coarse particles than were other commuters in the MASP, on weekdays and weekends. On weekdays, a commuter travelling through a MASP bus terminal can be exposed to a D_{pot} of coarse particles up to 128% higher than that to which a commuter travelling outside the same terminal is exposed, that difference being only up to 56% on weekends, although it was up to 186% on weekends for the D_{pot} of fine particles. The greater increase on weekends is related to the weekday-to-weekend decrease in the fine particle concentration being greater outside the terminals than inside the terminals, as shown in Fig. 1d and Fig. 1h. That can be explained by the fact that certain sources of fine particles, such as industrial processes, as well as the circulation of light- and heavy-duty vehicles, are reduced on weekends. The D_{pot} of fine particles estimated for bus commuters in the MASP on weekdays (0.11–0.27 μg kg^{-1} h^{-1}) is comparable to the weekday values reported for such commuters in Londrina (Moreira, Squizzato, Beal, Almeida, Rudke, et al., 2018). The authors of the Londrina study found that the D_{pot} of $PM_{2.5}$ for bus commuters was 0.18 μg kg^{-1} h^{-1}, compared with 0.16 μg kg^{-1} h^{-1} for car commuters.

Among the toxic metal elements evaluated in the present study, Cr showed the highest concentrations at all of the bus terminals and was found predominantly in the fine particle fraction. The high HQ for Cr indicates that it presents an intolerable risk of non-carcinogenic effects. However, the consideration that all of the Cr was hexavalent could be overestimating the HQ. The inhalation of Cr is associated with adverse health effects on the respiratory system (IRIS, 2019). Other toxic metals found in both particle fractions were V, Mn, Ni and Pb. The lower HQs for those elements indicate that they are not expected to have significant health effects in the exposed population. Mateos et al. (2018) studied the health risks associated with the inhalation of particles in areas of different urban land use in the city of Cordoba, Argentina. Those authors also found HQs < 1.0 for inhalation of seven chemical elements (Ba, Co, Cr, Cu, Mn, Pb and Zn). Sah et al. (2017) analysed $PM_{2.5}$ samples from urban areas in the city of Agra, India, and found HQs < 1.0 for inhalation of As, Cd, Cr, Ni and Pb in all age groups, although they reported an HQ of 1.48 for Co.

At GRU site, there was not only a high concentration of Cr but also a high concentration of Pb, which is a common contaminant that is considered highly neurotoxic for children and detrimental to foetal development. It is not known at what level Pb exposure begins to pose a risk to human health (i.e., there is no known safe level of Pb exposure), and the main public health agencies have not devised reference values because a clear threshold for some of the more sensitive effects in humans has yet to be identified (IRIS, 2019). The National Ambient Air Quality Standards established by the EPA set the allowable limit of Pb in air at 0.15 μg m^{-3} (US Environmental Protection Agency, 2019). Even low-dose exposure to Pb has been associated with various adverse health effects such as reduced intelligence, behavioural problems and attention-deficit/hyperactivity disorder (Braun, Kahn, Froehlich, Auinger, and Lanphear, 2006; Chen, Cai, Dietrich, Radcliffe, and Rogan, 2007; Hong, Im, Kim, Park, Shin, et al., 2015; Nevin, 2007; Olympio, Gonçalves, Günther, et al., 2009; Olympio, Oliveira, Naozuka, Cardoso, Marques, et al., 2010).

The adverse health effects of exposure to toxic elements are associated with several factors, such as the toxicity/concentration of the chemical, exposure time and exposure duration, as well as the age, body weight and health status of the individual. In polluted urban areas such as the MASP, many people can be exposed to an intolerable level of risk in several intra-urban spaces, even if the city-wide air quality is within the acceptable range.

The lifetime cancer risk was estimated for Cr, as well as for Ni, which is classified by the EPA as a human carcinogen (EPA group A), and Pb, which is classified as a probable human carcinogen (EPA group B2). The risk of Cr inhalation at GRU is quite high relative to the tolerability criterion of 1×10^{-6} and to the CETESB criterion for soil contamination in the state of Sao Paulo (1×10^{-5}). The cancer risk for Ni is also significant, given the tolerability criterion of 1×10^{-6}. Considering that the users of GRU are exposed to all three elements simultaneously, the pooled risk is 3.6×10^{-3}, which would correspond to an additional 140 cases of cancer in the population (of 39,000 users) studied.

Other studies conducted in cities in developing countries have also found high carcinogenic risks due to particulate inhalation in urban environments (Li, Wu, Wang, Yang, Li, et al., 2017; Mateos, Amarillo, Carreras, et al., 2018; Sah, Verma, Kumari, et al., 2017). Recent studies conducted in the MASP have also found that traffic-related air pollution correlates with the incidence of respiratory cancer and with the associated mortality (Ribeiro, Downward, Freitas, Chiaravalloti Neto, Cardoso, et al., 2019).

5. Conclusions

In general, the concentrations of fine particles in the MASP bus terminals were 1.3–2.0 times lower than the overall average of those reported in studies conducted inside bus terminals around the world. Despite this, considering the results of the present study, we can affirm that the inhalation of PM poses a high carcinogenic risk to the daily users of bus terminals in the MASP. It should be borne in mind that the risks can be greater for children and other susceptible groups. Although carcinogenic and non-carcinogenic risk assessment is not conclusive, it is a quite useful tool for supporting decision-making related to air quality management in urban areas. In several intra-urban scenarios, people are exposed to inhalation of fine particles and other contaminants, particularly in developing countries, where environmental data on toxic air contaminants are scarce.

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Table 1

Concentrations of metal elements in particulate matter with an aerodynamic diameter ≤ 10 μm at each of the bus terminals studied, together with the risk measures.

		ng m^{-3}					RfC			IUR	
Terminal	Element	Average	SD	Range	Median	*N*	(mg/m^3)	HQ	WOE[a]	(per μg m^{-3})	Cancer risk
SA		10.5	26.1	0.5–95.6	2.9	16		0.11			
GRU	V	3.9	2.5	0.5–10.1	1.9	10	0.0001[b]	0.04		-	-
CAM		3.5	0.9	1.8–5.1	3.6	7		0.03			
SA	Cr[c]	77.3	83.4	16.2–137.7	78.1	3	0.0001[b]	0.77			9.3E-04
GRU		430.6	404.4	3.7–1,041.6	246.3	8		4.31	A	1.2E-02	5.2E-03
SA		10.2	4.7	2.3–24.1	8.2	15		0.20			
GRU	Mn	19.4	7.9	6.9–38.7	18.1	13	0.00005[b]	0.39		-	
CAM		8.2	4.3	2.0–15.3	4.9	9		0.16			
SA		2.2	1.8	0.9–4.9	1.5	4		0.02			5.3E-07
GRU	Ni	23.8	24.5	2.5–70.8	10.4	9	0.00009[b]	0.26	A	2.4E-04	2.1E-06
CAM		1.6	1.1	0.7–3.2	1.3	4		0.02			3.9E-07

SA	Pb[c]	9.9	14.1	0.6–42.5	2.4	14	-[d]				1.2E-07
GRU		33.9	23.1	1.3–115.8	26.3	13		-	B2	1.2E-5	4.1E-07

RfC = Reference concentration (for chronic inhalation exposure), IUR = inhalation unit risk (IUR), HQ = hazard quotient, WOE = weight-of-evidence (category), SA = Santo Andre, GRU = Guarulhos, CAM = Campinas.

[a] Weight-of-evidence categorization according to the US Environmental Protection Agency (A = human carcinogen; B2 = probable human carcinogen).

[b] Source: ATSDR Minimal Risk Levels (MRLs) - June 2018 https://www.atsdr.cdc.gov/mrls/mrllist.asp#34tag).

[c] Not detected at CAM.

[d] No reference values for tolerability. Source: OEHHA (https://oehha.ca.gov/chemicals/lead-and-lead-compounds).

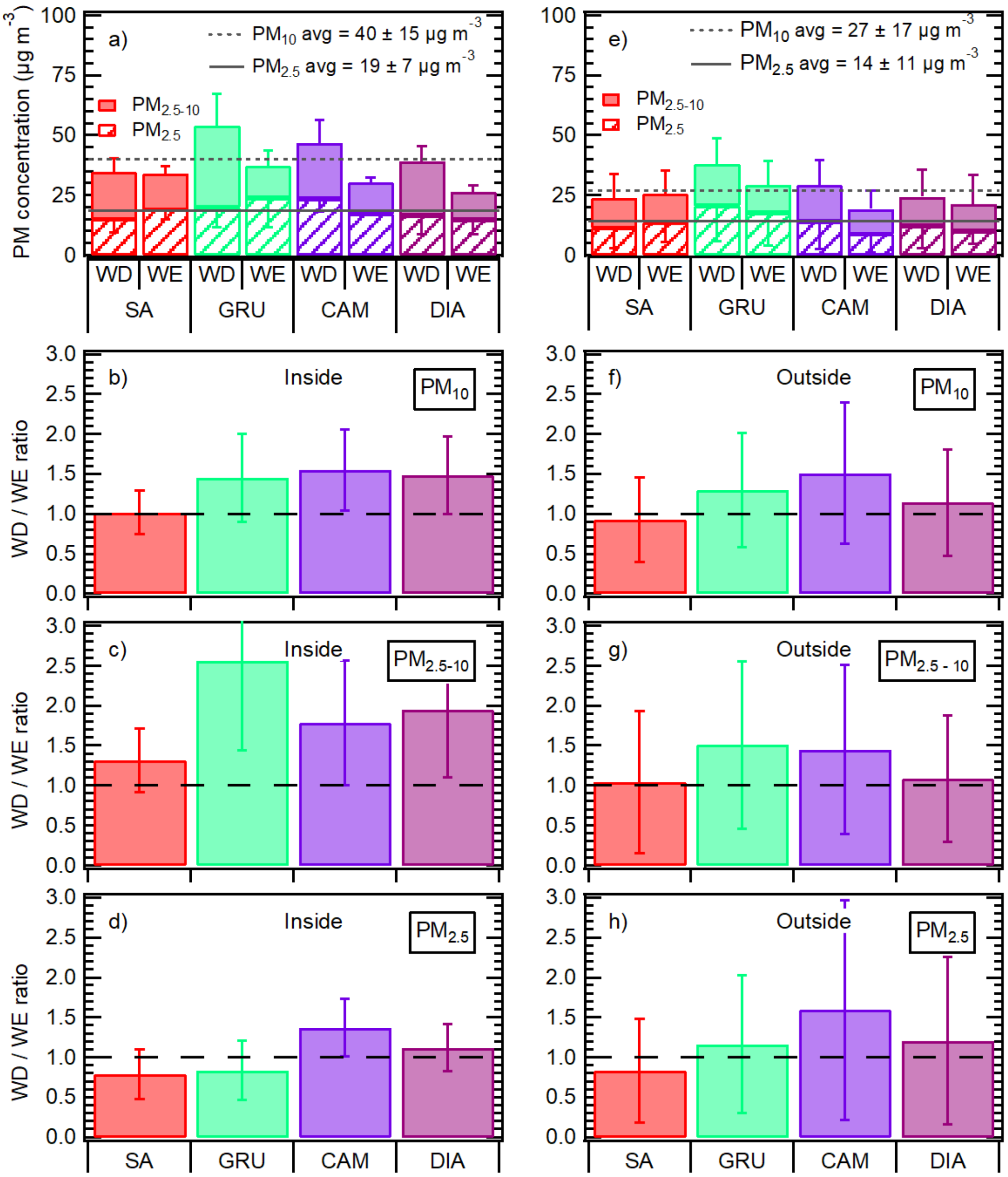

Fig. 1. Concentrations of coarse and fine fractions of particulate matter (PM) on weekdays (WD) and weekends (WE), together with the WD/WE ratios, inside and outside the bus terminals studied. For the average concentrations, only positive standard deviation bars are added to the coarse fraction values and only negative standard deviation bars are added to the fine fraction values.

PM_{10} = particles ≤ 10 μm in diameter, $PM_{2.5-10}$ = particles 2.5–10 μm in diameter, $PM_{2.5}$ = particles ≤ 2.5 μm in diameter, SA = Santo Andre, GRU = Guarulhos, CAM = Campinas, DIA = Diadema.

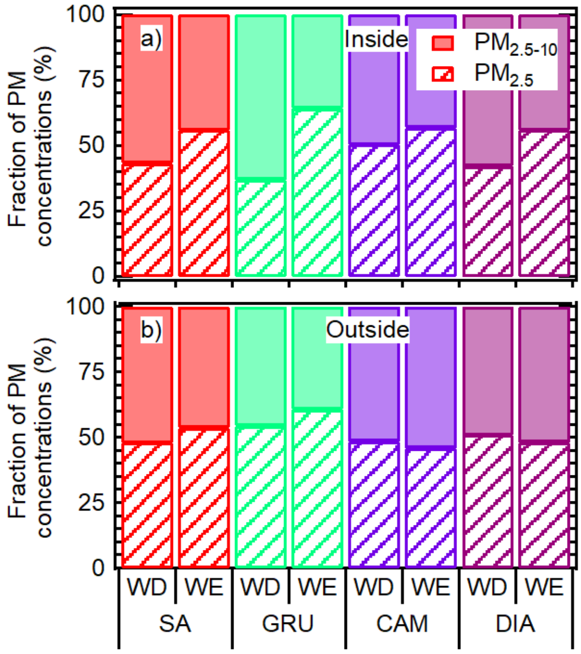

Fig. 2. Fractional contributions to the average concentrations of particulate matter (PM) on weekdays (WD) and weekends (WE), inside and outside the bus terminals studied.

$PM_{2.5–10}$ = particles 2.5–10 µm in diameter, $PM_{2.5}$ = particles ≤ 2.5 µm in diameter, SA = Santo Andre, GRU = Guarulhos, CAM = Campinas, DIA = Diadema.

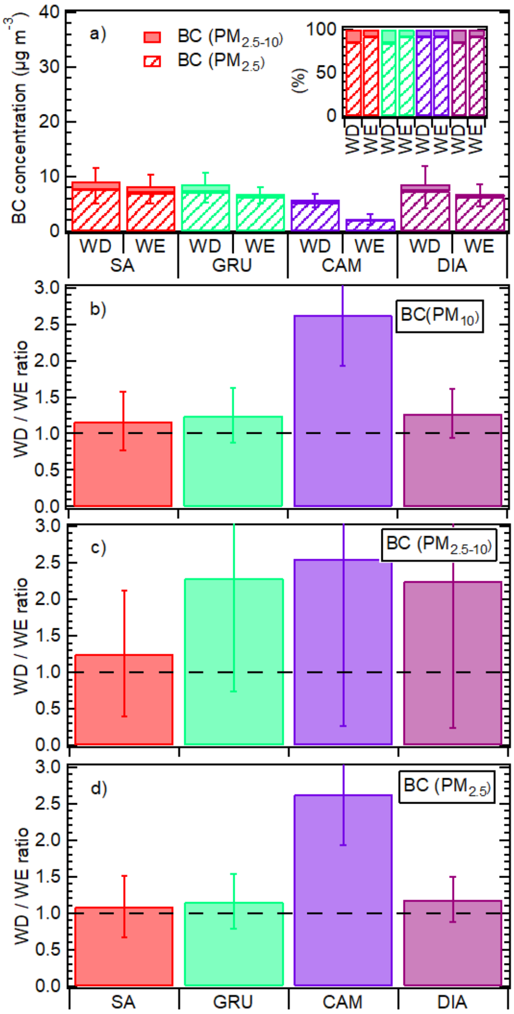

Fig. 3. (a) Black carbon (BC) concentration in the coarse and fine fractions, contributions of BC to the coarse and fine fractions is shown embedded in the upper right corner, (b) weekday/weekend ratio for BC concentration in PM_{10}, (c) weekday/weekend ratio for BC concentration in the coarse fraction, and (d) weekday/weekend ratio for BC concentration in the fine fraction. Error bars represent the standard deviation of the average value obtained at each bus terminal.

PM_{10} = particles ≤ 10 µm in diameter, $PM_{2.5–10}$ = particles 2.5–10 µm in diameter, $PM_{2.5}$ = particles ≤ 2.5 µm in diameter, SA = Santo Andre, GRU = Guarulhos, CAM = Campinas, DIA = Diadema.

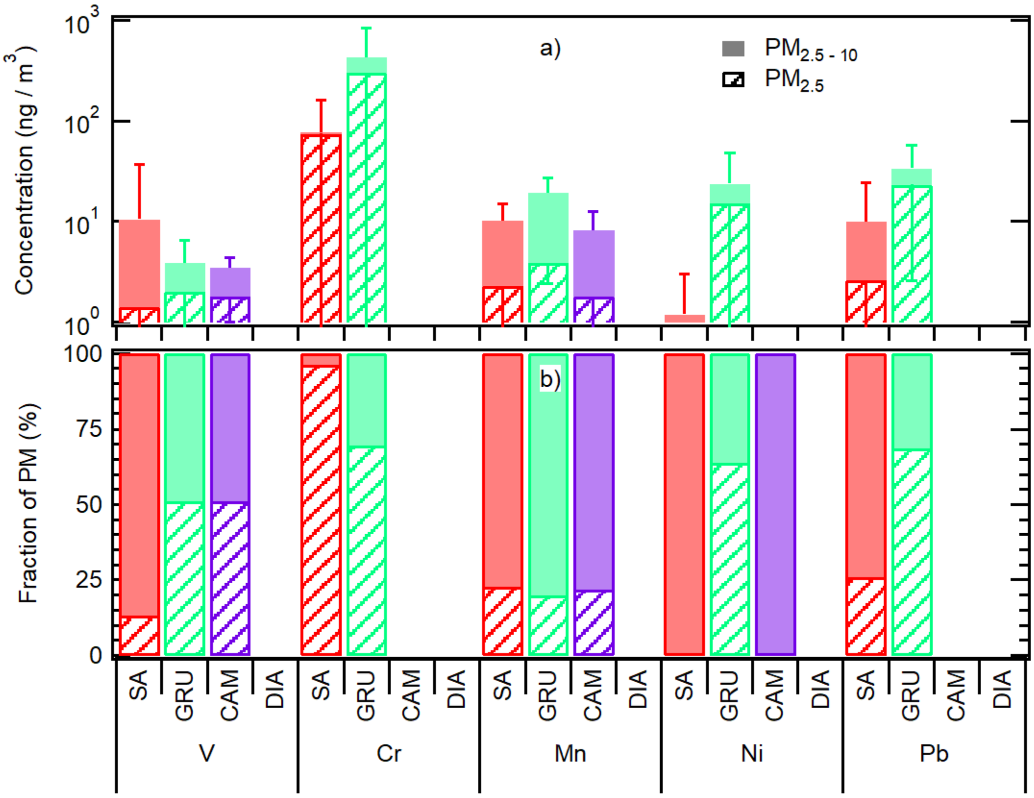

Fig. 4. a) Concentrations of selected toxic metals in particulate matter (PM), including particles with a diameter of 2.5–10 µm ($PM_{2.5–10}$, coarse fraction) and those with a diameter ≤ 2.5 µm ($PM_{2.5}$, fine fraction), at the Santo Andre (SA), Guarulhos (GRU) and Campinas (CAM) bus terminals; b) Fractional contribution of each toxic metal to the total concentration in the coarse and fine fractions. Error bars represent the standard deviation of the average value obtained at each bus terminal.

DIA = Diadema (no data).

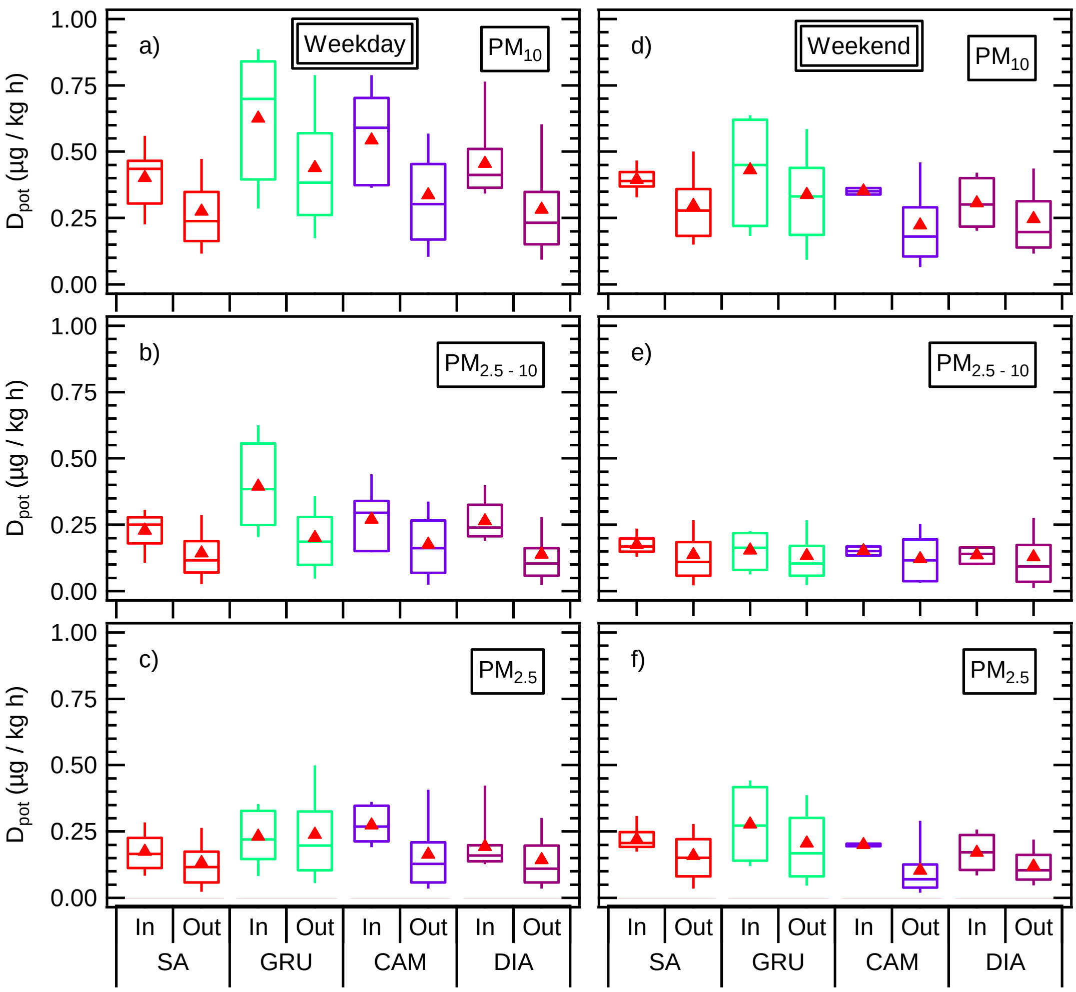

Fig. 5. Estimated potential dose (D_{pot}) for males inside and outside bus terminals (In and Out, respectively) on weekdays for a) PM_{10}, b) coarse, and c) fine particles; and on weekends for d) PM_{10}, e) coarse, and f) fine particles. The whiskers in the figure represent the 5th and 95th percentiles, whereas the box itself presents the 25th, 50th (median) and 75th percentiles. The arithmetic average is represented by triangles.

PM_{10} = particles ≤ 10 µm in diameter, $PM_{2.5–10}$ = particles 2.5–10 µm in diameter, $PM_{2.5}$ = particles ≤ 2.5 µm in diameter, SA = Santo Andre, GRU = Guarulhos, CAM = Campinas, DIA = Diadema.

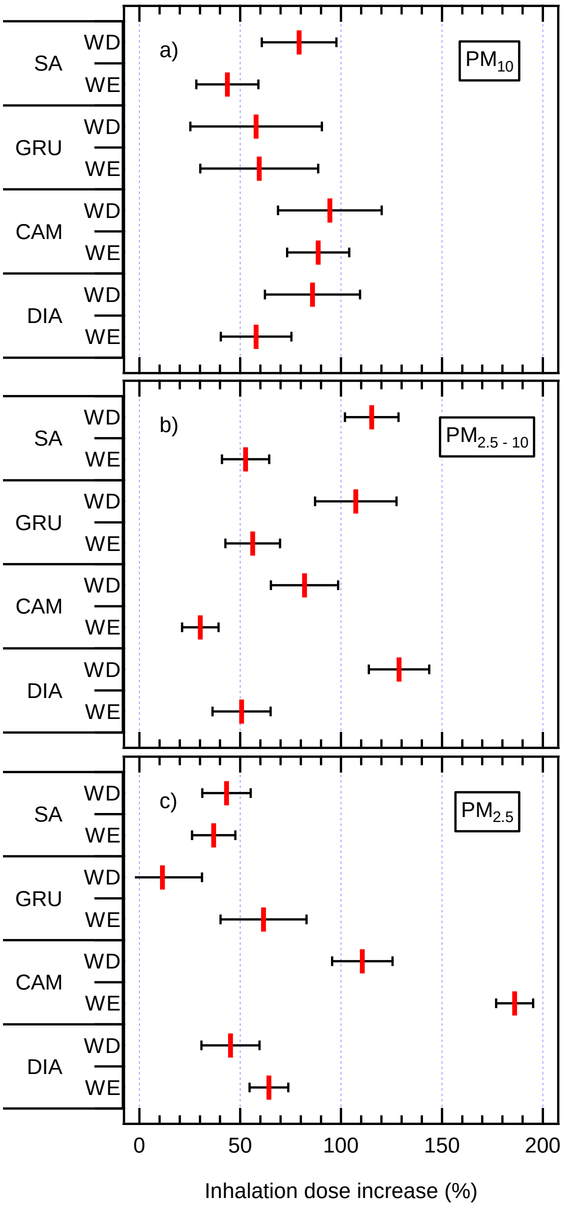

Fig. 6. Weekday (WD) and weekend (WE) percentage inhalation dose increase (%) estimated for commuters travelling through bus terminals in the Metropolitan Area of Sao Paulo, Brazil, in comparison commuters travelling outside those same bus terminals. Error bars represent the standard deviation of the average value obtained at each bus terminal.

SA = Santo Andre, GRU = Guarulhos, CAM = Campinas, DIA = Diadema, PM_{10} = particles ≤ 10 µm in diameter, $PM_{2.5–10}$ = particles 2.5–10 µm in diameter, $PM_{2.5}$ = particles ≤ 2.5 µm in diameter.

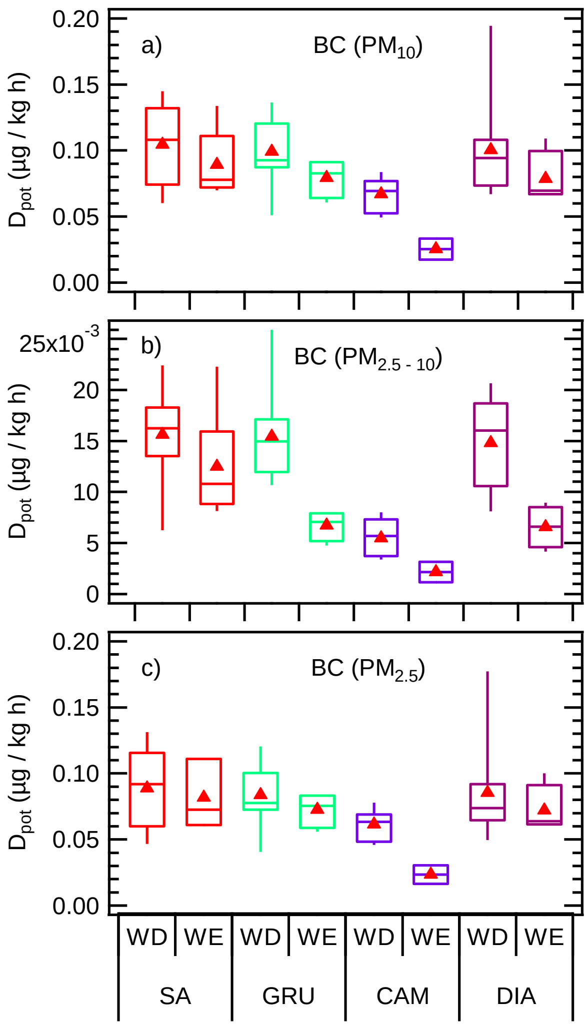

Fig. 7. Weekday (WD) and weekend (WE) potential dose (D_{pot}) of black carbon (BC), estimated for males, in a) particles ≤ 10 µm in diameter (PM_{10}), b) particles 2.5–10 µm in diameter ($PM_{2.5–10}$, coarse fraction) and c) particles ≤ 2.5 µm in diameter ($PM_{2.5}$, fine fraction), inside bus terminals. The whiskers in the figure represent the 5th and 95th percentiles, whereas the box itself presents the 25th, 50th (median) and 75th percentiles. The arithmetic average are represented by triangles.

SA = Santo Andre, GRU = Guarulhos, CAM = Campinas, DIA = Diadema.

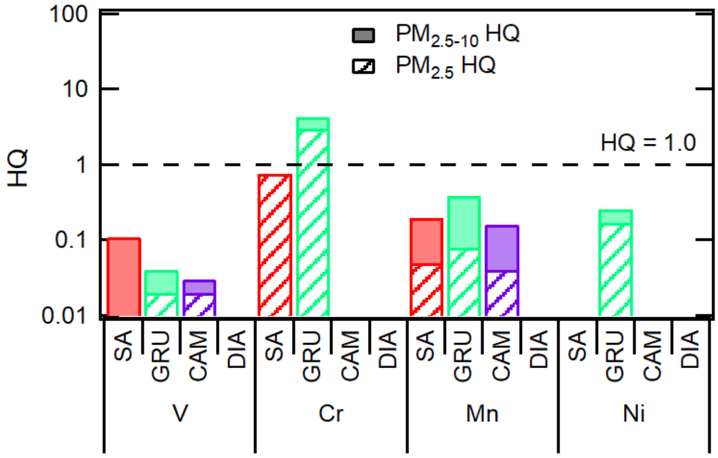

Fig. 8. Hazard quotient (HQ) values estimated for exposure to particles 2.5–10 µm in diameter ($PM_{2.5–10}$) or ≤ 2.5 µm in diameter ($PM_{2.5}$) containing the elements V, Cr, Mn and Ni.

SA = Santo Andre, GRU = Guarulhos, CAM = Campinas, DIA = Diadema.

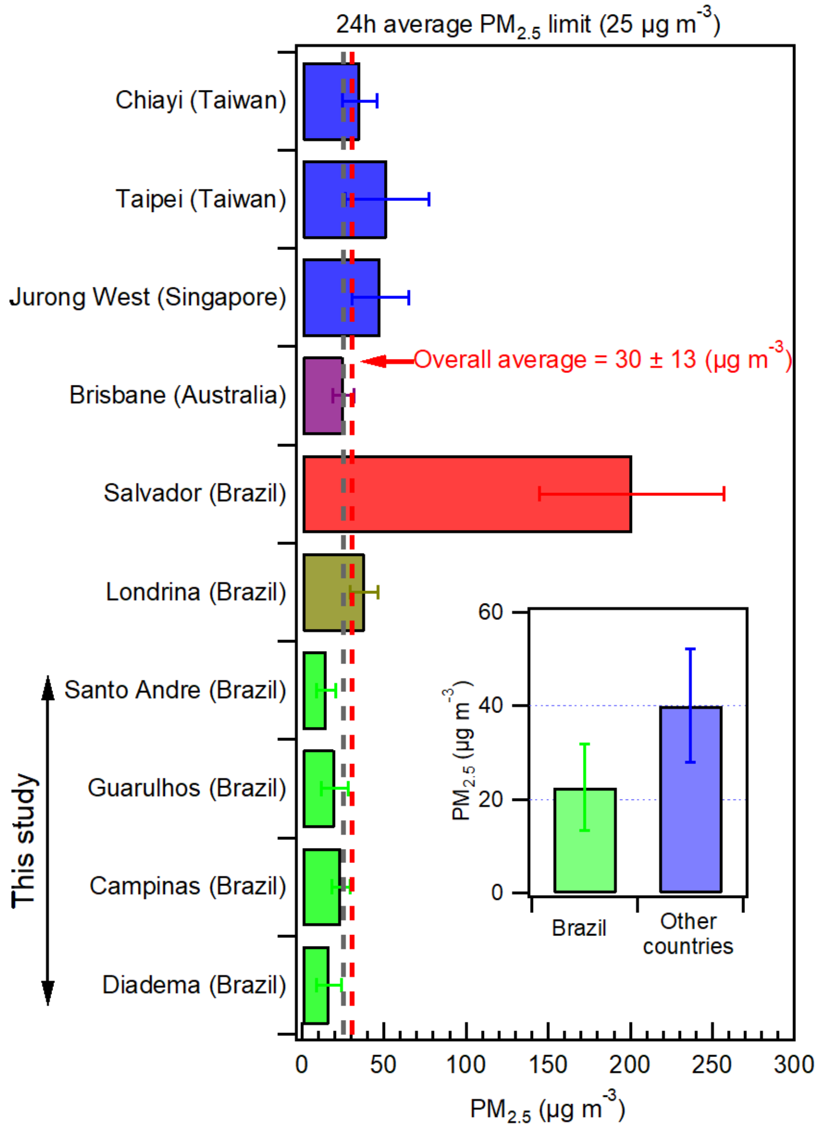

Fig. 9. Average concentrations of particles ≤ 2.5 µm in diameter ($PM_{2.5}$) inside bus terminals in the Metropolitan Area of Sao Paulo, Brazil, compared with those reported for other bus terminals around the world. Error bars represent the standard deviation of the average value obtained in each study. The embedded figure on the right presents the average value for all studies conducted in bus terminals in Brazil, excluding one conducted in the city of Salvador, in comparison with that for studies conducted in other countries. Error bars represent the standard deviation of the average values. For more details, see Table S2 in the Supplemental Material.

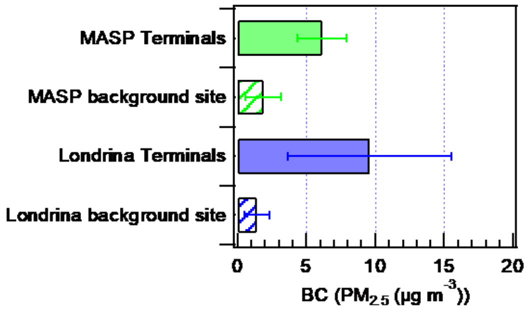

Fig. 10. Average concentrations of black carbon (BC) inside bus terminals in the Metropolitan Area of Sao Paulo and in the city of Londrina, compared with the concentrations reported for their respective background sites (dashed bars). Error bars represent the standard deviation of the average value obtained at each study. For more details, see Table S3 in the Supplemental Material.