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Health Risk Assessment Through Inhalation of Chemical Elements in Particulate Matter: A Case Study of Occupational Exposure in Highway Toll Plazas

Gabriel Pinheiro Machado [1], Marina Smidt Celere Meschede [2], Danilo Vitorino dos Santos [3], Guilherme Sgobbi Zagui [4,5], Murilo D. M. Innocentini [4,6], Carlos Eduardo Formigoni [4], Jordi Sierra [7,8], Joaquim Rovira [8], Martí Nadal [8], José Luis Domingo [8] and Susana Inés Segura-Muñoz [1,*]

1 Department of Maternal-Infantil Nursing and Public Health, Ribeirão Preto College of Nursing, University of São Paulo, Bandeirantes Avenue 3900, Ribeirão Preto 14040-902, Brazil; gabriel.pinheiromachado89@gmail.com
2 Institute of Collective Health (ISCO), University of Western Pará (UFOPA), Santarém 68035-110, Brazil; marina.meschede@ufopa.edu.br
3 Center of Chemical Waste Management, School of Pharmaceutical Sciences of Ribeirão Preto, University of São Paulo, Bandeirantes Avenue 3900, Ribeirão Preto 14040-903, Brazil; danilo@usp.br
4 Postgraduate Program in Environmental Technology, University of Ribeirão Preto, UNAERP, Ribeirão Preto 14096-900, Brazil; gszagui@unaerp.br (G.S.Z.); minnocentini@unaerp.br (M.D.M.I.); cformigoni@unaerp.br (C.E.F.)
5 School of Medicine, Department of Medicine, University of Ribeirão Preto, UNAERP, Ribeirão Preto 14096-900, Brazil
6 Centre for Regenerative Design and Engineering for a NEt Positive World (RENEW), Department of Architecture and Civil Engineering, University of Bath, Bath BA2 7AY, UK
7 Faculty of Pharmacy and Food Sciences, Universitat de Barcelona, Joan XXIII s/n Avenue, 08028 Barcelona, Catalonia, Spain; sierra@ub.edu
8 Laboratory of Toxicology and Environmental Health, School of Medicine, IISPV, Universitat Rovira i Virgili, Sant Llorenç 21, 43201 Reus, Catalonia, Spain; joaquim.rovira@urv.cat (J.R.); marti.nadal@urv.cat (M.N.); joseluis.domingo@urv.cat (J.L.D.)
* Correspondence: susis@eerp.usp.br

Abstract

(1) Background: Highway toll plazas are environments impacted by atmospheric pollutants that may affect workers' health. However, there are still few studies on these environments. This study evaluated particulate matter (PM) concentrations by size fraction ($PM_{10–9.0}$ to $PM_{0.43}$) and associated arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), manganese (Mn), nickel (Ni), lead (Pb) and vanadium (V) at two toll plazas in Brazil. (2) Methods: PM and trace element concentrations were compared between dry and rainy seasons, and a health risk assessment was conducted for toll collectors based on inhalation exposure. (3) Results: $PM_{10–2.5}$ concentrations ranged from 31.8 to 360 μg m^{-3} in the dry season and from non-detectable to 287 μg m^{-3} in the rainy season. $PM_{2.5}$ levels varied between 14.9 and 150 μg m^{-3} (dry) and 3.46–174 μg m^{-3} (rainy). Although trace element concentrations were within Occupational Safety and Health Administration (OSHA) limits, the hazard quotient (HQ) for manganese and arsenic exceeded unity (HQ > 1), indicating potential health risks. (4) Conclusions: These findings suggest that toll plaza workers may experience increased inhalation-related risk under the exposure assumptions used. Improved ventilation and protective measures, including the use of protective screens, are recommended to reduce occupational exposure.

Keywords: occupational exposure; particulate matter; metals; risk assessment

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1. Introduction

Annually, work-related illnesses affect approximately 160 million people worldwide and, along with workplace accidents, can be responsible for around 2 million deaths [1]. Health problems that arise or worsen in work environments can be caused by a series of physical, chemical and biological agents, movement repetition and/or stress [2,3]. Thus, occupational health emerges as an important field to carry out environmental, clinical–biological and social studies on workers' health, which can guide laws, regulations and public policies that promote occupational health [4]. Unfortunately, for some occupations, there are only a few studies focused on analyzing the risk factors for workers' health in their work environment, including road toll plaza collectors [3,5–10]. These workers operate inside cabins next to a vehicle corridor, charging fares to drivers who travel on highways, which have had their administration granted to the private sector. The road toll collectors are potentially exposed to various atmospheric pollutants from vehicle exhaust [9,11,12], like particulate matter, volatile organic compounds (VOCs) and NO_2. The proximity of the collectors to the emission sources, as well as the booth ventilation system, the number of vehicles crossing the toll and their acceleration and braking, are important factors that contribute to the increase in pollutant concentrations and the associated exposure for individuals working inside the cabins [9,12].

Particulate matter (PM) is among the air pollutants of traffic origin that can be considered risk factors for toll collectors. PM is defined as a mixture of liquid and solid compounds dispersed in the air as an aerosol; these compounds stand out for their ability to penetrate the respiratory tract and adsorb toxic components, such as metals and polycyclic aromatic hydrocarbons (PAHs) [13–15]. It has been demonstrated that exposure to coarse particulate matter ($PM_{10–2.5}$), with a diameter between 2.5 and 10 μm, and fine particulate matter ($PM_{2.5}$), with a diameter equal to or less than 2.5 μm, is related to chronic and acute respiratory and cardiovascular system diseases such as asthma, chronic obstructive pulmonary disease, lung cancer, heart attacks, and strokes [15–18]. The toxic components adsorbed into PM can act in different ways in workers. Metals act as mediators of airway damage, through the formation of Reactive Oxygen Species (ROS), in addition to being able to interact with various metalloproteins in biological systems and with cell DNA, becoming carcinogenic agents [19–24].

The present study aimed to evaluate the concentrations of nine size-segregated PM and associated metals in two different toll plazas in São Paulo State, Brazil. Based on the metal concentrations, the carcinogenic and non-carcinogenic risks derived from PM inhalation were also estimated for toll plaza workers. The study becomes relevant given that São Paulo state has a significant number of privatized highways (6600 km) that represent 30% of the national total (22,000 km of privatized highways) [25,26]. Unlike previous studies that focused only on $PM_{2.5}$, this research fills a critical gap by analyzing the detailed fractionation (nine stages) and seasonal variation (dry vs. rainy) of PM and metal concentrations, allowing for correlation between particle size and the anatomical site of pulmonary deposition and the specific health risk to Brazilian workers.

2. Materials and Methods

2.1. Sampling Site

The current study was carried out at two toll plazas (Toll 1 and Toll 2) that operate in São Paulo State (SP), in southeastern Brazil, approximately 50 km from Ribeirão Preto city (711,825 inhabitants) [27]. According to 2018 data, the average daily number of vehicles traveling through Toll Stations 1 and 2 were 19,519 and 12,788, respectively [28]. The proportion of small to large vehicles circulating between the toll plazas was 80–90% and 10–20%, respectively, for both sampling points [29]. The region's climate is characterized as

tropical with dry winters and rainy summers (Aw), based on the Köppen–Geiger classification. The precipitation, maximum and minimum temperature, wind speed and direction data recorded during the sampling period are presented in Table S1 in the Supplementary Material [30].

2.2. Particulate Matter Sampling

To characterize the dry and rainy seasons of the region, respectively, two campaigns were conducted in October 2020 and March 2021. In each campaign, four samplings were carried out. The collection equipment was placed in the center of the toll plaza, one meter in front of the booth, where there were two workers collecting fees from drivers traveling in both directions of the highway, at a height of approximately 150 cm from the ground. Samplings were carried out between 6 am and 2 pm, which represents the morning work shift at toll plazas.

Air sampling was carried out using an eight-stage cascade impactor (IMPAC8; 20–800, Tisch Environmental) fitted with 81 mm diameter glass fiber filters (A/E Fiber, 1 µm nominal; Pall Corporation). The impactor was operated at a nominal volumetric flow rate of 0.0283 m^3 min^{-1} (≈1700 L h^{-1}). The flow was set at the start of each sampling run using an in-line variable-area flow meter (rotameter; 0–2000 L h^{-1} range) with 50 L h^{-1} graduations, factory calibration, and a stated accuracy of ±5%. The particle-size fractions collected by the respective cascade impactor stages are shown in Figure 1.

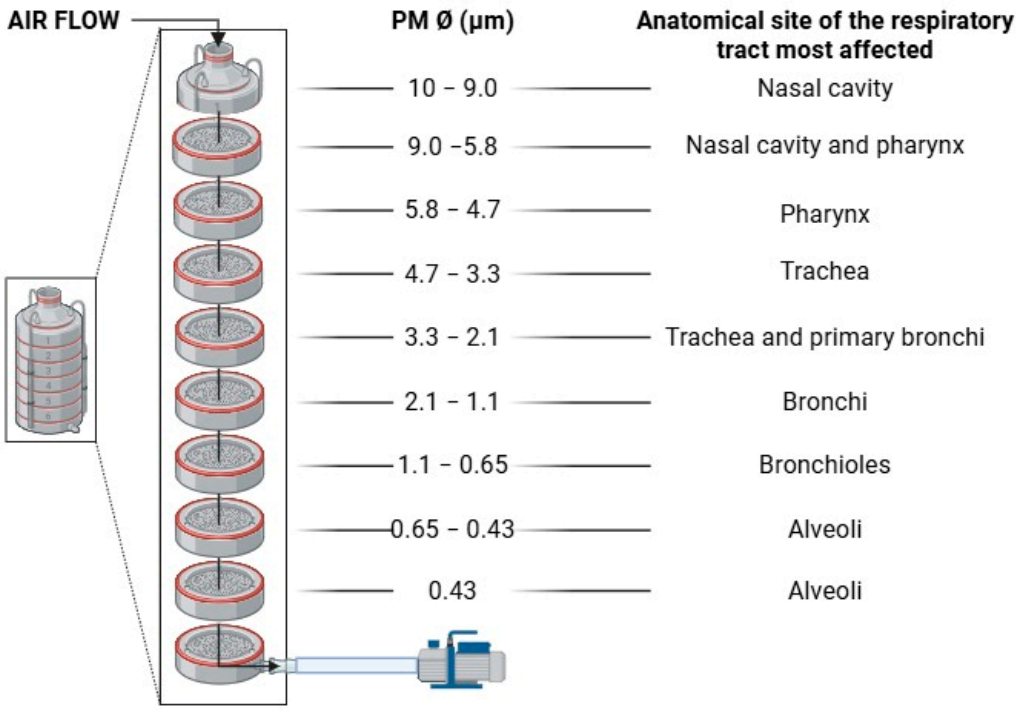


Figure 1. Eight-stage cascade impactor with respective layers for PM sampling and the most affected anatomical site for each PM fraction. Source: Adapted from Londahl et al. (2008) [31].

The equipment samples particles in eight different size ranges and a backup filter fraction ($PM_{0.43}$), as each one can penetrate different layers of the respiratory tract and, as previously stated, the effects are greater as the PM reaches the innermost parts of the lungs. Particle penetrability is shown in Figure 1, according to Londahl et al. (2008) [31].

2.3. Sample Treatment

Before sampling, the filters were previously conditioned in a desiccator (Energética Ind. e Com. Ltda., Rio de Janeiro, Brazil) with silica gel for 24 h. The temperature was

set at a range of 15–30 °C and the relative humidity was controlled at values <50%, with a variation of less than 5%, measured by a thermo-hygrometer (Instrutemp TH-5108, São Paulo, Brazil) coupled to the equipment.

After pre-reconditioning, each filter had its mass weighed gravimetrically three times before each collection and then packaged in the IMAPC8 layers, which was transported to the sampling points. The equipment was installed via a male rubber tube to a flow pump, which, in turn, was connected to an extension socket and operated within the specified time. The pump was turned on and off manually. After the samplings, the filters were conditioned again in the same way as before the collections and weighed three times each.

To evaluate PM concentrations, the average of the masses of each filter were considered. The calculation of PM concentrations was performed using Equation (1):

$$C = \frac{m_1 - m_0}{V} \cdot 10^6 \quad (1)$$

where $\boldsymbol{C}$ is the concentration of the particulate matter fraction (μg m^{-3}), $\boldsymbol{m_1}$ is the mass of the filters after sampling (g), $\boldsymbol{m_0}$ is mass of the filter before sampling (g), $\mathbf{10^6}$ is the conversion factor from grams (g) to micrograms (μg), and $\boldsymbol{V}$ is the final volume of air sampled (m^3).

For accuracy, the IMPAC 8 layers were washed with water and detergents before each collection, and the flow was evaluated using a flow meter.

2.4. Metal Quantification

After collection, the samples were submitted to metal quantification in $PM_{10–2.5}$ and $PM_{2.5}$. This separation was made because some occupational exposure limits for metals may differ for these two fractions of particulate matter. For this, 40.5 mm diameter surfaces were selected from each filter, in which samples with PM from the first five layers of the impactor were analyzed jointly (particles between 10 μm and 9.0 μm; 9.0 μm and 5.8 μm; 5.8 μm and 4.7 μm; 4.7 μm and 3.3 μm; 3.3 μm and 2.1 μm) and the last four (2.1 μm and 1.1 μm; 1.1 μm and 0.65 μm; 0.65 μm and 0.43 μm and below 0.43 μm).

Samples were digested with 2 mL of nitric acid (65% Suprapur, E. Merck, Darmstadt, Germany) and 3 mL of hydrofluoric acid (37.5%, Panreac SA, Castellar del Vallès, Barcelona, Spain) in Teflon pumps for 8 h at room temperature and additionally 8 h at 80 °C. Subsequently, the extracts were evaporated in a sand bath and reconstituted with 2.5 mL of nitric acid and 22.5 mL of ultrapure water [32]. After treatment, metals were measured by inductively coupled plasma mass spectrometry (ICP-MS, Perkin Elmer Elan 6000, Shelton, CT, USA). In all samples, the total concentrations of arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), manganese (Mn), nickel (Ni) and vanadium (V) of the elements were evaluated. The concentration of metals was obtained by subtracting the concentrations found in the blanks and considering the volume of the dilutions.

2.5. Method Validation

For air analysis, the accuracy of the instrumental methods was verified by triplicate samples, as well as by using blanks and a certified reference material (Urban Particulate matter, 1648a, National Institute of Standards & Technology, Gaithersburg, MD, USA) to be performed after every 5 samples. The detection limits (DLs) for metals were 0.25 ng m^{-3} for Cd, 0.50 ng m^{-3} for Mn, 1.00 ng m^{-3} for Cr, Cu, Pb, Ni and V, and 2.50 ng m^{-3} for As. Recovery rates ranged from 76% to 113%.

2.6. Exposure and Health Risk Assessment

The exposure to trace elements via inhalation was calculated by taking the total concentrations, in accordance with USEPA (2009) [33], as follows in Equation (2):

$$Exp = \frac{Cair \cdot ET \cdot EF \cdot ED}{AT} \quad (2)$$

where ***Exp*** is the exposure to trace elements via inhalation (μg m^{-3}); ***Cair*** is the mean concentration in PM_{10} of each trace element in air (μg m^{-3}); ***ET*** is the exposure time (8 working h/day); ***EF*** is the frequency of exposure (295 work days/year); ***ED*** is the duration of exposure (30 years of work); and ***AT*** is the averaging time (365 days·30 years·24 h). For ***ED***, the working period to retire in Brazil was considered, while for ***EF***, the working days per year, excluding holidays, vacations and weekends, was considered. For ET, an 8 h work shift was considered [34].

The hazard quotient (***HQ***) is a numerical estimate of the systemic toxicity potential of a single component through a single route of exposure. HQ was calculated according to Equation (3):

$$HQ = \frac{Exp}{(RfC \cdot 1000)} \quad (3)$$

where ***Exp*** is the exposure to trace elements via inhalation (μg m^{-3}); ***RfC*** is reference concentration for each metal (mg m^{-3}), and **1000** is the conversion factor from mg m^{-3} to μg m^{-3}.

In turn, the hazard index (HI) was calculated by summing the HQs of the metals. HI is a numerical estimate of the systemic toxicity potential of all agents that reach a receptor through a single route of exposure. Values of HQ ≥ 1 indicate that the exposed individuals may be subjected to health risks, and therefore, protective measures should be taken. For inhalation exposure, the carcinogenic risk was calculated according to Equation (4):

$$ELCR = Exp \cdot \ IUR \quad (4)$$

where ***ELCR*** is the Excess Lifetime Cancer Risk, an estimate of the increased incidence of cancer (probability) for a receptor, resulting from exposure to a chemical agent through a single route of exposure. In turn, ***IUR*** is the Inhalation unit risk, which is the carcinogenicity factor of each compound [35]. When the ELCR is above 10^{-4}, which means a probability of one individual among 10,000 exposed individuals can develop a cancer, it is considered an unacceptable carcinogenic risk. The total cancer risks, through inhalation, are calculated by the sum of ELCRs of each metal.

For metals that showed HQ ≥ 1 and/or ELCR $\geq 10^{-4}$, Monte Carlo simulations were performed to evaluate the uncertainties of the C_{air} and ED parameters, as these are the variables most susceptible to change. For each simulation, 10,000 random numbers were generated from a normal distribution for C_{air} and a discrete distribution for ED. Means and standard deviations were used for the simulations, with intervals of 2 to 30 years, respectively.

2.7. Data Analysis

An exploratory analysis was performed, based on statistical tests comparing the results found for PM and trace elements, for the dry and rainy seasons and tolls 1 and 2, respectively. The Shapiro–Wilk test was applied to evaluate the normal distribution. The *t* test (Student) was used between variables that presented normal distribution, while the Mann–Whitney test was used for those that did not present normal distribution. A p value < 0.05 was considered statistically significant. Values below the detection limit

were assumed to be one-half of the detection limit (ND = 1/2 DL). GraphPad Prism v 10.0 software was used for statistical analysis.

Total concentrations of $PM_{10–2.5}$ and $PM_{2.5}$ were also compared with national (State Decree no 59,113 of 2013 and Regulatory Standards nº 15) and Threshold Limit Value-Time Weight Average (TLV-TWA) of Occupational Safety and Health Administration (OSHA) [36–38]. The concentrations of trace elements were compared to Regulatory Standards nº 15 (NR-15), TLV-TWA from American Conference of Governmental Industrial Hygienists (ACGIH) and OSHA [37–39]. The state decree 59,113 refers to daily concentrations and was only used as a comparative assessment of air quality, not as an occupational exposure limit.

3. Results and Discussion

3.1. Particulate Matter

Figure 2 shows the PM concentrations during the dry and rainy periods, in both toll plazas and in Toll 1 and Toll 2, in both seasons.

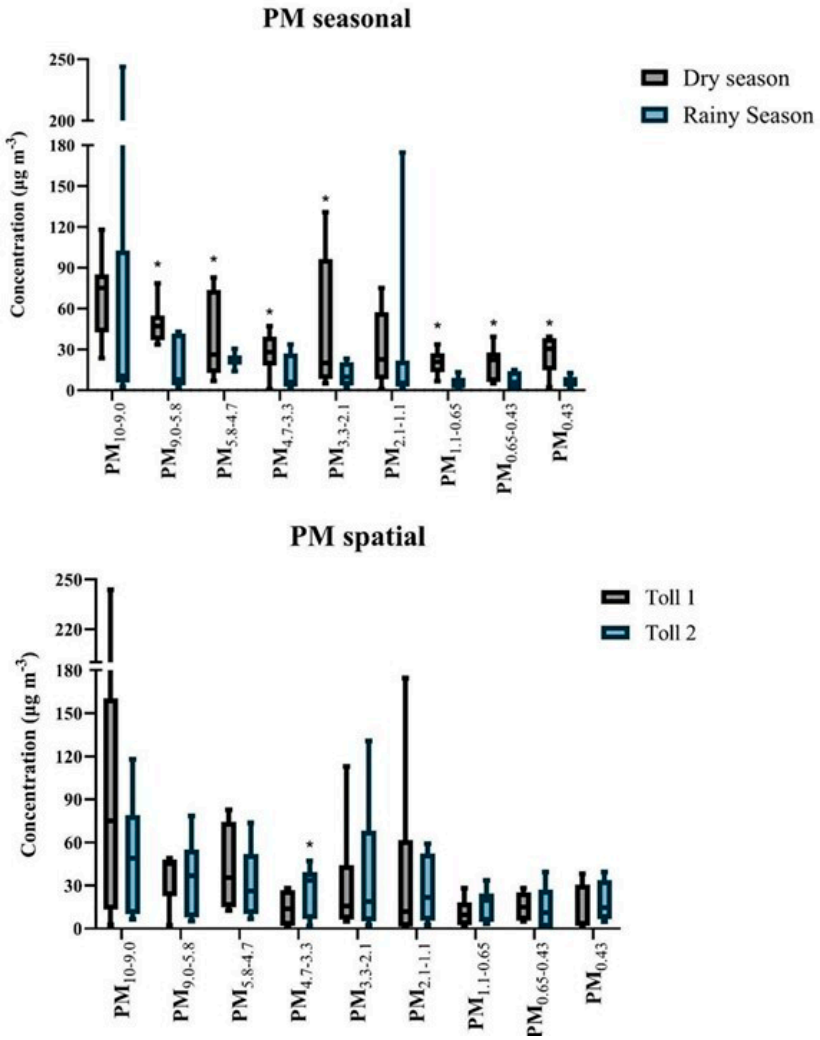


Figure 2. Concentrations of nine fractions of particulate matter in dry and rainy seasons (in both toll plazas) and in Toll 1 and Toll 2 (in both seasons). * An asterisk indicates significant differences between dry and rainy seasons.

The total PM concentrations ranged between 102 µg m^{-3} and 510 µg m^{-3} in the dry season, while in the rainy season the concentration varied from 3.46 µg m^{-3} to 461 µg m^{-3}.

These amounts, divided in $PM_{10–2.5}$, ranged from 31.8 μg m^{-3} to 360 μg m^{-3} in the dry season and 287 μg m^{-3} at concentrations absent in the rainy season, while $PM_{2.5}$ ranged from 14.9 μg m^{-3} to 150 μg m^{-3} in the dry season, and 3.46 μg m^{-3} to 174 μg m^{-3} in the rainy season.

Data on the PM distribution by diameter highlights a greater presence of particles between $PM_{10–9.0}$ and $PM_{2.1–1.1}$ (Figure 2), in agreement with previous findings in the scientific literature [40]. A greater predominance of finer fractions of particulate matter has been observed in areas impacted by vehicles and industrial emissions, as these sources release gases that can fuse and form particles. Studies show that the coarse fraction ($PM_{10–9.0}$, $PM_{9.0–5.8}$, $PM_{5.8–4.7}$, $PM_{4.7–3.3}$ and $PM_{3.3–2.1}$) can stem from soil and road dust suspended by vehicle traffic [40–42]. Toll plazas are semi-open places with a roof, but they are subjected to winds that can carry particles of different sizes, including larger ones, which are added to smaller particles originating from vehicle emissions. Noteworthily, highways are surrounded by agricultural areas that can also be a source of particulate matter, including coarser fractions such as $PM_{10–9.0}$ [43]. However, this information cannot be confirmed without an analysis of the sources.

The current results show significant differences between the dry and rainy seasons for $PM_{9.0–5.8}$ $PM_{5.8–4.7}$ $PM_{4.7–3.3}$, $PM_{1.1–0.65}$, $PM_{0.65–0.43}$, and $PM_{0.43}$, corroborating the results of previous studies carried out in the region [44,45]. These differences occur mainly due to the greater presence of rain and lower incidence of fires during the rainy season. Therefore, $PM_{10–9.0}$ and $PM_{2.1–1.1}$ did not show significant differences, which indicates that vehicles constantly influence toll plazas throughout the year, even in rainy seasons. The absence of significant differences in $PM_{10–9.0}$ also suggests the potential influence of soil and road dusts as vehicular emissions [9,41,42].

The daily vehicle traffic on Toll 1 was higher than that on Toll 2 (19,519 and 12,788, respectively). However, no significant differences were found between the two sampling points, except for $PM_{4.7–3.3}$, which was higher in Toll 2, although Toll 1 presents more traffic [28]. It must be noted that, in addition to the number of vehicles, air quality can be impacted according to the kinds of vehicles. For instance, older and large vehicles with faulty emission regulation systems tend to release more air pollutants. Therefore, the monitoring of concentrations of PM and other pollutants must be continuous, even during periods of low vehicle circulation.

In a study carried out at toll plazas in China, an average $PM_{2.5}$ concentration of 230.73 μg m^{-3} was found, while in the present study it was 65.82 μg m^{-3} [46]. As Li et al. (2019) did not report the average daily volume of vehicles in the plazas, it was not possible to assess the potential causes for the differences in pollutant concentrations [46]. As there are busier toll plazas in Brazil, which are located in the country's main metropolitan regions, such as São Paulo, more studies are required to evaluate the air quality in places with different average daily vehicle volumes in the country.

In none of the analyzed samples were the NR-15 standards (3 mg m^{-3} for PM_{10}, for 8 h) and Occupational Safety and Health Administration (OSHA) limits (15 mg m^{-3} for PM_{10} and 5 mg m^{-3} for $PM_{2.5}$, for 8 h) exceeded. However, the national daily standards of air quality (100 μg m^{-3} for PM_{10} and 50 μg m^{-3} for $PM_{2.5}$) for the health for the general population were exceeded for PM_{10} in all samplings from the dry season, as well as in two samples from the rainy season. For $PM_{2.5}$, threshold levels were also reached in seven samplings from the dry season and two samplings from the rainy season [36,37]. It should be noted that the standards are for 24 h environmental assessments, although they may indicate local air quality during the sampling period. It should be highlighted that recommended annual mean air quality guidelines for PM_{10} and $PM_{2.5}$ set by the World Health Organization are 15 and 5 μg m^{-3}, respectively [47]. A study performed in

Sweden that evaluated occupational exposure to PM demonstrated that these pollutants are associated with ischemic heart disease [48]. In a study carried out with waste collection workers in South Korea, it was shown that they are exposed to particles from vehicle diesel exhaust [49].

3.2. Trace Elements

The mean, maximum and minimum concentrations of trace elements in $PM_{10–2.5}$ and $PM_{2.5}$, in the dry and rainy seasons (in both toll plazas), and in Toll 1 and Toll 2 (in both seasons) are shown in Figure 3.

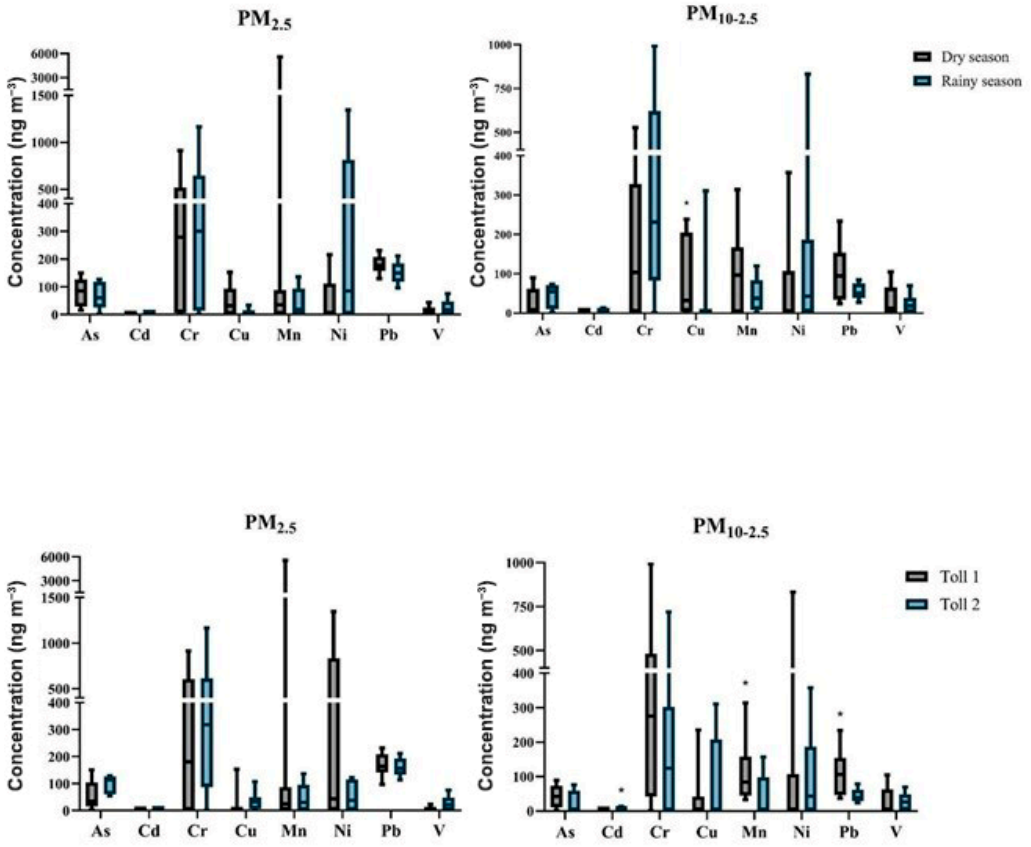


Figure 3. Trace element concentrations of $PM_{10–2.5}$ and $PM_{2.5}$, in dry and rainy seasons (in both toll plazas) and in Toll 1 and Toll 2 (in both seasons). * An asterisk indicates significant differences between dry and rainy seasons.

There were no significant differences in the concentrations of $PM_{10–2.5}$-associated metals according to the seasonal sampling, except for Cu, whose concentration was higher in the dry season. These results do not corroborate those found in PM, which were mostly higher in the dry season; however, as reported in some environmental studies in the region, there is no pattern between metal concentrations and seasonal period of sampling [44,45]. Therefore, the similarities found in the present study for metals may have been due to the sources of emissions of these metals being constant during the sampling period [50].

No significant differences in metal concentrations in $PM_{10–2.5}$ and $PM_{2.5}$ were found between the toll plazas, except for Pb and Mn, which were higher at Toll 1, and for Cd, with higher values at Toll 2. All differences between the sampling points occurred in the fraction of $PM_{10–2,5}$ that presents a large part of the elemental emissions from the crust, which are added to anthropogenic emissions. On the other hand, $PM_{2.5}$ comes mainly from sources of combustion and burning of materials [51]. These results might indicate that parts of these differences were not due to differences in vehicle emissions. Although Toll 1 had more

traffic, this was not enough to cause significant differences in PM concentrations between the sampling points.

All of the trace elements detected in the current study were also found in previous studies aimed at evaluating vehicle emissions, the main sources at toll plazas [52–54]. A study demonstrated that approximately 65.6% of $PM_{10–2.5}$ and 29.1% of $PM_{2.5}$ originating from vehicles is emitted from non-exhaustive sources, such as wear and tear of parts and brakes, lubricating oil, tires, and highway dust, which carry metals in their composition [55,56]. Manganese may be related to brake wear and chromium is related to the wear of engine parts, while Ni is present in mineral diesel, virgin engine oil and additives [49]. Lead and Cd are also found in vehicle emissions, as they are present in fuels and brake linings [50,57].

Table S2, in the Supplementary Material, summarizes the maximum pollutant concentrations, air quality standards, and TLV-TWA considered in this study. None of the trace elements presented concentrations higher than the NR-15, OSHA and ACGIH limits (8 h), but the World Health Organization's air quality guidelines (2022) were exceeded for Ni (25 ng m^{-3}), Cd (5 ng m^{-3}) and As (6.6 ng m^{-3}) [58]. Although these guidelines represent annual averages for the health of the general population and the exposure for workers at the toll plaza occurs for 8 h, it is possible to identify the low quality of the local air compared to other studies conducted in the region [45,46]. It must be considered that many effects caused by metals on the body are chronic; therefore, long-term exposure to the concentrations found in this study can cause—or worsen—health problems.

The analyzed elements can affect the exposed population through inhalation and cause carcinogenic and non-carcinogenic adverse effects. Cadmium is associated with breast and prostate cancer, while its non-carcinogenic effects mainly affect the kidneys (kidney stones and tubulointerstitial nephritis) [21,59]. Arsenic is associated with lung cancer, increased atherosclerosis and cardiovascular effects, while nickel causes bronchitis and asthma, lung cancer, and effects on the gums, mouth, and skin [21,59].

3.3. Health Risk Assessment

The risk quotients for the metals included in this study are given in Table 1.

Table 1. Risk quotients (HQ), Risk Index (HI) and exposure (Exp) in μg m^{-3} for metals at Tolls 1 and 2.

Metals	Toll 1			Toll 2		
	HQ	**ELCR**	**Exp. ****	**HQ**	**ELCR**	**Exp. ****
As	1.68 *	8.92×10^{-5}	2.07×10^{-2}	2.42 *	1.36×10^{-4} *	3.17×10^{-2}
Cd	0.19	3.41×10^{-6}	1.90×10^{-3}	0.27	4.87×10^{-6}	2.70×10^{-3}
Cr (VI)	0.22	1.88×10^{-3} *	2.24×10^{-2}	0.19	1.62×10^{-3} *	1.93×10^{-2}
Cu	-	-	1.29×10^{-2}	-	-	3.40×10^{-2}
Mn	3.73 *	-	1.86×10^{-1}	0.38	-	1.92×10^{-2}
Ni	0.56	1.21×10^{-5}	5.05×10^{-2}	0.37	8.12×10^{-6}	3.38×10^{-2}
Pb	-	-	7.57×10^{-2}	-	-	5.58×10^{-2}
V	0.08	-	7.85×10^{-3}	0.13	-	1.35×10^{-2}
Hazard Index	6.46 *	-	-	3.76 *	-	-

* HQ and HI > 1; ELCR > 10^{-4}. ** Exp. calculated from mean trace element concentrations.

Since the present study was only focused on air pollutants, inhalation was considered as the single exposure route. For non-carcinogenic risk assessment, some elements such as Cu and Pb do not have a reference concentration for this exposure route, so they were not considered for this analysis. In turn, no IUR values have been yet established for Cu, Mn, Pb or V. Therefore, these elements were not considered for carcinogenic risk assessment. Chromium presents reference values only for its hexavalent form (VI), which represents

approximately one-sixth of the total chromium concentration in soils [59,60]. Thus, for the risk analysis, 1/6 of the total Cr concentrations was considered.

Manganese and As were the trace elements with the greatest HQ, exceeding the unity in Toll 1 (Mn) or both tolls (As). The results for Mn corroborated previously published data from China, in which this element also presented the highest risk quotient in relation to the others [46]. However, the data differed regarding As, whose HQ was lower than 1. In the present study, the total concentrations of metals in the PM were considered, while in the study of Li et al. (2019) [46], only the $PM_{2.5}$-associated chemical elements were considered [46]. On the other hand, risks for toll workers were higher than those found for Ribeirão Preto's general population [45].

Manganese is an element that, at high concentrations, can trigger effects on the nervous system. Studies have revealed that Mn is associated with motor dysfunctions and Parkinson's disease [61–63]. As for arsenic, evidence of non-carcinogenic effects is mainly supported by oral exposure. However, various studies demonstrate effects on the central and peripheral nervous systems and thyroids also derived from inhalation exposure [61–63]. Although the concentrations of the elements did not exceed the occupational exposure limits, the risk assessment shows that even below the legal limit, the exposed population can be affected by exposure to metals [58,63,64].

The metals that presented carcinogenic risks above those recommended by the EPA were As in Toll 2, and Cr in both tolls. These elements may induce some carcinogenic effect in the exposed population, with a probability above 1:10,000, while the other elements have a probability below this proportion. The decreasing order of carcinogenic risks followed the same pattern in both toll plazas: Cr > As > Cd > Ni. The results for carcinogenic risks differed from the study conducted by Li et al. (2019), in which all elements were above the guidelines indicated by the EPA. In addition, the element that presented the greatest risk was Cd, followed by As and Ni [46]. These differences were mainly due to the concentrations found in each study.

Cr (VI) can cause lung and sinonasal cancer, as reported in studies that also evaluated occupational exposure [65–67]. Gastrointestinal tract, pancreas and breast cancer have also been observed to be associated with Cr exposure, but with less evidence [68–70]. The carcinogenic effects of As are mainly found in the lungs, skin, kidneys, bladder, liver, gastrointestinal tract and brain [71].

The risk distribution in different scenarios is presented in Figure S1 in the Supplementary Material. The ELCRs for Cr remained high, while for Mn and As, high risks were observed from the center of the distribution, reinforcing that it is possible to bring risks within acceptable limits by controlling some exposure factors, such as exposure time and pollutant emissions. However, it should be noted that the small number of samples limits this analysis.

The present study indicates that air pollution around toll booths can pose health risks to individuals exposed to it. However, other pollutants, also of vehicular origin, such as NO_2, SO_2, and volatile organic compounds (VOCs), may also be present in the toll plaza area, which can also expose workers there to further health risks [72]. Therefore, it is recommended that employers take proactive measures to promote the health and safety of workers in these locations, supported by public policies. Practical measures, such as the installation of exhaust systems, ventilation systems with filtered air, protective screens, and air curtains, along with personal protective equipment like disposable activated carbon masks, can help reduce occupational risks associated with exposure to air pollutants at toll booths. The uncertainty analysis also demonstrated that changes in exposure duration can reduce health risks below acceptable levels; therefore, altering workers' exposure time can become an effective measure, such as alternating shifts in toll booths among toll collectors

during the work period. Another effective measure would be to create public policies, laws, and regulations for non-exhaustive sources of trace elements in order to encourage vehicle manufacturers to incorporate technologies into their vehicles that reduce these forms of emissions.

3.4. Study Limitations

One of the limitations of this study is the low number of collected samples. It must be highlighted that the maximum concentrations of Mn differed from the others, which caused an increase in the respective risk quotients. Some sampling also revealed metal concentrations below detection limits. Therefore, it is suggested that future studies expand the sampling, as significant daily variations can occur and alter the risks. However, it should be noted that the study region has a tropical climate with dry winters and rainy summers, where the greatest climatic variation is in the amount of rainfall, with low temperature fluctuation throughout the year. Therefore, although the relatively low number of samples is a limitation, the fact that the collections covered both the dry and rainy seasons reduces the uncertainty in the analyses. Another limitation is that sampling was not carried out during the night shift, given that at other times there may be different weather and traffic conditions.

One additional limitation was the difficulty in determining a Cr VI ratio that would allow for a more accurate calculation of the carcinogenic risk associated with this element. Some sources suggest that this ratio may vary from 5 to 15%, while others have shown that it may vary from 30% to 40% in areas with high diesel vehicle traffic [73,74]. However, even considering the lowest proportion described in the cited studies, the carcinogenic risks remain above the acceptable value. The ELCRs in a scenario where the Cr VI proportion is 5% were 5.64×10^{-4} at Toll 1 and 4.88×10^{-4} at Toll 2 [73]. When considering the highest proportion of Cr VI described in the studies (40%), ELCRs of 4.51×10^{-3} were found for Toll 1 and 3.90×10^{-3} for Toll 2 [74]. These results reinforce the importance of adopting worker protection measures and technologies that reduce atmospheric Cr VI emissions.

4. Conclusions

The present study has shown that the concentrations of atmospheric pollutants monitored at two toll plazas on highways in São Paulo State did not exceed any legal value. However, for As, Cr, and Mn, risks were presented above acceptable levels, suggesting that they may pose a health risk to workers. The present results also highlight the need to establish measures that can minimize workers' exposure to air pollutants, such as improving air ventilation or adding exhaust mechanisms to prevent pollutants from entering the cabins. Having a rotation of professionals during the work shift and the expansion of electronic and automatic means for paying fares, as well as avoiding congestion at toll plazas, may also be important measures to be considered.

Supplementary Materials: The following supporting information can be downloaded at https://www.mdpi.com/article/10.3390/greenhealth2020013/s1: Table S1. Meteorological data during sampling (6 am to 2 pm), in the vicinity of the toll booths. Table S2. Maximum, state standards and TLV-TWA for PM_{10}, $PM_{2.5}$ ($\mu g\ m^{-3}$) and metals ($ng\ m^{-3}$). Figure S1. Monte Carlo simulations for trace elements that presented HQ > 1 and/or ELCR > 10^{-4} [30,37–39].

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