



Lung deposition, health risks, and composition of PM_{2.5} collected in an industrial area in Southern Brazil

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ABSTRACT

Joinville contains the third-largest industrial pole in the South region of Brazil. Studies about air quality and atmospheric composition are scarce. To further the discussions on the influence of anthropogenic sources on air pollution in the city and its impacts on human health, PM_{2.5} samples were collected within an industrial neighborhood during wintertime. Pollutants (ions, elements, polycyclic aromatic hydrocarbons and derivatives) were determined by gas and ion chromatography and inductively coupled plasma mass spectrometry techniques. Besides the composition, respiratory dose fluxes were calculated according to a model developed by the International Commission on Radiological Protection to estimate the mass of PM_{2.5} deposited in the lungs. Median PM_{2.5} concentrations surpassed (23 µg m⁻³) the limit recommended by the World Health Organization. Sulfate and nitrate were the most abundant water-soluble ions, indicating the importance of secondary reactions to PM_{2.5} concentrations. Cd, Sb, Mo, Zn, Cu, Pb, As, and Ni were enriched, and these species were associated with industrial activities and vehicular traffic. Among the PAHs, high-molecular-weight compounds were the most abundant species and were associated with fossil fuel combustion and industrial emissions. Oxygenated and nitrated hydrocarbon compounds were predominantly formed through secondary reactions. Chronic exposure to concentrations of carcinogenic elements, which showed enrichment during the studied period, may represent a moderate risk to human health. The benzo(a)pyrene equivalent index exceeded the safe limit in half of the samples. Furthermore, significant amounts of PM_{2.5} and components with carcinogenic and oxidative properties can reach the lungs, indicating a direct risk of exposure.

1. Introduction

The atmospheric particulate matter consists of heterogeneous particles suspended in the air, with aerodynamic diameters reaching up to 100 µm. Particles with a diameter equal to or smaller than 2.5 µm are classified as fine particulate matter (PM_{2.5}) and represent a threat to human health due to their ability to penetrate the lungs. The composition of atmospheric aerosols includes salts, metal oxides, elemental carbon, and organic compounds. Some of these species are known to be hazardous to human health and are associated with oxidative potential, carcinogenicity, and mutagenicity of PM_{2.5}. The toxic effects are attributed mainly to the presence of metals and carcinogenic and mutagenic organic compounds, such as polycyclic aromatic

hydrocarbons and their derivatives (oxy and nitro-PAH) (Seinfeld and Pandis, 2016).

The ability of PM_{2.5} to induce oxidative stress, formation of DNA adducts, and cell damage has been shown by *in vivo* and *in vitro* studies. PM_{2.5} exposure induces the activation of an inflammatory response and increases the levels of strand breaks and other DNA damage markers in human and animal cells (Cho et al., 2018). The exposure to PM_{2.5} was also associated with lung inflammation and pulmonary and myocardial fibrosis in mice. Epidemiological studies have also demonstrated the relationship between exposure to PM_{2.5} and hospital admissions and mortality due to cardiorespiratory diseases (Abe and Miraglia, 2016; Pan et al., 2017).

Inhalation is the main route of entry for atmospheric pollutants into

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the human organism. The respiratory system is highly affected by air pollution. The determination of the deposition flux of PM_{2.5} and its associated pollutants is important to evaluate the exposure due to inhalation and to assess the health risks. The International Commission on Radiological Protection (ICRP) developed a semi-empirical model for estimating the particle deposition in the human respiratory tract based on physical and biological parameters (such as lung morphology, particle size, and respiratory flux) (Hofmann, 2011). This model permits an estimate of the mass of PM_{2.5} deposited in three regions of the human respiratory system: extrathoracic or upper airway region, tracheobronchial and alveolar region (ICRP, 1994). Other models are available in the literature for determining pulmonary deposition of particulate matter, but the ICRP equations and the Multiple-Path Particle Dosimetry (MPPD) model are the most widely used (Can-Terzi et al., 2021). Although the MPPD software offers different models representing lung asymmetry and lung lobes, the ICRP was chosen in this work due to its more uniform parameters.

Studies on air pollution were already carried out in other urban and industrial sites in Brazil, mostly in the Southeast Region. These studies have shown the influence of a variety of sources, including vehicular traffic, biomass burning, industrial emissions, and secondary formation (Caumo et al., 2023; Pereira et al., 2017; Scaramboni et al., 2024). In Joinville, few studies have reported the chemical composition of particulate matter (Santos-Silva et al., 2023), and the presence of PAHs and their derivatives (oxy and nitro-PAHs) has never been investigated. An observational clinical study carried out in this city showed that residents of the industrial area exhibited changes in blood pressure and were prone to developing coronary artery disease (Schaidhauer et al., 2024). Furthermore, municipal reports have shown that diseases of the circulatory and respiratory systems are among the main causes of mortality in the city (Joinville, 2024a). Therefore, investigation of PM_{2.5}-bound pollutants, including toxic metals and carcinogenic organic compounds (e.g., PAHs and their derivatives), can provide insights into the health risks associated with exposure to fine particulate matter in Joinville during the winter season.

The city of Joinville contains the largest industrial pole, and it is the third in the South region of Brazil, comprising different types of industries (such as chemistry, textiles, plastics, metallurgy, and others) (Bonatti-Chaves et al., 2024). Despite its economic importance, few studies have investigated the air pollution in the city. Some biomonitoring studies conducted in the region showed a metal enrichment in pollen and leaf samples collected in residential and industrial sites (Bonatti-Chaves et al., 2024; Schaidhauer et al., 2024). Moreover, the region is prone to wind recirculation and stagnation regimes, which aggravate PM_{2.5} air pollution at industrial areas, where the local population is exposed to potentially toxic PM_{2.5}-bound elements (Santos-Silva et al., 2023).

The present study aims to provide a comprehensive investigation of PM_{2.5} composition (i.e., water-soluble ions, elements, PAHs, oxy-PAHs, and nitro-PAHs) collected during winter, at a site impacted by industrial activities. Furthermore, this work aims to deepen the discussion on the influence of industrial activities and vehicular traffic in the city, and to investigate the presence of markers of other pollution sources, such as biomass burning. Health risk indices and the masses of PM_{2.5}, metals, and PAHs deposited in the human respiratory tract were also calculated to evaluate the pulmonary exposure to these pollutants.

2. Methodology

2.1. PM_{2.5} sampling and meteorological conditions

The PM_{2.5} collections were carried out at the campus of the University of the Region of Joinville in the North Industrial Zone. Based on the classification of Köppen (1948), the urban area has a subtropical mesothermal humid climate with hot summers. Joinville is characterized by an average annual rainfall of 1600 mm–2200 mm (coast), and

2500 mm (near the mountain) (Mello et al., 2015; Mello and de Oliveira, 2016). During the sampling period, the average relative humidity and temperatures were 75 % and 21 °C.

The samples were collected every three days for 24 h, from June 11th to August 25th in 2022, in the winter season, when the meteorological conditions are not favorable to pollutant dispersion. Eighteen samples and one blank filter were obtained. The sampling was carried out using a high-volume sampler (1.13 m³ min⁻¹, Somar, Brazil) and quartz fiber filters (Whatman). The sampler was operated at ground level. Before sampling, the filters were decontaminated by heating in a muffle furnace (550 °C for 4 h), weighed in an environment with relative humidity controlled at 50 % (temperature = 20–25 °C), wrapped in aluminum foil, and kept in a desiccator until collection (Subramanian et al., 2004). The collected samples were folded, weighed (relative humidity = 50 %), wrapped in aluminum foil, stored in plastic bags, and frozen to avoid the loss of volatile compounds.

Meteorological parameters (wind speeds and directions, precipitation, relative humidity, and temperature) were obtained from the Santa Catarina Civil Defense meteorological stations' network.

2.2. Water-soluble ions

Water-soluble ions (WSIs) were extracted following the procedure described previously (Custodio et al., 2019). Briefly, punches of 5 cm² from the filters were extracted with 10 mL of ultra-pure water by ultrasound stirring (15 min). The extracts were filtered through a syringe filter (PTFE, 0.22 µm). The solutions were stored in a refrigerator until analysis.

Seven anions (F⁻, HCOO⁻, Cl⁻, NO₃⁻, PO₄³⁻, SO₄²⁻, and C₂O₄²⁻) and five cations (Na⁺, NH₄⁺, K⁺, Ca²⁺, and Mg²⁺) were quantified by ionic chromatography with conductivity detection (Metrohm AG, Switzerland). A Metrosep A Supp 5 column (250 × 4.0 mm) eluted with a solution of Na₂CO₃/NaHCO₃ (3.2/1.0 mmol L⁻¹) was used for anion determination. Cations were determined using a Metrosep C4 column (250 × 4.0 mm) eluted with a solution of dipicolinic acid (0.7 mmol L⁻¹) and nitric acid (1.7 mmol L⁻¹). External standards ranging from 0.1 to 3.6 µg mL⁻¹ were prepared from the dilution of certified solutions (SpecSol, Brazil).

The extracts of the samples and blank filters were analyzed in duplicate, and the contaminants of the blank filter were subtracted from the sample results. The limits of detection and quantification (DL and QL, Table S1) were determined by a visual method, following the procedure recommended by Shrivastava and Gupta (2011). Detection limits varied between 0.003 and 0.006 µg mL⁻¹ for cations and 0.003–0.050 µg mL⁻¹ for anions.

2.3. Elements

Elements were determined by the inductively coupled plasma mass spectrometry technique (Nexion 300D ICP-MS). The microwave-assisted extraction followed the methodology described elsewhere (Pereira et al., 2023a). Briefly, punches of 25 cm² from the filters were extracted with a mixture of HNO₃/H₂O (10 mL of HNO₃ + 15 mL of H₂O), as recommended by the American Environmental Protection Agency (USEPA, 1994). External standards varying from 0 to 150 ng m⁻³ were prepared by dilution of the multi-elemental stock solution (SPEX Certiprep™). Cd, Cu, Mn, Pb, Ni, Mo, Ce, La, Ti, Al, Fe, Zn, As, Rb, Sb, Ba, Sr, Co, and Sn were determined.

Enrichment factors (EF) of elements in relation to their Earth's crust abundance were calculated following Equation (1). Sr was chosen as the element reference.

$$EF = \frac{[X]_{PM2.5} / [Sr]_{PM2.5}}{[X]_{crust} / [Sr]_{crust}} \quad (\text{Eq. 1})$$

where: EF is the enrichment factor; [X]_{PM2.5} is the concentration of the

element “X” in $PM_{2.5}$; $[X]_{crust}$ is the abundance of the element “X” in the terrestrial crust; $[Sr]_{PM_{2.5}}$ is the concentration of Sr in $PM_{2.5}$; $[Sr]_{crust}$ is the abundance of Sr in the terrestrial crust. The relative abundances of elements in the Earth’s crust are given in ppm (equivalent to g/ton) (Lee, 1999).

Recovery rates were determined by enriching blank filters (triplicate) with a known amount of standard solutions. The enriched blanks were subjected to the same extraction process as the samples and the blank. The recovery was higher than 70 % for most elements (Table S1). The extracts of the samples and blank filters were analyzed in duplicate. The limits of detection and quantification (DL and DQ) were obtained following the procedure recommended by the National Institute of Metrology, Quality and Technology (INMETRO, 2018) and described in the supplementary material. Detection limits ranged from 0.01 to 1.99 ng g⁻¹ (Table S1).

2.4. Polycyclic aromatic hydrocarbons and derivatives (oxy- and nitro-PAHs)

Polycyclic aromatic hydrocarbons (PAHs) were extracted from the filters following the methodology described by Santos et al. (2016). Briefly, punches of 4.4 cm² of the filters, spiked with a deuterated chrysene, were extracted in a syringe-less microextraction device (Whatman MiniTM UniPrep Filters, Whatman, USA) with 500 µL of the mixture of dichloromethane and acetonitrile (82:18) by ultrasound agitation for 23 min. Then, the extracts were filtered (PTFE, 0.22 µm) and analyzed by gas chromatography coupled to mass spectrometry (GC-MS).

The PAHs derivatives (oxy and nitro-PAHs) were extracted from punches of 50 cm² of the filters, spiked with deuterated chrysene, by ultrasonic agitation (3 cycles with 60 mL of dichloromethane, 20 min each cycle). The extracts were concentrated and fractionated in a chromatographic column (internal diameter of 0.7 cm) filled with 2.5 g of silica gel, eluted with: (i) 15 mL of *n*-hexane, and (ii) 15 mL of a mixture of dichloromethane and acetone (2:1). The second fraction contained the PAHs derivatives. This fraction was concentrated and dried under N₂ flow, and dissolved in dichloromethane to determine oxy and nitro-PAHs by GC-MS with electron ionization (EI).

The samples were injected in splitless mode in a gas chromatograph coupled to a mass spectrometer (Agilent, GC 7820A and MS 5975). The analyses were performed using a DB-5ms (30m × 0.250 mm, film thickness 0.25 µm) and helium as gas carrier (0.9997 % purity, flow rate of 1.0 mL min⁻¹). The oven temperature started at 80 °C, heating (10 °C min⁻¹) up to 100 °C. Then, the temperature was increased up to 230 °C (8 °C min⁻¹), and then to 315 °C (2 °C min⁻¹). The ion source operates in electron impact mode (EI, 70 eV) and was kept at 250 °C. The transfer line temperature was set to 300 °C. The analysis was carried out in SIM mode, monitoring two ions m/z for each compound (Tables S2 and S3).

The analytes were quantified by the external standard method (analytical curves R² > 0.98, Tables S1 and S2), using the EPA 610 standard mix (Sigma Aldrich, St. Louis, USA), containing the sixteen priority PAHs of the US Environmental Protection Agency. The light-molecular-weight PAH naphthalene, acenaphthene, acenaphthylene, and fluorene were not quantified due to their poor recovery (<75 %). Individual standards of the PAHs retene (RET), benzo(e)pyrene (BeP), perylene (PER), coronene (COR), the oxy-PAHs 9-fluorenone (9-FO), 9,10-anthraquinone (9,10-AQ), 2-methylanthraquinone (2-MAQ), and 7,12-benzo(a)anthracenedione (BaAQ), and the nitro-PAH 9-nitroanthracene (9-NANT), 3-nitrofluoranthene (3-NFLT), and 1-nitropyrene (1-NPYR) purchased from Sigma Aldrich were also used.

The limits of detection and quantification were assessed by visual method. The recovery rates were determined by the enrichment of blank filters with standard solutions, followed by the extraction, fractioning, and analysis using the same procedure applied to the samples. The blank filter was also analyzed, but none of the compounds analyzed were detected. All samples were analyzed in duplicate. The analytical data

(curves, recovery, detection, and quantification limits) are presented in the supplementary material (Tables S2 and S3).

2.5. Health risks assessment

The non-carcinogenic and carcinogenic risks due to metal inhalation were estimated by the hazard quotient (HQ) and cancer risk (CR) indices, respectively (Alves et al., 2020; USEPA, 2009). The exposure concentrations by inhalation (EC_{inh}) were calculated by Equation (2):

$$EC_{inh} = \frac{C \times (ET \times EF \times ED)}{AT} \quad (\text{Eq. 2})$$

where: C is the element concentration; ET is the exposure time (24 h); EF is the exposure frequency (365 days); ED is the exposure duration (6 years for children and 24 years for adults); and AT is the average exposure time, which was estimated as ED × 365 days × 24 h/day for non-carcinogenic risk and equal to 75.5 years × 365 days/year × 24 h for carcinogenic risk. The lifetime of 75.5 years was chosen in the present study according to the average life expectancy in the state of Santa Catarina in 2022 (IBGE, 2022).

The hazard quotient (HQ) and carcinogenic risk (CR) were calculated by Equations (3) and (4):

$$HQ = \frac{EC_{inh}}{R_f C \times 1000} \quad (\text{Eq. 3})$$

$$CR = IUR \times EC_{inh} \quad (\text{Eq. 4})$$

where: R_fC is the reference concentration (mg m⁻³); and IUR is the inhalation unit risk (µg m⁻³) (Table S4).

To determine the risks to human health due to inhalation exposure to PAHs, benzo(a)pyrene-equivalent carcinogenic and mutagenic (BaP-TEQ and BaP-MEQ) were calculated. These indices were calculated by multiplying each carcinogenic and mutagenic PAHs by its potential in relation to BaP, as described in equations (5) and (6) (Durant et al., 1999; Nisbet and LaGoy, 1992).

$$\begin{aligned} \text{BaP} - \text{TEQ} = & ([\text{BaA}] \times 0.1) + ([\text{CHR}] \times 0.01) ([\text{BbF}] \times 0.1) \\ & + ([\text{BkF}] \times 0.1) + ([\text{BaP}] \times 1) + ([\text{IP}] \times 0.1) ([\text{DBA}] \times 5) \\ & + ([\text{BPE}] \times 0.01) \end{aligned} \quad (\text{Eq. 5})$$

$$\begin{aligned} \text{BaP} - \text{MEQ} = & ([\text{BaA}] \times 0.082) + ([\text{CHR}] \times 0.017) ([\text{BbF}] \times 0.25) \\ & + ([\text{BkF}] \times 0.11) + ([\text{BaP}] \times 1) \\ & + ([\text{IP}] \times 0.31) ([\text{DBA}] \times 0.29) + ([\text{BPE}] \times 0.19) \end{aligned} \quad (\text{Eq. 6})$$

The incremental lifetime cancer risk (ILCR) due to inhalation exposure to PAHs was calculated for children (10 years) and adults (75.5 years), following Equation (7) (USEPA, 2009).

$$ILCR_{inh} = CSF \times \frac{BaP - TEQ \times IR \times EF \times ED}{BW \times AT} \times 10^{-6} \quad (\text{Eq. 7})$$

where IR is the inhalation rate, EF is the frequency of exposure, ED is the duration of exposure in years, BW is the body weight, AT is the average time of exposure, and CSF is the inhalation cancer slope for BaP. Parameter values for children (10 years) and adults (75.5 years) are presented in the supplementary material (Table S5).

2.6. Lung deposition model

The respiratory deposition fractions (DF) of $PM_{2.5}$ and its components were calculated for three lung regions: the upper airway (UA), the tracheobronchial (TB) region, and the alveolar (AL) region, as described previously (Moniruzzaman et al., 2023). The inhalable fraction (IF) of

PM_{2.5} was calculated following Equation (8):

$$IF = 1 - 0.5 \left(1 - \frac{1}{1 + 0.0007 d_p^{2.8}} \right) \quad (\text{Eq. 8})$$

where d_p is the particle diameter (2.5 μm).

The deposited fractions for the three regions were calculated according to equations (9)–(11):

$$DF_{UA} = IF \times \left(\frac{1}{1 + \exp(6.84 + 1.83 \ln d_p)} + \frac{1}{1 + \exp(0.924 - 1.885 \ln d_p)} \right) \quad (\text{Eq. 9})$$

$$DF_{TB} = \left(\frac{0.00352}{d_p} \right) [\exp(-0.234(\ln d_p + 3.40)^2) + 63.9 \exp(-0.819(\ln d_p - 1.61)^2)] \quad (\text{Eq. 10})$$

$$DF_{AL} = \left(\frac{0.0155}{d_p} \right) [\exp(-0.416(\ln d_p + 32.84)^2) + 19.11 \exp(-0.482(\ln d_p - 1.362)^2)] \quad (\text{Eq. 11})$$

The total deposited fraction was given by the sum of the deposited fractions in the three regions:

$$DF = DF_{UA} + DF_{TB} + DF_{AL} \quad (\text{Eq. 12})$$

Finally, the respiratory deposition doses (RDD) for children and adults were estimated by Equation (13):

$$RDD = DF \times IR \times PM \quad (\text{Eq. 13})$$

where IR is the inhalation rate (0.5 m³/h for children and 0.65 m³/h for adults) and PM is the concentration of PM_{2.5} or associated pollutant.

2.7. Statistical analysis and backward air masses trajectories

The Spearman's rank correlation was applied to assess which species (WSIs, elements, and PAHs) exhibited similar sources or behavior. Spearman correlation coefficients ($p < 0.05$) for WSIs, elements, and PAHs were obtained using the Statistica software (version 13.5.0.17, Tibco Software Inc). Data below detection and quantification limits were replaced by DL/2 and QL/2, respectively. The Hysplit (Hybrid Single-Particle Lagrangian Integrated Trajectory) model was used through the READY platform from NOAA (National Oceanic and Atmospheric Administration) (Draxler and Rolph, 2003). The air masses backward trajectories were simulated for 96 h, using the meteorological data GDAS (1°) and starting point coordinates 26° 15' 00" S, 48° 51' 36" W. The height levels above the ground were set to 500, 1500, and 3000 m, to simulate trajectories near the ground, in the upper boundary layer, and lower troposphere (Pereira et al., 2017). The HYSPLIT model does not incorporate effects of chemical reactions, byproducts from fires, explosions, or chemical reactions, deposition, complex terrain, particulate transport, and variations of emission rate with time and height (NOAA, 2025). Nevertheless, backward air mass trajectories can be used to indicate the possibility of long-range transport. In this work, this model was used to investigate the influence of air masses coming from burning areas on days when biomass burning markers were detected.

The maps indicating the sampling location and wind rose were made in R software, using the *ggplot2*, *sf*, *geobr*, and *openair* packages.

3. Results and discussion

3.1. Fine particulate matter concentrations and sampling site characteristics

PM_{2.5} concentrations obtained in this study for Joinville, as well as those reported in other industrial sites by previous studies, are presented in Table 1. PM_{2.5} concentrations remained below the national 24-h average air quality standard of 50 $\mu\text{g m}^{-3}$, but surpassed the WHO 24-h AQG of 15 $\mu\text{g m}^{-3}$ on fourteen days, indicating inappropriate air quality in most sampling days (CONAMA, 2018; WHO, 2021a). The sampler was installed in the Industrial District neighborhood, next to a major avenue and large industries (2 km). According to the Urban Control-Territorial Planning Instrument, this neighborhood is surrounded by areas designated as special industrial interest zones (SE-06), mixed industrial zones (SE-06A), and priority densification zone 02 (SA-02). The sampling was carried out in a region composed of industries of different sizes and from a wide range of sectors, with highly congested traffic routes. The median concentration (23 $\mu\text{g m}^{-3}$) was lower than that reported in an important industrial site impacted by petrochemical activities in São Paulo state (average 32 $\mu\text{g m}^{-3}$) (Caumo et al., 2023); in a site (medium-sized industrial city) impacted by metallurgical, oil, fertilizer, and food industries in southern Brazil, the concentration was 12.06 $\mu\text{g m}^{-3}$ (Tavella et al., 2022).

In the largest metropolitan area in the South region of Brazil (~4 million inhabitants), the concentrations of PM_{2.5} (1.03–43.87 $\mu\text{g m}^{-3}$) collected from autumn to summer (2002) were within the range found in Joinville samples (9–49 $\mu\text{g m}^{-3}$) (Table 1). These concentrations were attributed mainly to vehicular traffic, with contributions of industrial activities (including coal-fired plants, metallurgical industry, and oil refinery) (Dallarosa et al., 2008).

The values observed in Joinville were also close to those reported in a previous study carried out in São Paulo (winter and spring months) (4.74 $\mu\text{g m}^{-3}$ – 52.70 $\mu\text{g m}^{-3}$) in an urban site with the influence of industrial emissions (Serafeim et al., 2023). The findings of this study underscore the significance of conducting air-quality research in smaller and medium-sized cities, which are often overlooked in pollution assessments. Although Joinville is classified as a medium-sized city, its PM_{2.5} concentrations during winter are comparable to those reported for some large urban centers. These findings emphasise the necessity of a thorough comprehension of anthropogenic activities and the dispersion mechanisms of pollutants within the designated study areas.

The city's climate is classified as humid subtropical, with high annual rainfall and elevated relative humidity throughout most of the year. Due to its proximity to the coast, local meteorological conditions are strongly influenced by maritime air masses, which contribute to frequent precipitation events and moderate thermal amplitude. The prevailing wind regime is dominated by northerly winds, as illustrated in the wind rose (Fig. 1a and b), which play an important role in pollutant dispersion and transport processes within the urban area. The marked topographic gradient exerts a significant influence on local airflow patterns, atmospheric stability, and pollutant accumulation, particularly under conditions of low wind speed and high humidity. These conditions have the potential to exert an influence on the dynamics of air quality in urban and industrial areas (Santos-Silva et al., 2023).

Industrial activities, mainly the metallurgical industry, play an important role in Joinville's economy. A total of 183 enterprises were identified within the specified sampling region. Of these, 78 were found to be engaged in activities related to metallurgy and metal products, chemicals, mechanical manufacturing, trade and storage of fuels, chemical or hazardous products, plastics, final waste disposal, and pharmaceuticals (Joinville, 2024a).

Regarding mobile sources, major traffic corridors with high volumes of both light- and heavy-duty vehicles are present near the sampling site. The city's vehicle fleet is over 460,000 vehicles. Light-duty vehicles

Table 1
PM_{2.5} concentrations in cities of South Brazil.

Site	Period	Min-max (µg m ⁻³)	Median (µg m ⁻³)	N. of samples	Ref.
Joinville, SC, Brazil (industrial)	June to August 2022	9–49	23	18	Present study
Porto Alegre, RS, Brazil (urban)	April to December 2002	1.03–43.87	–	40	Dallarosa et al. (2008)
Rio Grande, RS, Brazil (Industrial)	June 2009 to May 2010	8.19–19.62	12.06	12	Tavella et al. (2022)
Rio Grande, RS, Brazil (urban)	June 2009 to May 2010	7.26–24.74	10.52	12	Tavella et al. (2022)

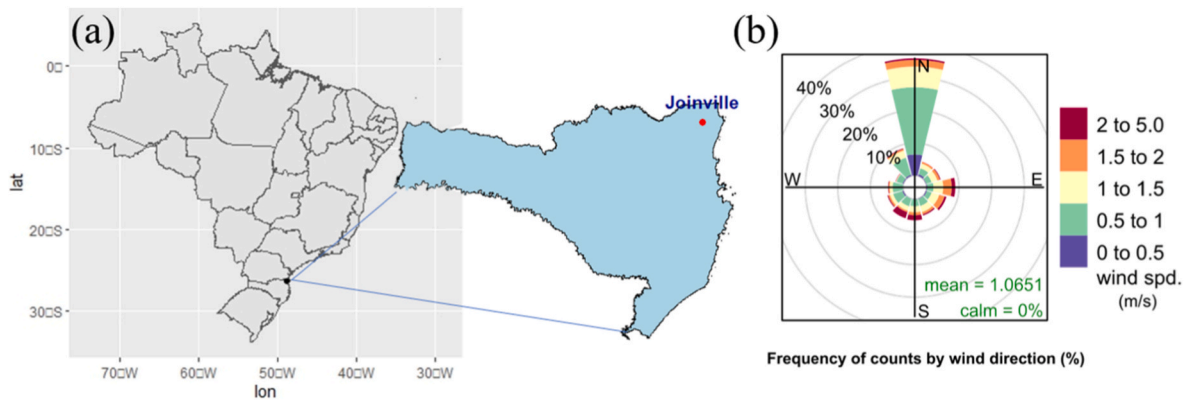


Fig. 1. Sampling site (a) and (b) wind roses.

comprise approximately 76 % of the total fleet. This is followed by motorcycles, which account for approximately 18 % of the fleet, and heavy-duty vehicles (HDV), which account for approximately 6 % of the total fleet (Ministry of Transport, 2022).

3.2. Inorganic species concentrations: water-soluble ions and elements

The concentrations of water-soluble ions (WSIs) and elements are presented in Table 2. Among ionic species, sulfate and nitrate were the most abundant species. Sulfate and nitrate were positively correlated with ammonium ($\rho = 0.9$ and 0.8 , respectively) (Table S5). These pollutants are formed through secondary reactions of gaseous pollutants (SO_2 , NO_2 , and NH_3) typically emitted by anthropogenic activities. Nitrogen and sulfur oxides are oxidized to nitric and sulfuric acid, which are neutralized by the ammonia, leading to the formation of fine particles of $(\text{NH}_4)_2\text{SO}_4$ and $(\text{NH}_4)_2\text{NO}_3$ (Seinfeld and Pandis, 2016). The $\text{NO}_3^-/\text{SO}_4^{2-}$ ratio varied from 0.3 to 1.3 (median = 0.7). Values lower than 1 are often attributed to the predominance of stationary sources, but high humidity and high temperatures can reduce the partitioning of NO_3^- in the particulate phase, due to the formation of HNO_3 , which is more volatile than NH_4NO_3 (Huang et al., 2016).

Cl^-/Na^+ ratios presented a large variation (0.01–63.00), with a median value of 2.60. Although sodium and chloride are associated mainly with the marine aerosol, Cl^-/Na^+ ratios greater than 1.8 indicate additional sources of chloride, such as the burning of waste or solid fuels (Souza et al., 2014). Sodium presented moderate ($\rho = 0.5$) and strong correlations ($\rho = 0.7$) with calcium and magnesium, respectively. This suggests that soil dust must be an important source of this ion, in addition to marine aerosol. Calcium, magnesium, and phosphate presented moderate to strong correlations ($\rho = 0.5$ – 0.7), which indicates the influence of dust resuspension.

The most abundant elements were $\text{Al} > \text{Fe} > \text{Zn} > \text{Cu}$. These elements are associated with soil resuspension (Al and Fe), metallurgical activities, and vehicular emissions (Cu, Fe, and Zn) (Pereira et al., 2023b; Yang et al., 2024). The enrichment factors (EF) were calculated to determine which species presented significant contributions from anthropogenic sources. $\text{EF} > 10$ indicates a significant anthropogenic contribution, while $\text{EF} < 10$ suggests mainly soil dust resuspension (Nayebare et al., 2018). Cadmium, antimony, and molybdenum (50 % of

Table 2
Water-soluble ions and elements concentrations in PM_{2.5} samples collected in a site in Joinville.

Water-soluble ions and elements	Range	Median
Concentrations (ng m ⁻³)		
F ⁻	2–27	6
HCOO ⁻	3–101	25
Cl ⁻	4–904	315
PO ₄ ³⁻	5–191	137
SO ₄ ²⁻	441–3443	1354
NO ₃ ⁻	296–2328	930
C ₂ O ₄ ²⁻	80–377	153
NH ₄ ⁺	1–1129	167
Ca ²⁺	60–528	299
Mg ²⁺	16–95	41
K ⁺	28–675	143
Na ⁺	5–338	130
Al	155–2430	525
As	1–4	1
Ba	3–22	9
Cd	0.3–2.2	0.6
Ce	0.3–1.8	0.5
Co	0.1–3.7	0.4
Cu	51–246	125
Fe	158–2079	530
La	0.3–1.0	0.4
Mn	5–70	18
Mo	2–9	5
Ni	0.3–32.3	1.3
Pb	3–28	11
Rb	0.5–3.9	16
Sb	1–7	2
Sn	1–5	2
Sr	0.3–5.3	1.7
Ti	3–69	17
V	0.4–2.9	1.1
Zn	31–731	229

the samples) presented the highest enrichment factors ($\text{EF} > 1000$). Most samples presented $10 \leq \text{EF} \leq 1000$ for the elements copper, zinc, lead, arsenic, and tin. EF values below 10 (Mn, Ni, La, Ti, Al, Fe, Rb, V, Ba, Sr, and Co) indicate mainly soil resuspension for most of the samples.

The city has a vehicle fleet of over 460,000 vehicles (Ministry of Transport, 2022), which contributes to metal concentrations in the air

through exhaustive and non-exhaustive emissions. In previous studies carried out in Brazilian road tunnels, copper was found as an ethanol/gasohol marker. This element can be emitted from engine abrasion, and is possibly present in ethanol due to the treatment of this fuel in copper tanks (La Colla et al., 2021; Pereira et al., 2023a).

Antimony is a marker of brake wear emissions. The abrasion of tires, brake linings, and metallic parts of vehicles can give some contribution to the emissions of other elements, including Cd, Pb, and Zn (Pereira et al., 2023b). Molybdenum is associated with lubricating oil, abrasion of vehicle parts, and is also present in the catalysts of ethanol-powered vehicles (Dabek-Zlotorzynska et al., 2019; La Colla et al., 2021).

According to a recent report, copper wire production accounts for more than 5 % of the city's industrial exports, highlighting the importance of this activity. Furthermore, refined and raw copper accounted for 11 % of total industrial imports (Joinville, 2024b). The secondary copper smelting is an activity present in Joinville and possibly contributed to the concentrations observed for this element. In China, studies showed that primary copper smelting industries are important sources of Cu, Zn, Pb, and As, while secondary copper smelting emitted more Cu, P, Pb, As, and Ni than other industries (Yang et al., 2024). In the present study, lead and cadmium showed moderate correlations with copper ($\rho = 0.6$ – 0.7) and may also be related to this activity.

Other elements that showed enrichment (Zn and Sn) may be associated primarily with industrial emissions. Zinc can be emitted by ferrous and non-ferrous metallurgical processes (Yang et al., 2024). Tin is not abundant in the Earth's crust, and its presence in the air is related to the burning of fossil fuels and industrial emissions (including glass production, electronics, and mechanical industries) (Correa et al., 2023). In a study conducted in an industrial pole in southeastern Brazil, the presence of zinc and tin in PM₁₀ and TSP samples was associated with iron and steel industries (Gioda et al., 2004). The foundries that process ferrous (i.e., iron and steel) and non-ferrous (i.e., aluminum, bronze, and brass) metals represent a significant economic activity in the city. This industrial activity may also have contributed to the metals enrichment in the atmosphere (Joinville, 2024b).

The concentrations of elements found in this study were between one and three orders of magnitude higher than those reported in studies conducted in industrial and urban areas in Europe and North America. Conversely, the values found in Joinville are comparable to those reported in studies conducted in Asia and Latin America (Liu et al., 2025; Maciejczyk et al., 2021). Notably, Cu showed higher values in this study (51–246 ng m⁻³) when compared to most worldwide studies. These concentrations are comparable with those already reported in studies conducted in Brazil (13–931 ng m⁻³ in São Paulo, Pereira et al., 2025) and in Latin America (Maciejczyk et al., 2021). It reinforces the influence of ethanol combustion emissions on the presence of Cu in the atmosphere.

Some diagnostic ratios can also be useful to distinguish between emission sources. The Zn/Pb ratio found in the present study (5–60, median 19) can indicate diesel combustion and cement plant emissions according to Arditoglou and Samara (2005).

A previous study carried out in Joinville showed that ventilation and stagnation/recirculation conditions may influence the concentrations of these elements in PM_{2.5}. It was shown that local specific wind regimes seemed to be able to reduce the contamination of Zn near a Metallurgical Industrial Complex, and local recirculation increased the contamination of Zn and Pb near the North Industrial District (Santos-Silva et al., 2023). Thus, the large range of Zn/Pb ratios found in the present study may reflect the influence of different industrial activities and atmospheric transport.

V/Ni ratios varied from 0.02 to 1.80 (median 1.10). Values varying from 1 to 3 were associated with crude oil combustion and residual fuel combustion in studies carried out in tunnels in São Paulo (Pereira et al., 2023b). Fe/Cu (3.6), Ba/Cu (0.07), Sb/Cu (0.02), and Sn/Cu (0.02) ratios are attributed to ethanol combustion and engine corrosion (Pereira et al., 2023b). In studies carried out in a Taiwanese tunnel

where light-duty cars and trucks emissions were investigated, these ratios were higher than those found in Brazilian tunnels. These ratios were attributed to brake wear (Lin et al., 2015).

Spearman coefficients were also calculated (Table S6); earth crust (Al, Fe, Mn, Sr, and Ti) and other elements associated with dust resuspension (EF < 10) present strong correlations ($\rho > 0.7$). Zn also presented a strong correlation ($\rho > 0.7$) with elements related to dust resuspension (Fe, Ti, Mn, Ba, Sr, and Ce), in addition to moderate correlation with Pb ($\rho = 0.7$) and Ni ($\rho = 0.5$). These results indicate that different anthropogenic activities influenced the concentrations of these elements in the particulate matter. Besides the industrial sources, dust resuspension, exhaust, and non-exhaust emissions strongly contributed to PM composition.

3.3. Polycyclic aromatic hydrocarbons and derivatives concentrations

The concentrations of PAHs and their derivatives (oxy and nitro-PAHs) are presented in Fig. 2 and Table S7. The total concentrations of PAHs varied from 0.4 to 10.3 ng m⁻³ (median 3.1 ng m⁻³). Joinville samples presented lower PAHs concentrations than those observed near a petrochemical industrial area in Southeast Brazil (average = 16.7 ng m⁻³) (Caumo et al., 2023). The PM_{2.5} samples collected in the petrochemical neighborhood presented BbF, BkF, and DBA as the most abundant PAHs, indicating strong vehicular influence and stationary emission sources. Similarly, Joinville samples presented PAHs coming from traffic (BPE, INP) and industrial marker (DBA). Yet, the concentrations were higher than those reported in a study carried out in another medium-sized and industrial city in Southern Brazil; the industrial complex is located on the coast, and the sea breeze may favor the pollutants dispersion (Tavella et al., 2022).

In studies carried out between 2006 and 2008, in a metropolitan region (~1.3 million inhabitants) strongly impacted by vehicular traffic, the PAHs concentrations (varied 2.11–3.70 ng m⁻³) were comparable to those found in this study. In this site, PHE and high molecular weight PAHs (HMW-PAHs) were the most abundant compounds, and the concentrations of HMW-PAHs were associated with heavy-duty vehicles (Teixeira et al., 2012). On the contrary, a study carried out in tunnels in São Paulo showed that gasohol and ethanol combustion predominantly emit CHR, BeP, and BaP (HMW-PAHs), while emissions from diesel and biodiesel burning are associated with low molecular weight PAHs (LMW-PAHs) (Pereira et al., 2023b).

COR, a HMW-PAH and marker for vehicular emission (range 0.1–1.1 ng m⁻³) presented low concentrations in samples collected on days that presented high PM_{2.5} concentrations (25 and 19 µg m⁻³) during vacation time (July 2nd and 20th). Differently, SNA concentrations (3600 ng m⁻³) were higher than the median values calculated for the whole campaign (2714 ng m⁻³), indicating secondary formation as the predominant source of PM_{2.5}.

The diagnostic ratios were also calculated among the PAHs (Table 3). BaP/(BaP + BeP) ratio (0.3–0.4) suggested photooxidation of PAHs on most sampling days. IP/(IP + BPE) (median 0.5) and BaA/(BaA + CHR) (median 0.35) indicated the predominance of the influence of fossil fuel combustion. FLT/(FLT + PYR) ratios above 0.5, as the values found in the present study, can be related to biomass burning, but these ratios were also observed in sites influenced by heavy-duty vehicle emissions (Dallarosa et al., 2008). The results indicate that vehicular traffic is the main source of PAHs in PM_{2.5} collected in this Joinville neighborhood. The vehicular fleet in the city is predominantly light-duty vehicles (~76 %), while heavy-duty vehicles (~6 %) account for a smaller portion of the traffic, which means that the combustion of gasoline may be the major source of these pollutants (Ministry of Transport, 2022). PAHs diagnostic ratios are useful in suggesting the processes that originated these pollutants, and are used cautiously (Tobiszewski and Namieśnik, 2012). Robust statistical analyses (such as PCA, Unmix, and PMF) are interesting tools to perform source-apportionment.

Retene, a biomass-burning marker PAHs presented low

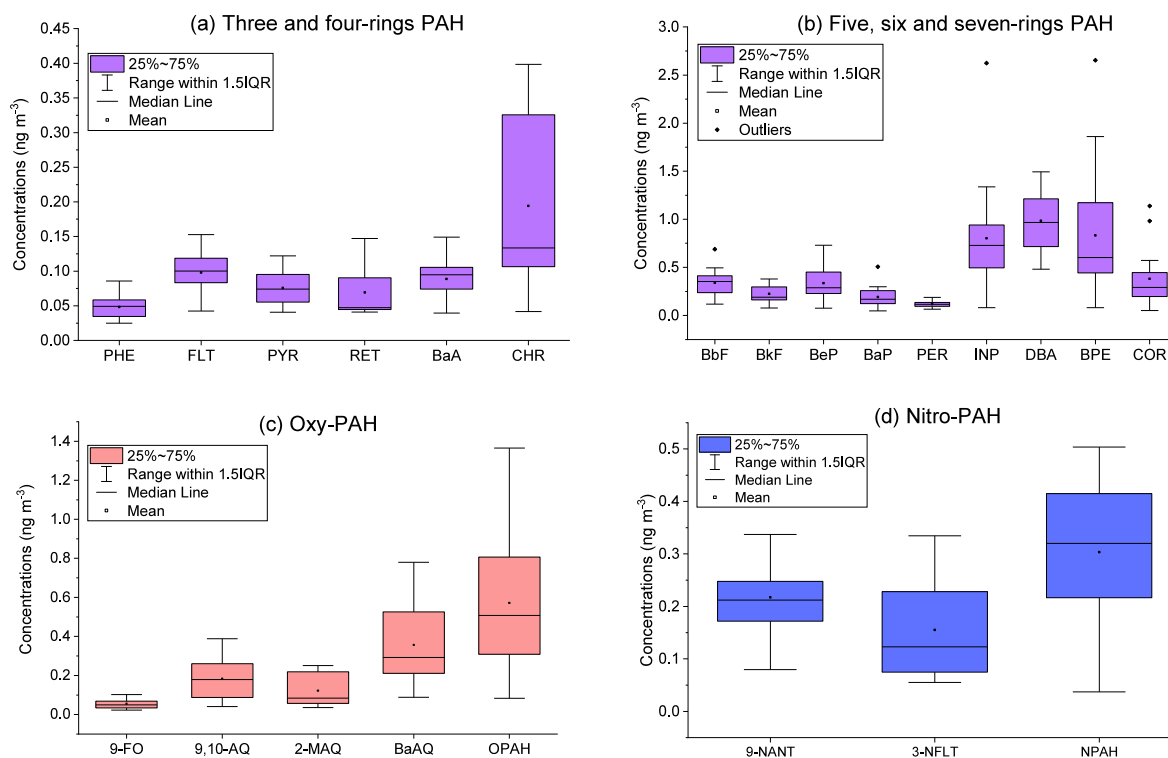


Fig. 2. Concentrations of polycyclic aromatic hydrocarbons and derivatives in PM_{2.5} samples collected in Joinville during the winter of 2022: (a) Three and four-rings PAHs: phenanthrene (PHE), fluoranthene (FLT), pyrene (PYR), retene (RET), benzo(a)anthracene (BaA), chrysene (CHR), (b) five, six and seven-rings PAHs: benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(e)pyrene (BeP), benzo(a)pyrene (BaP), perylene (PER), dibenzo(a,h)anthracene (DBA), benzo(g,h,i) perylene, and coronene (COR) (c) oxy-PAHs: 9,10-fluorenone (9-FO), 9,10-anthraquinone (9,10-AQ), 2-methylanthraquinone (2-MAQ), and 7,12-benzo(a)anthracene-dione (BaAQ), (d) nitro-PAHs: 9-nitroanthracene (9-NANT), 3-nitrofluoranthene (3-NFLT), and 1-nitropyrene (1-NPYR).

Table 3

Diagnostic ratios and sources of PAHs in the PM_{2.5} collected in Joinville.

	Range	Median	Source	Reference
BaP/ (BaP + BeP)	0.3–0.4	0.4	~0.5 Fresh emissions <0.5 Aged particles	Oliveira et al. (2011)
FLT/(FLT + PYR)	0.5–0.6	0.6	<0.4 Petrogenic 0.4–0.5 Fossil fuel combustion >0.5 Coal, wood, and Grass combustion	De La Torre-roche et al. (2009)
BaA/ (BaA + CHR)	0.18–0.60	0.35	<0.2 Petrogenic 0.2–0.35 Mixed sources >0.35 Combustion sources	Yunker et al. (2002)
IP/(IP + BPE)	0.2–0.6	0.5	<0.2 Petrogenic 0.2–0.5 Petroleum combustion >0.5 Coal, wood, and Grass combustion	Yunker et al. (2002)

concentrations (0.04–0.15 ng m⁻³) in one third of the samples, indicating a low influence of biomass burning on PAHs levels. The backward air masses trajectories, obtained by the Hysplit Model, indicated the influence of the transport of air masses from regions with fire spots reported by INPE data (Fig. 3) during 4 days during the sampling (from 1st to 4th August). In this period, over 2800 fires were observed (INPE, 2022; Ramdahl, 1983).

Oxy-PAHs and nitro-PAHs were detected and quantified in 89 % and 61 % of the samples, respectively. These compounds present higher mutagenicity and carcinogenicity than their parent PAHs (Idowu et al., 2019). The sum of PAHs derivatives varied from 0.08 to 1.40 ng m⁻³ for oxy-PAHs and 0.04–0.50 ng m⁻³ for nitro-PAHs. These values are lower

than those found in Brazilian major cities, including São Paulo ($\sum_4$ Oxy-PAHs = 74.9–2137 pg m⁻³ and $\sum_8$ Nitro-PAHs = 90.2–1002 pg m⁻³, winter and spring, Serafeim et al., 2023) and Belo Horizonte ($\sum_6$ Oxy-PAHs = 0.26–2.76 ng m⁻³ and $\sum_4$ Nitro-PAHs = 0.51–1.77 ng m⁻³, one-year campaign, Santos et al. (2020), and higher than those found in other cities, such as Ribeirão Preto, Brazil (58–383 pg m⁻³, winter, Scaramboni et al., 2024), Mexico City ($\sum_8$ Nitro-PAHs = 58–383 pg m⁻³, spring to winter, Valle-Hernández et al., 2010).

The most abundant oxy-PAHs were 9,10-AQ and BaAQ. It is known that 9,10-AQ can be directly emitted by diesel combustion or formed through secondary reactions of anthracene with gaseous pollutants and radicals in the atmosphere (Inomata et al., 2015; Nocun and Schantz, 2013). These compounds were also the most abundant oxy-PAHs found in São Paulo studies (Pereira et al., 2017; Serafeim et al., 2023). 9,10-AQ was also found in abundance in a tunnel impacted by biodiesel combustion in São Paulo (Pereira et al., 2023a), which suggests the possible influence of high-duty vehicles.

9-NANT and 2+3-NFLT were the most abundant nitro-PAHs. 3-NFLT is emitted directly, and the isomer 2-NFLT is formed exclusively through secondary reactions. 1-NPYR, a nitro-PAH emitted exclusively by diesel combustion (Inomata et al., 2015), was detected in only two samples (Table S7). 9-NANT was also found in abundance in a study carried out in Mexico City, where the concentrations were attributed to both secondary reactions and primary emissions (Valle-Hernández et al., 2010).

The samples were collected only during the winter season. Lower concentrations and different profiles may be found in seasons with a greater influence of meteorological variables that facilitate the dispersion of pollutants and photochemical reactions (relative humidity, precipitation, and solar radiation).

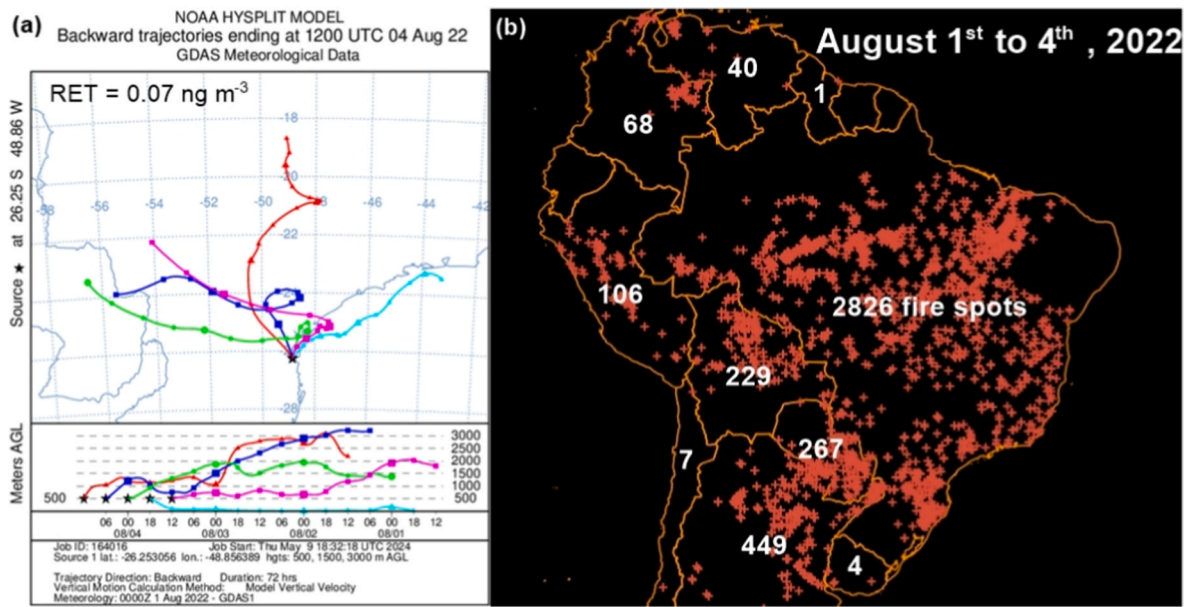


Fig. 3. Influence of air masses transport and fire spots on retene concentrations: (a) HYSPLIT backward trajectories on August 4th, 2022, (b) fire spots detected from August 1st to 4th, 2022.

3.4. Health and risk assessments

The health risk values were calculated assuming chronic exposure to the pollutant concentrations found from June to August 2022 (winter). However, it is important to note that the concentrations of these pollutants may vary between seasons and over the years.

The hazard quotient (HQ) and the cancer risk (CR) due to toxic metals inhalation during winter season in Joinville are presented in Table 4. The Environmental Protection Agency of U.S. (EPA) recommends a non-carcinogenic risk (HQ) value smaller than one (USEPA, 2009). The median HQ value of the sum of all metals per day of sampling was found to be 0.7, with the safe limit being exceeded on seven sampling days of the campaign. Individual hazard quotient (HQ) values for each toxic metal revealed that, except for manganese (Mn) on a single campaign day, none of the metals exceeded the safe limit. Manganese is associated mainly with reactive oxygen species formation in particulate matter (Pietrogrande et al., 2021). In samples collected previously in a site heavily impacted by traffic (in São Paulo city), HQ was over 1.1, and Ni presented the highest individual values (HQ > 1 in most sampling days) (Alves et al., 2020) (see Table 4).

The median index found for cancer risk due to metal inhalation (CR) surpasses the limit recommended by EPA (1×10^{-6}) for children and

Table 4
Hazard quotient (HQ) and cancer risk (CR) indexes of toxic metals in PM_{2.5} collected in Joinville.

Element	Median HQ (Range)	Median CR _{children} (Range)	CR _{adults} (Range)
Mn	0.36 (0.10–1.40)	–	–
Ni	0.01 (0.004–0.360)	2.6×10^{-8} (6.8×10^{-9} – 6.7×10^{-7})	1.1×10^{-7} (2.7×10^{-8} – 2.7×10^{-6})
As	0.08 (0.04–0.27)	4.3×10^{-7} (2.3×10^{-7} – 1.4×10^{-6})	1.7×10^{-6} (8.8×10^{-7} – 5.6×10^{-6})
Pb	–	6.8×10^{-8} (2.1×10^{-8} – 1.8×10^{-7})	2.7×10^{-7} (8.3×10^{-8} – 7.0×10^{-7})
Cd	0.06 (0.03–0.22)	9.0×10^{-8} (5.0×10^{-8} – 3.2×10^{-7})	3.6×10^{-7} (2.0×10^{-7} – 1.2×10^{-6})
Co	0.07 (0.01–0.62)	3.1×10^{-7} (4.3×10^{-8} – 2.7×10^{-6})	1.2×10^{-6} (1.7×10^{-7} – 1.1×10^{-5})
Sum	0.70 (0.20–1.80)	1.1×10^{-6} (1.0×10^{-7} – 3.7×10^{-6})	4.6×10^{-6} (4.0×10^{-7} – 1.5×10^{-5})

adults (USEPA, 2009). The individual indexes calculated for As (1.7×10^{-6}) and Co (1.2×10^{-6}), were higher than those recommended (for adults). The carcinogenicity of As and Co present in airborne particulate matter was proven by different studies. The low pH within lysosomes (cell organelles) may favor partial solubilization of cobalt, leading to the release of cobalt ions into the cytoplasm and cell nucleus (Ortega et al., 2014). Inorganic arsenic species (As^{3+} and As^{5+}) are very reactive and are easily absorbed by the human organism (Chung et al., 2014). Arsenic induces DNA double-strand breaks in lung fibroblasts and epithelial cells (Xie et al., 2014).

BaP, the most studied PAH, was found in all samples (0.05 – 0.51 ng m^{-3}). The World Health Organization (WHO) recommends a BaP concentration below 1 ng m^{-3} as a safe limit (WHO, 2021b). Although the concentrations of BaP did not surpass this value during the sampling period, the calculated BaP-TEQ index (0.1 – 8.2 ng m^{-3} , median 1.5 ng m^{-3}) (Table 5) exceeded this limit in nine days, indicating potential cancer risk in 50 % of the samples.

The median ILCR index Caumo et al., 2023; Tavella et al., 2022 in Joinville samples were 4.1×10^{-7} for children and 1.2×10^{-6} for adults. This index exceeded the limit recommended by the EPA ($<1 \times 10^{-6}$) in eight days for children and nine days for adults. This result indicated a moderate risk of cancer due to inhalation of carcinogenic PAHs on half of the sampling days. The ILCR index in Joinville was higher than those reported in the urban and industrial areas in Southern Brazil (6.88×10^{-8} and 4.72×10^{-8} , respectively), but lower than those reported near a petrochemical industrial area (6.4×10^{-4}) (Caumo et al., 2023; Tavella et al., 2022).

3.5. Respiratory deposition flux

The Respiratory Deposition Fluxes (RDD) of PM_{2.5}, PAHs, and

Table 5
BaP-TEQ and ILCR indexes of carcinogenic PAHs found in Joinville PM_{2.5} samples collected in the winter season.

	Range	Median
BaP-TEQ	0.1–8.2	1.5
ILCR (Children, 10 years)	2.0×10^{-8} – 2.3×10^{-6}	4.1×10^{-7}
ILCR (adults, 75.5 years)	5.7×10^{-8} – 6.4×10^{-6}	1.2×10^{-6}

elements were calculated, and the results are summarized in Table 6. These values represent the deposition of pollutants in the lungs during winter. The DF (deposition fraction) was higher in the upper airway (UA), followed by the alveolar (AL) and tracheobronchial (TB) regions. Most PM_{2.5} is deposited in the UA through interception, sedimentation, and impaction mechanisms. Despite the lower deposition in the TB and AL regions, significant concentrations of PM_{2.5} and bound pollutants still reach the lungs through diffusion mechanisms (Hofmann, 2011).

The level of inhaled pollutants may vary with physical and biological factors, such as lung morphology, pre-existing illness, type of breathing (nasal and oronasal), and occupational exposure (Hofmann, 2011). The masses of pollutants deposited in the respiratory system were higher for adults than for children, due to the higher inhalation rate difference. Adults often are exposed to air pollution for longer periods than children and to higher levels of pollution (Khan et al., 2022).

In the upper airway, particles can be eliminated by coughing or sneezing. In the UA and TB regions, there is particle clearance due to the presence of mucociliary cells. Mucociliary activity is greatest in the upper airway and decreases in the tracheobronchial region. In the alveolar region, mucociliary cells are absent due to the need for gas exchange, and clearance occurs mainly through the absorption of particles by alveolar macrophages. This process is slow, and the accumulation of substances in this region can cause long-term damage (Khan et al., 2022).

The literature reports that cardiovascular mortality risk in children is associated with higher deposition of particulate matter in the lungs (Khan et al., 2022). In Joinville, a clinical study showed that residents of the industrial site, the most polluted area of the city, are prone to present changes in blood pressure levels and to develop coronary artery disease (Schaidhauer et al., 2024). Diseases of the circulatory system are the main cause of morbidity in the city (Joinville, 2024a).

The RDD of carcinogenic PAHs (estimated as BaP-TEQ) calculated in PM_{2.5} samples collected in Joinville are presented in Fig. 4. The total of BaP-equivalent carcinogenic PAHs deposited in the lungs (TB + AL regions) per day for children varied from 0.15 to 17 ng, and from 0.19 to 22 ng for adults. These pollutants are mainly found in fine and ultrafine particles, which can reach deeper regions of the respiratory system, causing higher deposition. The deposition of these PAHs and derivatives in the TB and AL regions represents a great threat to human health. Metabolic activation of PAHs by cytochrome P450 enzymes, epoxide hydrolases, and other enzymes results in the formation of quinones capable of interacting with macromolecules, leading to mutations and cancer (Rossner et al., 2016). PAHs metabolites induce genotoxic effects on alveolar and bronchial human lung cells by combining oxidative stress with energy depletion (Gurbani et al., 2013; Rossner et al., 2016).

Metals are also associated with the toxic effects of PM_{2.5}. Several studies showed the ability of these species to induce ROS formation through the Fenton reaction (Pietrogrande et al., 2021). In addition,

transition metals (such as Fe, Cu, Mn, and Ni) were associated with the inflammatory response, oxidative stress, and reduction of cell viability of alveolar and bronchiolar human lung cells exposed to PM_{2.5} *in vitro* studies (Cho et al., 2018). The sum of metals deposited in the lungs (TB + AL regions) varied from 1030 to 11,357 ng per day for children and 1339–14,764 ng per day for adults. Iron and copper presented the highest deposition levels. The median mass of copper deposited in the lungs was 252 ng per day for children and 327 ng per day for adults, and for iron was 1070 ng per day for children and 1391 ng per day for adults.

Although there are no reference doses for inhalation of these metals, Fe and Cu are known as the main drivers of the oxidative effects of atmospheric particulate matter, and these values present a concern to human health (Pietrogrande et al., 2021). Different mechanisms are proposed in the literature for the Fenton-like reactions of these metals. These mechanisms include the interaction of Cu (II) and Fe (II) with H₂O₂, a byproduct of cellular metabolism. This reaction produces reactive oxygen species (ROS, e.g., O₂[•] and OH[•]) (Wei et al., 2019). The imbalance between antioxidant defenses and ROS production favors the reaction of these species with cellular macromolecules (nucleic acids, proteins, and lipids), promoting oxidative stress (Mascio et al., 2019).

The total respiratory deposition doses (RDD) of PM_{2.5} range from 4 to 21 µg h⁻¹ (0.07–0.36 µg min⁻¹) for children and 5–28 µg h⁻¹ (0.09–0.46 µg min⁻¹) for adults. These values were notably lower than those reported in cities of China and India, where this pollutant is typically found in high concentrations (PM_{2.5} > 100 µg m⁻³) (An et al., 2022; Singh et al., 2025). In a study conducted in Delhi, India, from 2019 to 2022, the RDD ranged from 0.35 µg min⁻¹ (female, sitting, 2020) to 2.76 µg min⁻¹ (male, walking, 2019). In that study, the RDD values were higher in industrial/commercial areas than in residential sites, which showed that these anthropogenic activities contributed significantly to the PM_{2.5} deposition. Besides, the factors affecting deposition were time of day, gender, and activity level (Singh et al., 2025). In Jinan, China, a study conducted between 2018 and 2020 applied the ICRP model to show the total PM_{2.5} deposition during locomotion (walking). During the winter, RDD ranged from 1.6 µg min⁻¹ (morning, route B) to 3.8 µg min⁻¹ (afternoon, route A), showing that direct exposure to vehicular traffic can significantly increase deposition. The RDD values in Jinan were higher in winter than in the spring, showing that deposition is also affected by seasonal values, and that sampling over a short period does not represent annual values (An et al., 2022).

4. Conclusions

PM_{2.5} concentrations remained below the national air quality standards, but exceeded the WHO guideline, which showed inappropriate air quality on most sampling days. This represents a greater risk of exposure to toxic components and adverse health effects.

The inorganic pollutants abundance and ratios showed the influence

Table 6
Respiratory Deposition Flux of PM_{2.5} and bound pollutants for children (10 years) and adults (75.5 years).

Pollutant RDD	Children			Adults		
	UA	TB	AL	UA	TB	AL
PM _{2.5} (µg h ⁻¹)	3–17	0.3–1.5	0.5–2.7	4–22	0.4–2.0	0.6–3.5
Pollutants (ng h ⁻¹)						
BaP-TEQ	0.025–2.842	0.002–0.247	0.004 0.453	0.033–3.695	0.003–0.321	0.005–0.589
Mn	2–24	0.1–2.1	0.3–3.8	2–32	0.2–2.8	0.3–4.9
Ni	0.1–11.1	0.01–0.98	0.02–1.74	0.2–14.4	0.01–1.27	0.02–2.26
As	0.2–1.4	0.02–0.12	0.03–0.22	0.3–1.8	0.03–0.16	0.05–0.29
Pb	1–9	0.1–0.8	0.2–1.5	1.5–12.3	0.1–1.0	0.2–1.9
Cd	0.1–0.8	0.01–0.07	0.02–0.12	0.2–1.0	0.01–0.09	0.02–0.16
Co	0.02–1.28	0.002–0.113	0.003–0.200	0.03–1.66	0.002–0.146	0.004–0.260
Cu	17–85	2–8	3–13	23–110	2–10	4–17
Fe	54–715	5–63	8–112	70–930	6–82	11–145
ΣElements	175–1933	15–171	27–303	228–2513	20–222	36–393

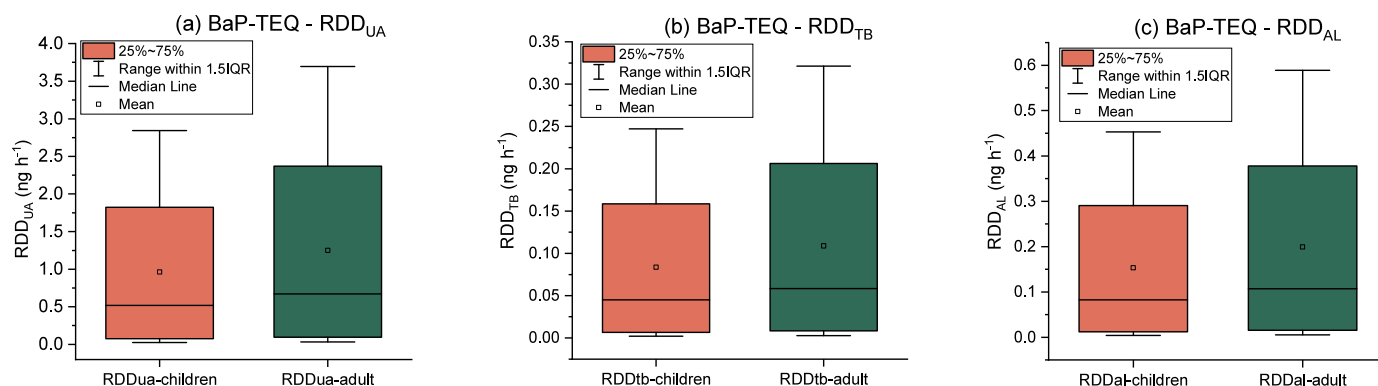


Fig. 4. Respiratory deposition fluxes (RDD) for BaP-TEQ: (a) upper-airway, (b) tracheobronchial, and (c) alveolar RDD.

of fossil fuel combustion, dust resuspension, vehicular traffic, and industrial activities. Some elements showed enrichment, indicating that industries (mainly metallurgical activities) and vehicular traffic (including non-exhaust and exhaust emissions) are the most important sources of $PM_{2.5}$ in this city. The high content of copper in the samples was attributed to emissions from ethanol-powered vehicles and copper foundry activities.

This is the first study presenting concentrations of PAHs, oxy, and nitro-PAHs in Joinville's $PM_{2.5}$. The results showed a higher abundance of compounds with high molecular weight, associated with fossil fuel combustion. The emissions profile and diagnostic ratios showed that vehicular emissions were the main sources. Oxy- and nitro-PAH were predominantly formed through secondary reactions.

The hazard quotient (HQ) and the cancer risk (CR) indices showed that both non-carcinogenic and carcinogenic risks due to inhalation exposure to toxic elements surpass the safe limits in most samples. Furthermore, the individual CR indexes calculated for As and Co exceed the safe threshold for adults, indicating that these elements may play an important role in the toxicity of these samples. The health risk assessments showed that the concentrations of carcinogenic PAHs remained below safe limits, although the ILCR exceeded the limit on half of the sampling days.

The respiratory dose fluxes, calculated according to the ICRP model, showed that most of the $PM_{2.5}$ mass is deposited on the upper airway, but significant amounts still reach the tracheobronchial and alveolar region of the human lungs, where $PM_{2.5}$ and its components can cause adverse health effects. Copper and iron, which are known to be important contributors to the oxidative potential of $PM_{2.5}$, presented high deposition levels.

This study was conducted only during the winter season and cannot be extrapolated to annual and seasonal interpretations. The ICRP model and health risk indexes are empirical approaches that do not consider lung asymmetry and physiological particularities between individuals. Despite the limitations, this approach can be applied in preliminary/exploratory studies in other sampling sites to orient further studies related to health effects (e.g., oxidative potential, genotoxicity, cytotoxicity, etc.).

CRedit authorship contribution statement

Camila N. Farias: Writing – original draft, Validation, Methodology, Investigation, Formal analysis, Conceptualization. **Gabriel D. Barp:** Visualization, Formal analysis, Conceptualization. **Eduardo Karnopp:** Formal analysis. **Katarina O. Rodrigues:** Formal analysis. **Marcos A. Hortellani:** Formal analysis. **Jéssica C. Santos-Silva:** Writing – review & editing. **Jorge E.S. Sarkis:** Resources, Funding acquisition. **Mariane Bonatti-Chaves:** Conceptualization, Funding acquisition, Investigation, Writing – review & editing. **Sandra H.W. Medeiros:** Resources. **Pérola C. Vasconcellos:** Writing – review & editing, Supervision, Resources,

Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.apr.2026.102901>.

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