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Health impacts of $PM_{2.5}$-bound metals and PAHs in a medium-sized Brazilian city

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Abstract Rio Grande is a medium-sized industrial city located in the extreme south of Brazil, and previous studies in this city have shown contamination by metal(loids) and polycyclic aromatic hydrocarbons (PAHs) in water, soil, and sediment and in the atmosphere. In Brazil, the incorporation of $PM_{2.5}$ monitoring in environmental legislation is recent (2018) and, like other developing countries, the number of studies is still small. This study aimed to investigate the levels of $PM_{2.5}$ in the industrial and urban area of Rio Grande, to determine the concentration of metal(loid)s As, Cd, Cu, and Pb and of 16 PAHs in the samples of $PM_{2.5}$, to perform the health risk assessment for these contaminants and the health impact assessment for two possible scenarios of reduction of $PM_{2.5}$ levels. Our main findings regarding the $PM_{2.5}$ samples include the following: (1) The levels of this pollutant in the city of Rio Grande were higher than those allowed in current Brazilian legislation, in both the industrial and urban areas; (2) the existence of non-carcinogenic and carcinogenic risks for metals present in all samples; (3) the absence of carcinogenic risk for the assessed PAHs; and (4) the reduction scenarios proposed pointed to a reduction of up to 22 deaths annually in conjunction with reductions in health-related expenditures. Thus, these results may serve as a basis for the development of public health policies aimed at improving air quality, jointly assisting health surveillance and directing future studies towards a better intrinsic approach to the problem.

Keywords Particulate matter · Human health risk assessment · Health impact assessment · Brazil

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Introduction

In the current scenario of frequent infrastructural, monetary, and social advances, exposure to air pollution has become a major concern for the environment and public health (Mondal & Singh, 2021). The global burden of disease associated with air pollution exposure exacts an enormous toll on human health worldwide: the World Health Organization (WHO) (2021) estimates that exposure to air pollution causes approximately 7 million deaths annually. In face of this worrisome context, particulate matter with an aerodynamic diameter of 2.5 µm or less ($PM_{2.5}$) is the center of attention, since, as many clinical studies have shown, it is the most critical factor of air quality degradation, with a significant positive correlation between airborne particulate matter and detrimental human health outcomes (Alessandrini et al., 2013; Xing et al., 2016; Landrigan, 2017; Sharma et al., 2020; EEA, 2021; WHO, 2021; Zang et al., 2022), even being considered as the 5th-highest risk factor for human health (State of Global air, 2019).

Numerous natural and anthropogenic processes, such as volcanic eruptions, soil dust, combustion of fossil fuels for different purposes, vehicle emissions, construction residues, and waste incineration, may generate $PM_{2.5}$ in the atmosphere (EEA, 2021; WHO, 2021). Due to its small particle size and large specific surface area, the $PM_{2.5}$ is a complex mixture of chemical components that include metals and polycyclic aromatic hydrocarbons (PAHs), which are of interest for our study, and other compounds, such as elemental carbon, other organic carbon, sulfate and nitrate salts, and water (Zereini & Wiseman, 2010; Kim et al., 2013; Faraji Ghasemi et al., 2020; WHO, 2021). Previous studies have reported that some metals and PAHs are the major $PM_{2.5}$ components that are associated with harmful and toxic effects on human health (Kim et al., 2013; Landrigan, 2017; Sharma et al., 2020; Xing et al., 2016; Zereini & Wiseman, 2010; Zhang & Cao, 2015). In the case of metals, it is acknowledged that long-term exposure to some, mainly As, Cd, Cu, and Pb, in $PM_{2.5}$ can lead to higher carcinogenic risks, as well as chronic adverse effects on the respiratory, circulatory, and nervous systems (Hu et al., 2012; Xing et al., 2016; Sharma et al., 2020; Sui et al., 2020; Zang et al., 2022). As for the PAHs, despite the fact that the composition and concentration of PAHs may vary depending on the season and region (Longhin et al., 2013), it is also well established that, due to their mutagenic and carcinogenic characteristics, many of these compounds are considered to be priority pollutants in face of human health by several government agencies, including the United States Environmental Protection Agency (USEPA), International Atomic Energy Agency (IAEA), and International Agency for Research on Cancer (IARC), with existing studies proving negative human health outcomes due to the presence of these compounds in the air (Kim et al., 2013; Larrea Valdivia et al., 2020; Sharma et al., 2020). Hence, it is evident there is a need for continuous monitoring and evaluation of these compounds in $PM_{2.5}$ so that these results assist in the public policy decision-making, with consequent reporting and improvement of the human health in any region.

In view of this context, it is difficult to believe that in Brazil, $PM_{2.5}$ was only started to be introduced in the current legislation on air quality in 2018 (CONAMA, 2018), establishing as concentration limit the levels adopted by the WHO in 2006 in its *Air quality guideline for Europe* of 10 µg m^{-3} annual average (WHO, 2006). In addition, there are no established parameters for controlling contaminants in $PM_{2.5}$, with only limits for Pb in total suspended particles (TSPs). Moreover, to this day, measuring $PM_{2.5}$ in Brazil, despite its danger, is still rare. The survey performed by Vormittag et al. (2021) points to alarming data on air monitoring in Brazil, with only 2% of the Brazilian territory having active monitoring stations (371 stations in total) of which only 25.9% assess $PM_{2.5}$, and with none of these stations located in the southern region of Brazil, the second largest region in terms of gross national product and the third in terms of the country's population size.

Rio Grande City (32° 01′ 40″ S; 52° 05′ 40″ W) is located in the Rio Grande do Sul State, the southernmost Brazilian state. Rio Grande houses more than 200,000 inhabitants, and the economy relies mainly on a large industrial complex that is composed of fertilizer, oil, food, fish, and metallurgical industries, being also characterized by its high port activity, with one of the main ports in Brazil (IBGE, 2012). Previous studies in this city have shown the impact of the industrial atmospheric emissions on pollutant levels in soil (Da Silva Júnior et al., 2013; Penteado et al., 2022) and air (Mirlean et al., 2000; Da Silva Júnior et al., 2020; Gutierrez et al., 2020), especially for contamination by metallic elements. Regarding $PM_{2.5}$ levels, there is only one study, whereupon Gutierrez et al. (2020) identified that more than 50% of daily measurements performed in Rio Grande exceeded the legal limit for this pollutant. Furthermore, it is important to mention that since 2016, the local environmental agency has not monitored the levels of air pollutants in Rio Grande (FEPAM, 2021). Moreover, this city is considered a high-risk area for air pollution, especially since most production sites are located not far away from urban areas. In addition, although previous studies have observed possible toxicological effects accrue the industrialization in this region, little has been investigated on atmospheric pollution in this locality, and further assessments on $PM_{2.5}$ have not yet been performed.

Considering the adverse effects of some metals and PAHs in $PM_{2.5}$ on human health, the scenario in which Rio Grande is considered makes it an excellent object of study for the assessment of risk to human health from these contaminants. Thus, in addition to measuring $PM_{2.5}$ levels in this region, our study also proposes to assess the risk to human health of the main contaminants present in $PM_{2.5}$, metals, and PAH, through tools developed and recognized by the USEPA, the human health risk assessment (HHRA) (USEPA, 1989, 2009, 2022), and the incremental lifetime cancer risk (ILCR) (USEPA, 2005, 2009), and to estimate health impacts and benefits resulting from the possible decrease in the concentrations of this pollutant through a tool derived from the WHO-HIA general method (WHO, 2006), the health impact assessment (HIA) (Abe & Miraglia, 2016). Therefore, in this study, our aims are (1) to investigate the levels of $PM_{2.5}$ in the industrial and urban area of Rio Grande; (2) to determine the concentration of metal(loid)s As, Cd, Cu, and Pb and of 16 PAHs in the samples of $PM_{2.5}$; (3) to perform the HHRA for metals and the ILCR for PAHs; and (4) to evaluate an HIA for two possible scenarios developed based on the analyses.

Material and methods

Study site description and sampling of $PM_{2.5}$

$PM_{2.5}$ samples were collected in two main regions of the city of Rio Grande. The first represented the industrial area, located in a region with strong industrial activity, close to the entrance to the industrial complex, located next to a petrochemical refinery and fertilizer industries. The second represented the urban area, located in a region with strong urban activities and vehicular traffic, and with an approximate distance of 10 km from the entrance to the industrial complex, thus far from the contamination coming from the factories. Figure 1 shows the two locations where the samples were taken in the city of Rio Grande.

Sampling was conducted monthly from June 2009 to May 2010 for a period of 12 months. The samples were collected on quartz fiber filters (8 in. × 10 in.) by using a high-volume air sampler at a flow rate of 1.5 $m^3\ min^{-1}$. The quartz fiber filters were previously kept in a closed chamber for 24 h, to stabilize its temperature and humidity, and the high-volume air sampler was installed with a final height of approximately 5 m above the ground. After the end of $PM_{2.5}$ collection, each filter membrane was stored in an airproofed polystyrene cartridge and taken to the laboratory, subjected to controlled temperature and humidity, and then re-weighed using an analytical balance of one in 100,000 accuracies. Finally, all the samples were stored at −20 °C for further analysis.

The following meteorological parameters were monitored during the study: total precipitation (mm), atmospheric pressure (mB), temperature (°C), average wind speed (m/s), maximum wind speed (m/s), and wind direction (°). These parameters were obtained through the Brazilian National Institute of Meteorology (*Instituto Nacional de Meteorologia*, INMET, 2022), which has a database with daily information on meteorological conditions in the region.

Analysis of the composition of $PM_{2.5}$

Determination of metals As, Cd, Cu, and Pb

The determination of As, Cd, Cu, and Pb was performed according to the methodology described in USEPA (1999a). Initially, the acid attack was carried out with aqua regia (HNO_3 and HCl 3:1) on a plate at a temperature of 80 °C. Subsequently, the extract was filtered and diluted in ultrapure water (Milli-Q); finally, the dosage was performed using traditional methods of atomic absorption

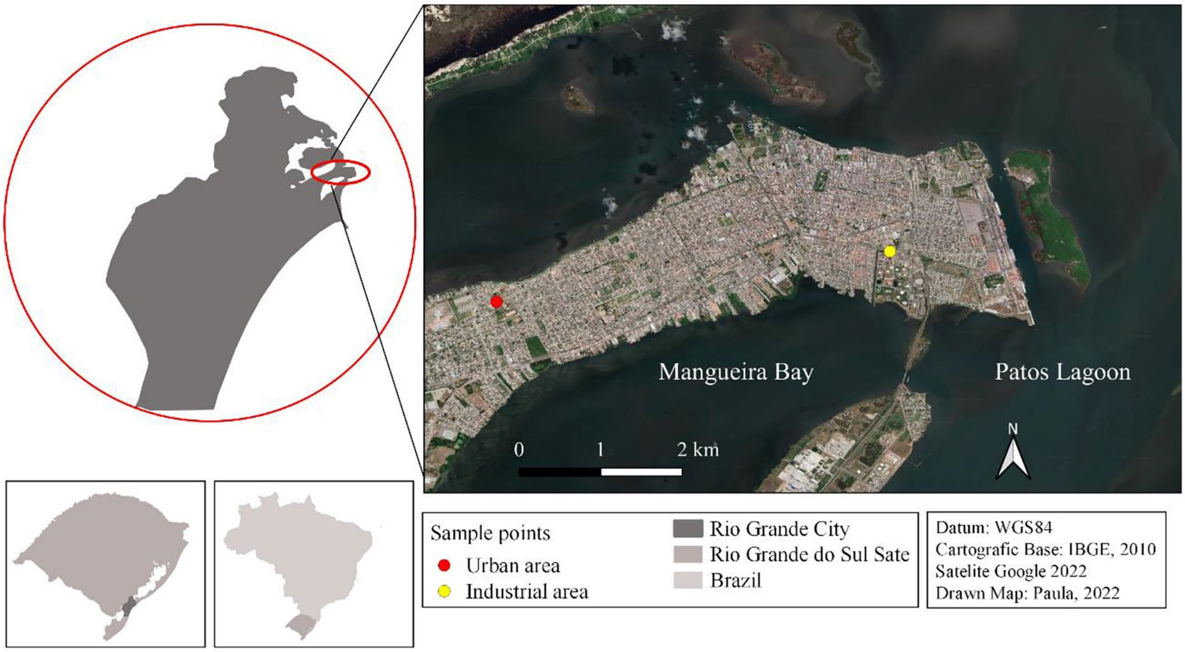

Fig. 1 Location of the $PM_{2.5}$ sampling sites in the industrial and urban areas

spectrophotometry by graphite furnace in a Perkin Elmer Analyst 800 model.

Determination of PAHs

The determination of PAHs was performed according to the methodology described in USEPA (1999b). A gas chromatograph (Perkin Elmer Clarus 600) was used, coupled with a mass spectrometer and an Elite-5MS column (5% diphenyl/95% dimethylsiloxane). The heating ramp used was 40 °C, with an increase of 10 °C per min to 60 °C, followed by heating of 5 °C per min until 290 °C and, finally, the same initial rate to 300 °C. A source temperature of 200 °C and a transfer line temperature of 280 °C were used for the detector. The samples were injected in a volume of 1 µl in splitless mode with a flow of 50 ml of helium, with an inlet temperature of 280 °C and a mobile phase flow (helium) of 1.5 ml min^{-1}. The PAHs were identified using the selected ion recording method, in which the characteristic ions corresponding to the mass/fragmentation charge of each compound were selected and monitored.

HHRA of metals in $PM_{2.5}$

To assess the potential contamination and the human health risk presented to adults in the metals As, Cd, and Pb bound to $PM_{2.5}$ in the industrial and urban area of the city of Rio Grande, we used the risk assessment methodology for the inhalation pathway described by the USEPA in its *Risk assessment guidance for superfund* (*Part F, Supplemental guidance for inhalation risk assessment*) (USEPA, 2009). We chose to use only the inhalation pathway for the mathematical model because this route exerts a strong influence on the final result, with the other pathways (dermal and oral) producing risk results that are possible to be disregarded. For this purpose, the equations and parameters used for the HHRA via inhalation pathway are described in Table S1.

The reference dose for inhalation toxicity (reference concentration, RfC) for As, Cd, and Pb is 1.5×10^{-5}, 10^{-5}, and 2×10^{-4}, respectively. In turn, the inhalation unit risk (IUR) for these same metals was 4.3×10^{-3}, 1.8×10^{-3}, and 1.1×10^{-5}, respectively. It is important to mention that the HHRA was not performed for the metal Cu because it does not have an RfC. The potential risk of non-carcinogenic effects is estimated by the hazard quotient (HQ). HQ values above threshold 1 acknowledge the presence of non-carcinogenic risk. In addition, the sum of the HQ can be performed to obtain the hazard index (HI) and verify the presence of risk in the entire sample. Concomitantly, the carcinogenic risk is recognized when the value resulting from Eq. 3 (Table S1) is greater than 10^{-4} (USEPA, 1989, 2009). Thus, through this mathematical model, it is possible to infer the possibility of risk to human health in face of the exposure to these metals in $PM_{2.5}$.

Health risk assessment of PAHs in $PM_{2.5}$

In order to assess the carcinogenic risk of $PM_{2.5}$-bound PAHs, the ILCR model was employed in our study according to USEPA (2005, 2009). This is an effective evaluation model based on benzo[*a*] pyrene equivalent concentration (BaP_{eq}) to assess human health risk. Inhalation is a crucial pathway for exposure to PAHs; therefore, the ILCR for PAHs in $PM_{2.5}$ is based mainly in this one pathway (Zhang et al., 2009; Wang et al., 2020). Firstly, BaP_{eq} was calculated by multiplying the mass concentration of individual PAH species with their corresponding toxic equivalency factor (TEF) (Eq. S4, Supplementary material). TEF has been widely adopted as the relative carcinogenic potency of corresponding PAHs. Different PAHs are assigned different TEF values. All the PAHs corresponding toxic equivalency factor are presented in Table S2.

After obtaining the BaP_{eq} of PAHs, it is possible to apply the mathematical model of the ILCR through Eq. (1).

$$\mathrm{ILCR} = \mathrm{CSF} \cdot \mathrm{cf} \cdot \frac{\left(\mathrm{BaP_{eq}} \cdot \mathrm{IR} \cdot \mathrm{ET} \cdot \mathrm{EF} \cdot \mathrm{ED}\right)}{\mathrm{BW} \cdot \mathrm{AT}} \tag{1}$$

where CSF is the inhalation cancer slope factor of BaP which is 3.14 kg day^{-1} mg^{-1}; cf is the conversion factor of 10^{-9} mg pg^{-1}; BaP_{eq} is the BaP equivalent concentration, in ng m^{-3}; IR is the inhalation rate for adults (16.68 m^3 day^{-1}); ET is the exposure time (24 h day^{-1}); EF is the exposure frequency (365 days $year^{-1}$); ED is the exposure duration (70 years); BW is the average body weight (70 kg); and AT is the average exposure time (613,200 h). According to the USEPA, an ILCR lower than 1×10^{-6} can be regarded as negligible, and an ILCR above 1×10^{-4} is likely to be harmful to human beings. An ILCR value within a range of 1×10^{-6} to 1×10^{-4} indicates a tolerable risk for the public, and lower values do not indicate risk.

Health impact assessment

In this study, we also evaluated the health benefits that could be achieved if $PM_{2.5}$ concentrations were decreased. These benefits that can be calculated include the number of deaths avoided, gain in life expectancy, life years gain (for adults above 30 years of age), and a monetary evaluation that allows to approximate how much is saved with this reduction in pollution. Our approach followed the guidelines and presentation defined by Abe and Miraglia (2016), which is based on the methodology, concentration response functions, and equations that are available at the guidelines for performing an HIA of the health impacts of urban air pollution (WHO, 2006).

For this evaluation, two $PM_{2.5}$ reduction scenarios were built. The two scenarios were built as follows: (1) a decrease in the annual mean by a fixed amount of 5 µg m^{-3} and (2) a decrease of the annual mean down to the current annual Brazilian standards, 10 µg m^{-3} (CONAMA, 2018). The results of the predictive scenarios were represented as the number of avoided deaths in each scenario and the additional life expectancy at age 30, using the data reported in the Brazilian health system database (DATASUS, 2021) involving total and cardiovascular deaths as recommended by Abe and Miraglia (2016), and the monetary benefits in US$ were determined as recommended by Corá et al. (2020), attributing 1,000,000 € as value of a statistical life and then converted into dollars (Bickel & Friedrich, 2005).

Data analysis

Levels of $PM_{2.5}$, metals, and PAHs were analyzed and presented as median, and their maximum and minimum values obtained during the study period. Mathematical models of HHRA, ILCR, and HIA were performed as described above, and their data are presented accordingly.

Results

The concentrations of $PM_{2.5}$ in the 12 months of analysis, as well as the composition of the metals and PAHs studied, are shown in Table 1. It can be seen that there are no differences between the concentrations of $PM_{2.5}$ in the industrial and urban areas. This result was similar in the analyzed metal(loid)s, with no differences between the two areas. In turn, the same was observed for the PAHs, with benzo[*a*]pyrene and pyrene being the PAHs with the highest median concentration in all analyzed samples from the industrial and urban areas, respectively. Moreover, the results regarding the meteorological variables are presented in Table S3.

According to the levels of metals observed in the $PM_{2.5}$ samples, the HHRA was performed. The HHRA showed that there is a non-carcinogenic risk for As, Cd, and Pb in all samples from the industrial area. In the urban area, only one Cd sample did not show an HQ value greater than 1 (sample point #8), so all other samples presented a non-carcinogenic risk for the evaluated metals. Furthermore, the sum of the hazard quotients for each metal indicates that there is a non-carcinogenic risk in all samples studied in the two exposure scenarios (Table 2).

On the one hand, the HHRA for carcinogenic risk in adults showed that all samples of As and Cd in the industrial setting exceeded the threshold value for risk (1×10^{-4}). On the other hand, in the urban setting, only sample #8 of Cd did not present a carcinogenic risk. No Pb sample presented a carcinogenic risk; however, considering the sum of the risks among all the evaluated metals, both exposure scenarios presented a carcinogenic risk (Table 3).

The concentrations of PAHs from the two study areas were used to calculate the risk to human health from this set of compounds (Table 4). Despite the

Table 1 Medians, minimums, and maximums observed in urban and industrial areas for $PM_{2.5}$ and its metal(loid)s and PAH components

	Industrial area			Urban area		
	Median	Min	Max	Median	Min	Max
Particulate matter (µg m^{-3})						
$PM_{2.5}$	12.06	8.19	19.62	10.52	7.26	24.74
Metals						
As (ng m^{-3})	1.93	0.60	18.24	2.57	0.11	7.60
Cd (ng m^{-3})	4.70	2.01	28.47	8.10	1.25	51.75
Cu (µg m^{-3})	5.46	1.36	11.42	4.67	0.64	20.66
Pb (µg m^{-3})	1.44	0.38	5.44	0.86	0.32	25.45
PAHs (ng m^{-3})						
Benzo[*a*]pyrene	0.0535	ND	0.0967	0.0656	ND	0.1263
Dibenzo[*a*,*h*]anthracene	0.0071	ND	0.0155	0.0057	ND	0.1331
Benzo[*a*]anthracene	–	ND	0.0054	0.0007	ND	0.0156
Benzo[*b*]fluoranthene	0.0043	ND	0.2142	0.0043	ND	0.0147
Benzo[*k*]fluoranthene	0.0016	ND	0.2162	0.0029	ND	0.0225
Indeno[1,2,3-*c*,*d*]pyrene	0.0007	ND	0.0018	0.0009	ND	0.0087
Anthracene	–	ND	0.0025	–	ND	0.0017
Benzo[*g*,*h*,*i*]perylene	0.0043	ND	0.0188	0.0055	ND	0.0602
Chrysene	0.0007	ND	0.0009	0.0008	ND	0.0169
Acenaphthene	–	ND	0.0002	0.0109	ND	0.0183
Acenaphthylene	–	ND	0.0028	–	ND	0.0040
Fluoranthene	–	ND	0.0150	–	ND	0.0889
Fluorene	–	ND	0.0002	–	ND	0.0120
Naphthalene	–	ND	0.0037	–	ND	ND
Phenanthrene	–	ND	0.0381	–	ND	0.0028
Pyrene	0.0435	ND	0.1116	0.0415	ND	0.1494
Σ HPAs	0.0961	ND	0.5864	0.1249	ND	0.5048

Table 2 Hazard quotient (HQ) and hazard index (HI) for adults

Sample number	Urban				Industrial			
	As	Cd	Pb	HI	As	Cd	Pb	HI
#1	2.18×10^{2}	9.82×10^{2}	4.18×10^{0}	1.20×10^{3}	1.17×10^{3}	1.02×10^{3}	7.50×10^{0}	2.19×10^{3}
#2	1.49×10^{2}	3.47×10^{2}	2.30×10^{0}	4.98×10^{2}	1.64×10^{2}	6.24×10^{2}	1.05×10^{1}	7.99×10^{2}
#3	4.86×10^{2}	3.24×10^{3}	1.11×10^{1}	3.73×10^{3}	4.28×10^{2}	2.73×10^{3}	2.61×10^{1}	3.18×10^{3}
#4	4.23×10^{2}	4.96×10^{3}	6.06×10^{0}	5.39×10^{3}	1.72×10^{2}	3.85×10^{2}	2.69×10^{0}	5.60×10^{2}
#5	7.24×10^{1}	2.38×10^{3}	1.72×10^{1}	2.46×10^{3}	9.04×10^{1}	1.41×10^{3}	1.30×10^{1}	1.51×10^{3}
#6	2.84×10^{2}	8.96×10^{2}	6.84×10^{0}	1.19×10^{3}	2.44×10^{2}	3.80×10^{2}	8.90×10^{0}	6.33×10^{2}
#7	1.93×10^{2}	3.16×10^{3}	1.22×10^{2}	3.47×10^{3}	7.23×10^{1}	5.46×10^{2}	6.31×10^{0}	6.24×10^{2}
#8	7.18×10^{0}	2.48×10^{-1}	1.53×10^{0}	8.95×10^{0}	3.86×10^{1}	1.92×10^{2}	2.38×10^{0}	2.33×10^{2}
#9	2.78×10^{1}	2.54×10^{2}	1.99×10^{0}	2.83×10^{2}	1.12×10^{2}	4.53×10^{2}	1.04×10^{1}	5.75×10^{2}
#10	6.98×10^{1}	3.60×10^{2}	4.04×10^{0}	4.33×10^{2}	1.34×10^{2}	2.04×10^{2}	2.82×10^{0}	3.42×10^{2}
#11	1.80×10^{2}	6.57×10^{2}	3.72×10^{0}	8.41×10^{2}	8.69×10^{1}	4.49×10^{2}	3.92×10^{0}	5.40×10^{2}
#12	6.41×10^{1}	2.64×10^{2}	1.76×10^{0}	3.30×10^{2}	6.75×10^{1}	3.75×10^{2}	1.83×10^{0}	4.44×10^{2}
RfC	1.50×10^{-5}	1.50×10^{-5}	2.00×10^{-4}	–	1.50×10^{-5}	1.50×10^{-5}	2.00×10^{-4}	–

RfC reference concentration

Table 3 Individual and total cancer risk (CR) for adults

Sample number	Urban				Industrial			
	As	Cd	Pb	Total	As	Cd	Pb	Total
#1	4.82×10^{-3}	6.06×10^{-3}	3.15×10^{-6}	1.09×10^{-2}	2.58×10^{-2}	6.29×10^{-3}	5.66×10^{-6}	3.21×10^{-2}
#2	3.29×10^{-3}	2.14×10^{-3}	1.74×10^{-6}	5.43×10^{-3}	3.63×10^{-3}	3.85×10^{-3}	7.95×10^{-6}	7.49×10^{-3}
#3	1.07×10^{-2}	2.00×10^{-2}	8.38×10^{-6}	3.07×10^{-2}	9.46×10^{-3}	1.68×10^{-2}	1.97×10^{-5}	2.63×10^{-2}
#4	9.35×10^{-3}	3.06×10^{-2}	4.57×10^{-6}	4.00×10^{-2}	3.81×10^{-3}	2.38×10^{-3}	2.03×10^{-6}	6.19×10^{-3}
#5	1.60×10^{-3}	1.47×10^{-2}	1.30×10^{-5}	1.63×10^{-2}	2.00×10^{-3}	8.70×10^{-3}	9.80×10^{-6}	1.07×10^{-2}
#6	6.27×10^{-3}	5.53×10^{-3}	5.16×10^{-6}	1.18×10^{-2}	5.40×10^{-3}	2.35×10^{-3}	6.72×10^{-6}	7.75×10^{-3}
#7	4.28×10^{-3}	1.95×10^{-2}	9.20×10^{-5}	2.38×10^{-2}	1.60×10^{-3}	3.37×10^{-3}	4.76×10^{-6}	4.97×10^{-3}
#8	1.59×10^{-4}	1.53×10^{-6}	1.15×10^{-6}	1.61×10^{-4}	8.53×10^{-4}	1.19×10^{-3}	1.80×10^{-6}	2.04×10^{-3}
#9	6.14×10^{-4}	1.57×10^{-3}	1.50×10^{-6}	2.18×10^{-3}	2.48×10^{-3}	2.79×10^{-3}	7.83×10^{-6}	5.29×10^{-3}
#10	1.54×10^{-3}	2.22×10^{-3}	3.04×10^{-6}	3.77×10^{-3}	2.97×10^{-3}	1.26×10^{-3}	2.12×10^{-6}	4.23×10^{-3}
#11	3.98×10^{-3}	4.06×10^{-3}	2.81×10^{-6}	8.03×10^{-3}	1.92×10^{-3}	2.77×10^{-3}	2.96×10^{-6}	4.69×10^{-3}
#12	1.42×10^{-3}	1.63×10^{-3}	1.33×10^{-6}	3.05×10^{-3}	1.49×10^{-3}	2.32×10^{-3}	1.38×10^{-6}	3.81×10^{-3}
IUR	4.30×10^{-3}	1.80×10^{-3}	1.10×10^{-5}	–	4.30×10^{-3}	1.80×10^{-3}	1.10×10^{-5}	–

IUR inhalation unit risk

Table 4 PAH exposure cancer risk in Rio Grande urban and industrial $PM_{2.5}$

Study site	ILCR
Industrial area	4.72×10^{-8}
Urban area	6.88×10^{-8}

values for the urban area being slightly higher than the values for the industrial area, as both ILCR values were lower than 1×10^{-6}, they can be regarded as negligible, thus demonstrating the absence of risk in face of these compounds in the $PM_{2.5}$ of the city of Rio Grande.

Finally, HIA was developed using the median $PM_{2.5}$ found in the industrial area (12.06). From the mathematical model, a number of 22.3 premature deaths related to air pollution annually were estimated, which is equivalent to 1.61% of the total deaths for the population over 30 years old in the city. Faced with this, two scenarios were created. In the first scenario (5 μg m^{-3} reduction in mean $PM_{2.5}$), HIA estimated approximately 13 and 8 avoided deaths, considering total mortality and cardiovascular mortality for people over 30 years of age, respectively. In the second (reduction of the annual average of $PM_{2.5}$ to 10 μg m^{-3}), HIA estimated approximately 6 and 4 deaths avoided annually using the same considerations. Moreover, the average increase in life expectancy in the first and second scenarios was 0.9 month and 0.5 month, respectively, while the economic value related to preventable deaths in the scenarios was over 17 million USD in the first and over 9 million dollars in the second (Table 5).

Discussion

Air pollution has a widely recognized impact on human health, and there is an increasing body of evidence that relates the exposure to $PM_{2.5}$ and a range of adverse effects (Alessandrini et al., 2013; Xing et al., 2016; Landrigan, 2017; Sharma et al., 2020; EEA, 2021; WHO, 2021; Zang et al., 2022). It is also well recognized that the monitoring of this pollutant on a global scale needs advances and improvements as it can still be considered poor compared to other atmospheric pollutants, and this problem increases in countries considered to be in developing and underdeveloped (WHO, 2021). At the same time, these countries also have the highest level of $PM_{2.5}$ pollution. This fact is directly related to outdated legislation and the lack of infrastructure for monitoring air quality. In view of this, both the scientific community, environmental protection agencies, and the WHO have highlighted the importance of monitoring and evaluating this pollutant in these regions (EEA, 2021; WHO, 2021) and have also developed tools that allow assessing the health risk associated with the components of this pollutant. With this, our study gains importance not only for performing this monitoring, but also for providing a health risk assessment of the main components present in the samples of $PM_{2.5}$ and an estimate of the health impacts and benefits resulting from the possible decrease in the concentrations of this pollutant. Our main findings regarding the $PM_{2.5}$ samples include the following: (1) The levels of this pollutant in the city of Rio Grande were higher than those allowed in current Brazilian legislation (CONAMA, 2018), and by current and former WHO parameters (WHO, 2006, 2021), in both the industrial and urban areas; (2) the existence of non-carcinogenic and carcinogenic risks for metals present in all samples; (3) the absence of carcinogenic risk for the assessed PAHs; and (4) the reduction scenarios proposed pointed to a reduction of up to 22 deaths annually in conjunction with reductions in health-related expenditures.

Initially, we observed that both areas of this study presented annual medians higher than those permitted

Table 5 Potential health benefits of reducing daily $PM_{2.5}$ levels on total mortality and cardiovascular mortality, in Rio Grande, Brazil

Health outcome	Annual number of deaths avoided	Annual number of deaths per 100,000	Gain in life expectancy (months)	Life years gain	Monetary Benefits, US$*
Decrease by 5 μg m^{-3} in $PM_{2.5}$ levels					
Total mortality	13.3	12.4	0.9	231.5	17,632,000.00
Total cardiovascular mortality	8.2	7.7			
Decrease to 10 μg m^{-3} in $PM_{2.5}$ levels					
Total mortality	6.7	6.2	0.5	116.4	8,882,285.00
Total cardiovascular mortality	4.1	3.9			

*Taking into account the dollar exchange rate in 2010 by current Brazilian legislation of 10 µg m^{-3} annually (CONAMA, 2018). However, this legislation presents considerable acceptable "intermediate values" until 2023, and the values observed in our study are about these intermediate values. Within this context, it is important to note that the inclusion of $PM_{2.5}$ in this legislation occurred only after its update in 2018 (CONAMA, 2018), and before that, there were no limits for this pollutant in the Brazilian territory (CONAMA, 1990). The truth is that the monitoring of air pollution in Brazil is still something rare, with monitoring stations in less than 2% of its national territory, and in this topic, the monitoring of $PM_{2.5}$ is still something even rarer, where less than 26% of these stations monitor this pollutant (Vormittag et al., 2021). This situation obviously generates massive concern, of which only greater investments and an increase in the seriousness of how this issue is treated in Brazil can change this reality.

It is well established that $PM_{2.5}$ comprises multiple components of which the most related to its toxicity and negative health outcomes are metals and PAHs. A number of recent systematic reviews and meta-analyses have demonstrated the effect of these components of PM (Landrigan, 2017; Shah et al., 2015; Sharma et al., 2020; Xing et al., 2016) on all-cause and cause-specific mortality. In this regard, the most direct way to assess human exposure to contaminants present in $PM_{2.5}$ is to measure the actual body burden through biomonitoring. However, in practice, there are multiple limitations to this approach. Therefore, we used the knowledge of concentrations and mathematical models of exposure to investigate how these components can affect human health.

As our study assessed two main components, metals and PAHs, we shone light to the two classic mathematical models that are commonly used to assess their risk to human health. First, the health risks of potentially contaminated $PM_{2.5}$ with metals can be calculated based on a conceptual model of exposure developed by the United States Environmental Protection Agency (USEPA, 1989, 2009), which estimates the nature and probability of adverse human health effects, the HHRA. Although this model allows assessment for different exposure pathways, our approach focused on the inhalation pathway as this is the main source of $PM_{2.5}$ exposure. Second, USEPA (2005) standard models for determining ILCR are used to understand the role of exposure to PAHs in $PM_{2.5}$ in cancer incidence. In addition to assessing the possible risks of exposure to these contaminants present in $PM_{2.5}$, we performed an investigation into the impacts of $PM_{2.5}$ in the health system as a whole. For this purpose, there is the HIA methodology, which is derived from the WHO-HIA general method (WHO, 2006) and quantifies the impact of air pollution exposure on health using some successive steps that eventually leads to health indicators and calculates the number of attributable mortality and morbidity cases. To our knowledge, although there are studies involving up to two of these mathematical models, this complete approach involving risks to human health from metals and PAHs present in $PM_{2.5}$ with consequent assessment of the impacts on the health system has never been performed.

According to the Global Burden of Disease (GBD) study estimates, around 4.58 million deaths were directly attributable to $PM_{2.5}$ ambient air pollution in 2017 (Bu et al., 2021). Studies indicate that the levels of this pollutant are directly related to all-cause and cause-specific mortality, the latter being mostly due to problems in the respiratory and cardiovascular systems (Landrigan, 2017; Shah et al., 2015; Sharma et al., 2020; Xing et al., 2016). As previously mentioned, the risk of toxicity of this compound may be closely related to the presence of metals and PAHs in this compound. Our study showed that all monthly samples collected during the study period presented non-carcinogenic risk and carcinogenic risk for metals, for both urban and industrial areas. The presence of these compounds in the city of Rio Grande is perpetuated throughout its territory, regardless of the proximity to the industrial zone. On the contrary, PAHs did not present a risk in any of the evaluated areas. This behavior is expected due to the low concentration of PAHs present in the evaluated $PM_{2.5}$.

It is believed that the presence of high levels of metals in $PM_{2.5}$ in the city of Rio Grande may be linked to the large number of petrochemical and fertilizer industries in the city, characterized by using formulations rich in metals as their inputs (Mirlean et al., 2000; Da Silva Júnior et al., 2013; Gutierrez et al., 2020). Concerns about air quality in the Rio Grande region are not new. The only study ever performed evaluating $PM_{2.5}$ in this region (Gutierrez et al., 2020) showed high levels of this pollutant when compared to the air quality guidelines of the WHO (2006) and current Brazilian legislation (CONAMA, 2018), providing evidence that this worrisome scenario remains unchanged. Moreover, it is important to note that the contamination and risk panorama in the city of Rio Grande is recurrent in both the industrial and urban areas (Da Silva Júnior et al., 2013; Penteado et al., 2022). In addition, studies indicate that the effects of air pollution caused by industrial complexes are similar between industrial and urban areas, even if they are in different areas in a limited distance, including not only effects on adults, but also effects on cognitive performance and lung function in children (Bigliardi et al., 2022; Dupont-Soares et al., 2021).

These data reinforce the idea and concern of the scientific community that the responsible personnel need to focus on developing comprehensive policies for air pollution, which include and care about people living outside the industrial zone. This effect of perpetuation and dispersion of atmospheric pollution within an industrial/urban scenario is already known and is directly related to the meteorological and seasonal conditions to which a region is subjected; however, it is also important to take into account the automotive sources as they contribute to a part of the contamination and air pollution in an urban environment (Britter & Hanna, 2003; Li et al., 2021). In fact, recent studies carried out in the city of Rio Grande involving the monitoring of air quality showed that the urban region can suffer even more than the industrial zone in the face of other atmospheric pollutants (Tavella et al., 2021; Ceglinski et al., 2021), and this effect is directly related to places with increased traffic of motor vehicles.

The potential benefits associated with the decrease in the $PM_{2.5}$ levels demonstrated by the health impact assessment of our study are fundamental to demonstrate to entrepreneurs and government authorities that the adoption of stricter air pollution regulations in conjunction with continuous monitoring of air quality can have positive economic and social impacts, improving the quality of life and reducing expenses with the health system at different levels of society. In this sense, Li and Gibson (2014) proved how the combination of stricter environmental laws and the commitment to different industrial sectors can generate effective reductions in air pollution, with consequent health benefits. In a study performed in the state of North Carolina (USA), it was demonstrated how the application of state policies which are stricter than the federal policies led to a reduction in air pollution with consequent 1700 deaths avoided in 2012. Therewithal, in Brazil, the impacts of air pollution on health services are still poorly understood. Studies that estimate these impacts are often restricted to large national metropolises (Abe & Miraglia, 2016; Leão et al., 2021); however, the study by Honscha et al. (2022) carried out in the state of Rio Grande do Sul, in the region of the largest Brazilian coal mine, highlighted how this analysis proved to be a useful tool to demonstrate the beneficial effects of reducing air pollutants on different aspects of health.

The current study showed not only the levels of $PM_{2.5}$ pollution in the city of Rio Grande, but also how the concentrations of metal(loid)s and PAHs in its composition may be linked to the risk imposed by this pollutant in this location. The existence of a non-carcinogenic and carcinogen risk for the metal samples raises a red flag that needs an in-depth investigation aimed not only at reducing $PM_{2.5}$ as a whole, but also at mitigating the high levels of metals in its composition. Furthermore, we demonstrate how a mere reduction in $PM_{2.5}$ concentrations causes exponential improvements in the population's quality of life with a consequent reduction in the amounts of expenditures on the health system. We hope that these unprecedented findings may serve as a basis for the development of public health policies aimed at improving air quality, jointly assisting health surveillance and directing future studies towards a better intrinsic approach to the problem.

Conclusion

Our findings allowed us to identify that the levels of $PM_{2.5}$ in the urban and industrial areas of the city of Rio Grande, Brazil, were higher than the limits allowed by the current Brazilian legislation and, consequently, far superior than those recommended by the World Health Organization. As for the risks to human health, the metals quantified in this pollutant presented carcinogenic and non-carcinogenic risks in all monthly samples. In turn, the PAHs did not present concentrations that could impose a carcinogenic health risk. Finally, the scenarios created to assess the impacts of reducing $PM_{2.5}$ pollution in the city demonstrated significant health benefits with reduction in the number of deaths and also in public health spending. Therefore, we emphasize how our results should serve as a case for the development of public health policies and thus guarantee improvements in the quality of life of this community, and also guide other regions to follow in this direction.

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Author contribution RAT was responsible for preparing the first version of the manuscript text. RLB and JEKS were responsible for the risk assessment of the metal(loid)s. RBC and BM were responsible for the risk assessment of PAHs. PFR was responsible for the map elaboration and performed the health impact assessment and data review. VMFV and PRMB were responsible for acquiring financing, in addition to the infrastructure for chemical analysis. FMRSJ was the study supervisor. All authors read and approved the final version of the manuscript.

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Availability of data and material The datasets used and/or analyzed during the current discussion are available and from the corresponding author upon reasonable request.

Declarations

Ethics approval and consent to participate Not applicable.

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