

## CHARACTERIZATION OF PM<sub>2.5</sub> ELEMENTAL COMPOSITION IN RESIDENTIAL HOMES: SOURCES AND HEALTH RISK ASSESSMENT

Caracterización de la composición elemental de PM<sub>2.5</sub> en viviendas residenciales: fuentes y evaluación del riesgo para la salud

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Key words: indoor air quality, trace metals, exposure assessment, enrichment factors, human health effects, residential environments.

### ABSTRACT

Understanding indoor air pollutant levels is essential to evaluate potential health risks and inform mitigation strategies. This study quantified indoor concentrations of suspended particulate matter with a diameter of 2.5 micrometers (PM<sub>2.5</sub>) and elemental composition (As, Zn, Pb, Cr, and 17 others) in 15 homes—five each from urban, suburban, and rural areas—in Córdoba province (Argentina) during summer and winter. The highest PM<sub>2.5</sub> levels were found in rural homes during winter (mean: 14.78 µg/m<sup>3</sup>), followed by suburban (8.93 µg/m<sup>3</sup>) and urban homes (8.10 µg/m<sup>3</sup>). Despite detectable concentrations, all PM<sub>2.5</sub> levels remained below the United States Environmental Protection Agency's 24-hour standard. Health risk assessment revealed that arsenic (As) was the main contributor to carcinogenic risk, with values exceeding  $1 \times 10^{-6}$  in some homes, particularly during summer. Non-carcinogenic risks for most elements remained within acceptable limits. Elemental source attribution using enrichment factors indicated that indoor PM<sub>2.5</sub> originated from both outdoor sources—mainly vehicular traffic (Co, Cr, As, Zn, Pb)—and indoor activities such as cooking (Co, Cu), paint use (Mn, Cr, Pb), plastic materials (Zn), and electronics (Mo). Seasonal differences also influenced elemental profiles, with some metals enriched during winter due to reduced ventilation and biomass combustion. These findings emphasize the relevance of both external and indoor sources in shaping indoor air quality and underscore the need for seasonally tailored risk mitigation. This study contributes to a better understanding of indoor PM<sub>2.5</sub> exposure in residential environments and supports the development of targeted strategies to reduce health risks associated with airborne particles in low- and middle-income settings.

Palabras clave: calidad del aire interior, metales traza, evaluación de la exposición, factores de enriquecimiento, efectos sobre la salud humana, entornos residenciales.

## RESUMEN

Comprender los niveles de contaminantes en ambientes interiores es esencial para evaluar los riesgos potenciales para la salud e implementar estrategias de mitigación. Este estudio cuantificó las concentraciones de partículas suspendidas con un diámetro de 2.5 micras ( $PM_{2.5}$ ) y su composición elemental (As, Zn, Pb, Cr, y otros 17) en 15 viviendas —cinco de zonas urbanas, suburbanas y rurales— de la provincia de Córdoba (Argentina), durante el verano y el invierno. Las concentraciones más altas de  $PM_{2.5}$  se observaron en viviendas rurales durante el invierno (media:  $14.78 \mu\text{g}/\text{m}^3$ ), seguidas por las suburbanas ( $8.93 \mu\text{g}/\text{m}^3$ ) y urbanas ( $8.10 \mu\text{g}/\text{m}^3$ ). A pesar de los niveles detectables, todas las concentraciones se mantuvieron por debajo del estándar de 24 horas de la Agencia de Protección Ambiental de EUA. La evaluación del riesgo para la salud reveló que el arsénico (As) fue el principal contribuyente al riesgo carcinogénico, superando en algunos casos el valor de  $1 \times 10^{-6}$ , especialmente durante el verano. Los riesgos no carcinogénicos para la mayoría de los elementos se mantuvieron dentro de los límites aceptables. El análisis de factores de enriquecimiento indicó que el  $PM_{2.5}$  en interiores se originó tanto en fuentes externas —principalmente el tráfico vehicular (Co, Cr, As, Zn, Pb)— como en actividades internas como la cocina (Co, Cu), el uso de pinturas (Mn, Cr, Pb), materiales plásticos (Zn) y dispositivos electrónicos (Mo). Las diferencias estacionales también influyeron en los perfiles elementales, con mayor enriquecimiento de algunos metales en invierno debido a la menor ventilación y a la combustión de biomasa. Estos resultados subrayan la importancia de considerar tanto fuentes internas como externas al abordar la calidad del aire interior y los riesgos asociados.

## INTRODUCTION

The fine fraction of indoor aerosols, known as  $PM_{2.5}$ , originate from diverse sources such as cooking, smoking, and cleaning activities (Satsangi et al. 2014). The respiratory system serves as the primary entry pathway for particles (Zhang et al. 2021), allowing  $PM_{2.5}$  to deeply penetrate into the lungs and cause adverse health effects (Hu et al. 2012). These effects are influenced by the physical properties of the particles, including size, number, total surface area, and electrostatic properties, as well as their chemical and biological composition (Taner et al. 2013). Due to its aerodynamic size,  $PM_{2.5}$  exhibits a larger specific surface area and higher adsorption ability than coarse particle fraction, facilitating the binding of toxic compounds to its surface (Li et al. 2017). Moreover, trace concentrations of various metals in the atmosphere have experienced significant increases in recent years to the point where industrial and vehicular emissions now dominate the natural biogeochemical cycle in many urban environments (Chang et al. 2018, Gaonkar et al. 2020, Vithanage et al. 2022).

Although inorganic compounds constitute only a small fraction of particulate matter (PM) mass, even small quantities can have a detrimental impact on human health (Zereini and Wiseman 2011). Furthermore, the inhalation of trace metals adsorbed

to  $PM_{2.5}$  has been associated with lung cancer incidence, cardiovascular damage, atherosclerosis, and hypertension (Fang and Zheng 2014, Tong et al. 2016, Zhang et al. 2016, Vohra et al. 2021), and the potential carcinogenic effects of Cr, Ni, Cu, Zn, Cd, and Pb adsorbed on PM have been confirmed (WHO 2016). Additionally, trace amounts of heavy metals such as Pb and Cd are neurotoxic to living organisms, while Mn, Cd, and Zn are known promoters of carcinogenic activities in animals (Timothy and Tagui Williams 2019, Rahman et al. 2022). Therefore, since 2013, the International Agency for Research on Cancer (IARC 2013) has classified atmospheric particulates as Group 1 contaminants (i.e., carcinogenic to humans).

Air quality standards have been established primarily for outdoor environments. However, significant human exposure to air pollutants occurs indoors, as individuals spend approximately 90% of their time indoors, with around 65% spent at home (Ścibor et al. 2019, Tofful et al. 2021). Despite the potential for indoor environments to serve as significant sources of heavy metals emissions (Li et al. 2017), there have been limited studies examining the potential health risks associated with the inhalation of indoor metals adsorbed onto PM (Abdel-Salam 2021). For instance, yellow wall paint has been associated with elevated levels of Cd, Cu, Pb, and Zn; purple color has been related to high levels of Zn and Pb; and green color

contributes to elevated levels of Cu (Tong and Lam 2000, Chattopadhyay et al. 2003). Therefore, it is crucial to assess indoor human exposure to heavy metals (Jones et al. 2000), particularly considering that the most vulnerable population groups (i.e., young children and the elderly) spend most of their time indoors, primarily within their homes (Laumbach et al. 2015, Lizana et al. 2020).

The indoor air quality (IAQ) index refers to the state of air quality in and around buildings and structures, specifically focusing on the well-being and comfort of occupants (USEPA 2022). Numerous studies conducted worldwide have evaluated the elemental composition of different PM fractions in diverse indoor environments, including educational institutions (Hassanvand et al. 2015), offices (Kurt-Karakus 2012, Saraga et al. 2017), restaurants (Taner et al. 2013, Niu et al. 2021), and residential homes (Kurt-Karakus 2012, Satsangi et al. 2014, Gao et al. 2015, Zhang et al. 2016, Jorquera et al. 2018, Abdel-Salam 2021, Tofful et al. 2021). Therefore, further investigation into IAQ is necessary, considering the complex characteristics of indoor environments and the various indoor sources of pollutants in general, particularly PM<sub>2.5</sub> (Li et al. 2017). Additionally, there is currently a lack of IAQ data from homes in Argentina, and there is no information regarding the comparison between air quality in urban and rural household environments.

Hence, the objectives of this study were to: i) determine the concentration and elemental composition of 21 elements adsorbed onto PM<sub>2.5</sub> collected from indoor environments situated in areas with different land uses, ii) estimate the human health risk associated with the inhalation of indoor particles, and iii) analyze the potential sources of each element. As an initial methodology for assessing the origins of particles collected in indoor environments, enrichment factors (EF) were calculated for each element, which compares the enrichment of an element in the environment with its natural abundance.

## MATERIALS AND METHODS

### Study area

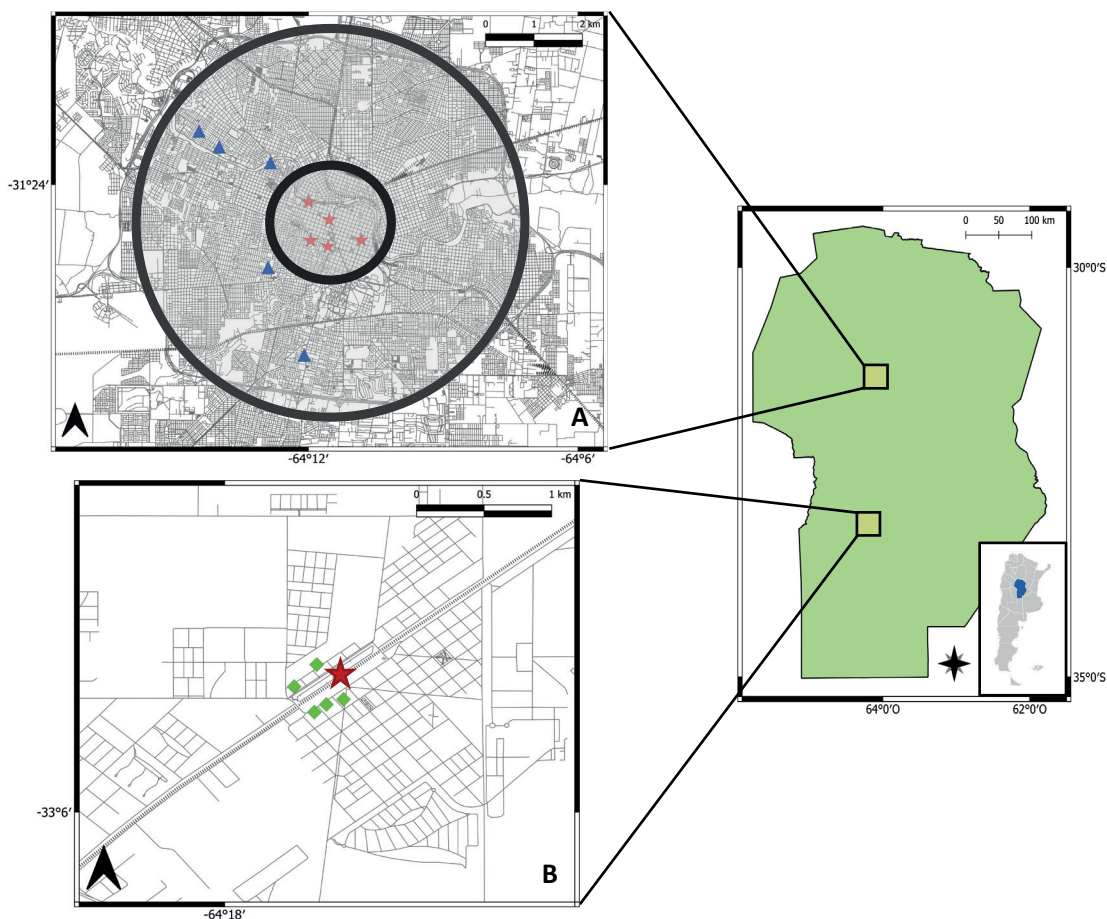
The sampling sites were in two study areas within the Córdoba province (Argentina): Córdoba city and Las Higueras. Córdoba city, the second largest city in Argentina, is situated in the central part of the country (31° 24' S, 64° 11' W, ~ 400 m above sea level), with a population of nearly 1.6 million people (INDEC 2022). Its concave topography restricts air circulation, resulting in frequent thermal inversions

during cold periods (Olcese and Toselli 2002). The climate of the region is characterized as sub-humid, with an average annual rainfall of 790 mm, primarily occurring in the southern summer months (January to March). The mean annual temperature is 17.4 °C, and prevailing winds typically originate from the northeast (NE), south (S), and southeast (SE) directions (SMN 2023). In Córdoba city, vehicular traffic constitutes the primary source of air pollution, although there is also some contribution from the metallurgical and mechanical industries (Mateos et al. 2019). During winter days, PM<sub>2.5</sub> concentrations often exceed the air quality guideline values set by the Córdoba Government (35 µg/m<sup>3</sup> 24-h mean) around 2.8 times (GC 2017, Tavera Busso et al. 2018). The city was divided into two sampling zones: the urban zone, represented by the downtown area characterized by limited vegetation and high vehicular traffic, and the suburban zone, characterized by low population density, abundant natural vegetation, and limited vehicular traffic (**Fig. 1**).

Las Higueras (33°5'32 S, 64°17'20 W) is a small town situated in the southern part of Córdoba province. Located in the heart of an expansive agricultural region, the town has a population of 9867 inhabitants (INDEC 2022). Due to its rural setting, this site was designated as a rural sampling zone. The primary economic activities in the area turn around extensive agriculture and livestock farming, with a few agro-based industries also present. The climate of the region is characterized as sub-humid, with warm and humid summers and short, cold, and dry winters. The annual mean temperature is 16.8 °C, and prevailing winds predominantly originate from the north and west between August and December. The mean annual rainfall amounts to 809 mm, with a concentration during summer (**Fig. 1**; SMN 2023).

### Sampling method

Sampling was conducted during both winter (from 5/6/2019 to 8/6/2019) and summer (from 10/21/2019 to 12/30/2019) seasons in all households while inhabitants were present and engaged in their regular activities. A random selection of households was performed within each study area from those that agreed to participate in the study. Five homes were selected within each study zone, resulting in a total of 15 households being sampled. Only households with non-smoking occupants were selected for the study. In each household, a sampler was installed in the living room, positioned approximately 1.5 m above the floor (at breathing zone level), and situated



**Fig. 1.** Study areas and sampling sites in Córdoba. **A:** Córdoba city (inner circle: urban area; outer circle: suburban area); **B:** Las Higueras, rural area (red star: grain elevator facility).

at least 1 m away from doors, windows, and other openings. The living room was chosen as a representative location for measuring the  $PM_{2.5}$  concentration throughout the entire house. Active sampling was carried out for one month using a Harvard impactor connected to an air pump operating at a constant flow rate ( $12.5 \pm 2$  L/min).  $PM_{2.5}$  was collected on 47 mm diameter polytetrafluoroethylene (Teflon<sup>®</sup>) filters with a pore size of 1.0- $\mu$ m (Zefluor, Millipore; Oeder et al. 2012), previously oven-dried at 65 °C for at least 72 h ( $n = 8$  per house). The filters were replaced every seven days to ensure enough PM was sampled to quantify the analyzed compounds. Thus, a total of 120 samples were collected (40 samples per sampling site, considering that there are three sampling sites, or 60 samples per sampling season, considering that samples were collected during two seasons).

In addition, a survey was conducted in each home to gather information on potential indoor sources of  $PM_{2.5}$ . The survey included questions regarding the

number and ages of occupants, the type of fuel used for cooking, the type of heating system, and the use of aerosols, insecticides, or air fresheners. Additionally, the height of the house from the ground and the distance to the main source of particle emissions (such as a street, cultivated area, or green space) were recorded (Appendix A, Supplemental Material – SM).

#### **$PM_{2.5}$ mass concentration**

The teflon filters were weighed before and after sampling using an electronic microbalance (Precisa XR205SM-DR, Dietikon, Switzerland) to determine the gravimetric PM mass (Al-Jeelani 2017). The PM concentration was subsequently calculated by dividing the mass by the sampled air volume, expressed in  $\mu$ g/ $m^3$  (Tavera Busso et al. 2017).

#### **$PM_{2.5}$ elemental composition**

Each teflon filter was placed in a closed reflux tube with 5 mL of 65% m/v nitric acid ( $HNO_3$ ; Emsure,

Merck). The tubes were hermetically sealed, and the filters were left for at least two weeks, or until no nitrogen dioxide (NO<sub>2</sub>) release was observed. To accelerate digestion, the tubes were heated on a hot plate at 130 ± 10 °C and the accumulated gas was periodically purged. After digestion, the liquid content of each tube was quantitatively transferred to a 25 mL flask and rinsed with MilliQ water. The sample was then filtered through a 0.22 µm pore size Teflon (Millipore, Merck). Finally, 1.5 mL of each sample was collected and utilized to determine the elements of interest (Tavera Busso et al. 2017).

The concentration of 21 elements (As, B, Ba, Be, Bi, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Sr, Tl, V and Zn) was determined by inductively coupled plasma mass spectroscopy (ICP-MS; Agilent 7500cx). Three calibration curves of high (200 ppb), medium (100 ppb) and low (1 ppb) concentration were generated using standards (ICP Multielement Standard VI, Certipur, Merck). In all cases, the R<sup>2</sup> values for all elements exceeded 0.9983 (p < 0.005), indicating a strong correlation. Dilutions, when necessary, were carried out using MilliQ water. Sample blanks were prepared containing only 5 mL of 65% m/v HNO<sub>3</sub> (Emsure, Merck; Tavera Busso et al. 2017). Additionally, the limit of detection (LOD) and limit of quantification (LOQ) values were determined (table B1, Appendix B, SM).

### Enrichment factor (EF)

The analysis of the EF shows the degree of enrichment of a given element compared to its abundance in nature. This method is commonly used as a first approach to estimate the origin, whether natural or anthropogenic, of an element (Gao et al. 1992). Additionally, its application has expanded to include the analysis of emission sources of particles in indoor environments in order to estimate their origin. In this study, the EF was calculated using the following equation (1):

$$EF_i = (i/j)_{\text{air}} / (i/j)_{\text{crust}} \quad (1)$$

where EF<sub>i</sub> is the enrichment factor of each element *i*, *j* is the reference element of the earth's crust material, (i/j)<sub>air</sub> is the coefficient of element *i* in element *j* in the sample, and (i/j)<sub>crust</sub> is the coefficient of element *i* in element *j* of the crust (Chao and Wong 2002). An EF < 10 indicates a natural origin, whereas an EF > 10 indicates some anthropogenic influence (Vasconcellos et al. 2011).

Sr was used as a reference element (Mirzaei Aminiyani et al. 2018). Concentrations of Na, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Ba and Pb in the earth's

crust were obtained from total metal determinations for the Córdoba city soil (Bermudez 2011). For the remaining elements, available information on average crustal composition on a regional and global scale was combined (Rudnick and Gao 2005, Kabata-Pendias and Mukherjee 2007). The values of element concentrations in the earth's crust used for calculations are summarized in Supplementary Material (Appendix C, SM).

### Health risk assessment

Equations presented by the United States Environmental Protection Agency (USEPA) were used for health risk assessment (USEPA 2011). Briefly, the chemical risks were calculated considering the average daily dose (ADD) and the slope factor (SF). The equations used for calculations, the values of the cancer potency factor for each metal, and the parameters employed for risk exposure assessment, are summarized in Supplemental Material (Appendix D, SM).

Regarding health risk assessment, a risk of 10<sup>6</sup> (when the risk of developing cancer over a human lifetime is 1 in 1 000 000) represents a negligible cancer risk, a value between 10<sup>6</sup> and 10<sup>4</sup> is defined as a potential cancer risk (USEPA 2004), while a risk that exceeds 10<sup>4</sup> (when the risk of developing cancer over a human lifetime is 1 in 10 000) is a significant cancer risk (Maharjan et al. 2022).

### Statistical analysis

To analyze PM<sub>2.5</sub> concentration, a one-way analysis of variance (ANOVA) was performed, with a linear mixed model, random effects, nested factors, and a VarIdent-type heteroscedasticity modeling. For the analysis of elemental composition, an ANOVA was performed considering the sampling periods and zones. In addition, means were compared using a Fisher's least significance difference (LCD-Fisher) test with p < 0.05 (Di Rienzo et al. 2020). The association between indoor PM<sub>2.5</sub> elemental composition and the different land uses was assessed using a principal component analysis (PCA), considering sampling zones as classification criterion. The Info-Stat v.2020/e software, coupled to the R 3.6.3 environment, was used to perform all statistical analyses.

## RESULTS

### PM<sub>2.5</sub> concentration

The following results are based on the statistical tests described in the Statistical analysis section.

**Figure 2** shows  $PM_{2.5}$  concentration ( $\mu\text{g}/\text{m}^3$ ) for each sampling period and zone, respectively. Although there were no statistical differences, a small increase in  $PM_{2.5}$  was observed during the summer. Notably, the rural zone exhibited  $PM_{2.5}$  levels more than twice as high as those in the urban and suburban zones. The Supplemental Material, table E1 (Appendix E), shows detailed results of  $PM_{2.5}$  concentrations for each sampling period and zone, categorized by household characteristics. Overall, higher  $PM_{2.5}$  concentrations were observed in ground-level homes compared to apartments. In addition, homes located at longer distances from green areas generally had higher  $PM_{2.5}$  concentrations. Furthermore, homes with pets generally showed higher  $PM_{2.5}$  concentrations. Smaller differences were observed between homes with and without children, occasional smokers, air conditioners, exhaust fans, air fresheners, or aerosols. However, it is important to note that despite selecting only non-smoking homes, some households reported having visitors who smoked inside the house during the sampling period.

### Elemental composition and EF

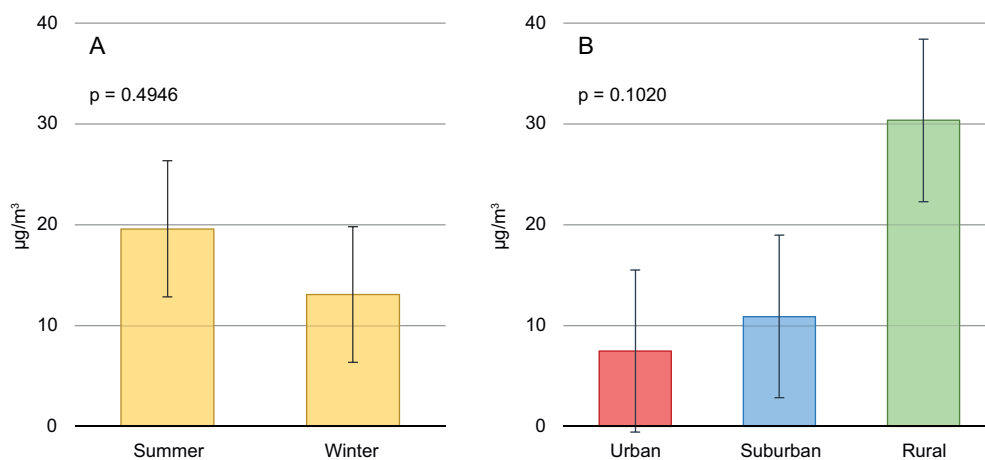
The results presented below are supported by the statistical tests detailed in the Statistical analysis section. In urban homes, the highest concentration of As, Cd, Cr, Mo and Zn were recorded, whereas the highest concentrations of B, Bi, Co, K, Mn, Na, Pb, Sr, V, and Zn were found in the suburban zone, and the highest concentrations of B, Ba, Be, Fe, Mg, Ni, and Tl were observed in the rural zone. Throughout all zones, the concentrations of most elements were

higher in winter compared to summer, respectively (**Table I**).

Regarding the PCA, two components were retained, explaining 99.7% of the total variance of the data. The first component (PC 1: 84.7%) included high loadings of B, Ba, Be, Bi, Cu, Fe, K, Mg, Mn, Na, Ni, Sr, Tl, V, and Zn. These elements are typically associated with soil resuspension and natural sources; however, some of them (e.g., Cu, Zn, B, and Ni) may also originate from anthropogenic activities, particularly in urban environments. Notably, Cu and Zn exhibited a negative correlation with the other elements in PC 1, suggesting a distinct behavior possibly linked to vehicular and industrial emissions. This is consistent with previous studies identifying Cu and Zn as markers of anthropogenic sources such as traffic-related emissions and wear of mechanical components (Bermudez et al. 2012, Mateos et al. 2018).

The second component (PC 2: 15.3%) was represented by As, Cd, Co, Cr, Mo, and Pb, all of which are well-known anthropogenic elements, often related to industrial processes and fuel combustion. These components reflect the complex mixture of emission sources impacting indoor environments across the studied zones (**Table II**; Bermudez et al. 2012, Pan et al. 2015).

The contribution of elements in each sampling zone is presented in **figure 3**. Each zone was characterized by a distinct group of elements: PC1 was more strongly associated with the rural zone, while PC2 contributed to the differentiation of suburban and urban zones, where anthropogenic emissions are expected to be more prevalent.



**Fig. 2.**  $PM_{2.5}$  concentration ( $\mu\text{g}/\text{m}^3$ )  $\pm$  standard deviation in each sampling period (A) and in each sampling zone (B), respectively.

**TABLE I.** ELEMENTAL COMPOSITION OF PM<sub>2.5</sub> IN SAMPLING ZONES DURING SUMMER AND WINTER.

Elemental composition (ng/m <sup>3</sup> ) ± standard deviation	Urban		Suburban		Rural	
	Summer	Winter	Summer	Winter	Summer	Winter
As	0.41±0.06	0.52±0.14	0.30±0.05	0.30±0.08	0.06±0.02	0.07±0.02
	ns		ns		ns	
B	0.15±0.02	0.09±0.03	0.95±0.21	1.57±0.35	0.34±0.28	1.57±0.31
	ns		ns		**	
Ba	0.83±0.11	1.85±0.27	2.16±0.29	3.45±0.43	2.77±0.71	4.18±0.72
	**		*		ns	
Be	0.02±0.01	0.03±0.01	0.03±0.01	0.05±0.01	0.06±0.01	0.06±0.01
	ns		ns		ns	
Bi	0.25±0.06	0.57±0.08	0.43±0.09	0.63±0.15	0.63±0.12	0.55±0.13
	**		ns		ns	
Cd	0.10±0.02	0.15±0.03	0.07±0.01	0.14±0.02	0.07±0.02	0.11±0.02
	ns		**		ns	
Co	0.004±0.01	0.004±0.01	0.005±0.01	0.03±0.01	0.01±0.01	0.03±0.01
	ns		***		ns	
Cr	0.58±0.10	1.02±0.23	0.52±0.06	0.99±0.10	0.66±0.11	0.71±0.11
	ns		***		ns	
Cu	0.96±0.16	2.26±0.44	1.61±0.29	1.05±0.53	2.82±0.36	2.75±0.36
	**		ns		ns	
Fe	26.18±2.71	25.30±4.16	89.69±12.38	124.61±18.42	163.13±33.48	204.86±34.67
	ns		ns		ns	
K	30.99±5.63	100.44±16.60	88.03±15.29	218.12±25.33	70.73±23.69	140.29±25.16
	**		***		ns	
Mg	12.23±2.93	18.98±4.27	35.83±6.95	59.03±10.68	66.31±19.66	107.61±20.49
	ns		ns		ns	
Mn	0.99±0.14	1.96±0.24	3.01±0.42	4.00±0.63	1.57±0.48	3.14±0.53
	**		ns		*	
Mo	0.13±0.01	0.14±0.014	0.10±0.01	0.11±0.02	0.08±0.02	0.11±0.02
	ns		ns		ns	
Na	52.76±8.37	61.43±12.58	62.58±10.79	121.21±16.61	49.20±14.09	95.71±15.37
	ns		**		*	
Ni	0.10±0.01	0.24±0.032	0.18±0.03	0.33±0.06	0.44±0.07	0.49±0.07
	***		*		ns	
Pb	2.56±0.28	2.96±0.39	1.91±0.25	3.36±0.40	1.73±0.38	2.31±0.39
	ns		**		ns	
Sr	0.39±0.05	0.66±0.07	0.76±0.10	0.99±0.16	0.54±0.16	0.97±0.18
	**		ns		ns	
Tl	0.0012±0.01	0.027±0.01	0.04±0.01	0.06±0.01	0.08±0.01	0.08±0.01
	***		*		ns	
V	0.09±0.01	0.10±0.02	0.16±0.03	0.27±0.04	0.10±0.03	0.21±0.04
	ns		*		*	
Zn	13.71±4.09	20.86±6.85	12.58±3.06	21.25±5.04	12.08±1.75	14.67±1.77
	ns		ns		ns	

\* denotes statistical significance at  $p < 0.05$ ; \*\* denotes statistical significance at  $p < 0.01$ , \*\*\* denotes statistical significance at  $p < 0.001$ , "ns" denotes non-statistical differences.

To complement this analysis, the EF was also calculated, helping to distinguish between natural and anthropogenic sources based on the degree of

enrichment relative to crustal abundances. EF results revealed that elements such as B, Tl, Cr, As, Mo, Pb, Zn, Cu, Cd, and Bi exhibited significant enrichment,

**TABLE II.** EIGENVECTORS VALUES FOR THE ELEMENTAL COMPOSITION OF PM<sub>2.5</sub> OBTAINED WITH PRINCIPAL COMPONENT ANALYSIS (PCA). THE ELEMENT VALUES THAT HAVE MORE WEIGHT FOR EACH EIGENVECTOR ARE HIGHLIGHTED WITH ASTERISKS.

Variable	PC1	PC2
As	-0.17	-0.38*
B	0.24*	-0.06
Ba	0.24*	-0.04
Be	0.24*	0.00
Bi	0.23*	-0.16
Cd	0.21	0.24*
Co	-0.11	0.49*
Cr	-0.18	0.36*
Cu	-0.24*	0.06
Fe	0.24*	0.03
K	0.22*	-0.2
Mg	0.24*	0.07
Mn	0.24*	-0.03
Mo	-0.21	0.25*
Na	0.24*	0.07
Ni	0.23*	0.14
Pb	-0.13	-0.47*
Sr	0.23*	0.09
Tl	0.24*	-0.03
V	0.24*	0.03
Zn	-0.23*	-0.15

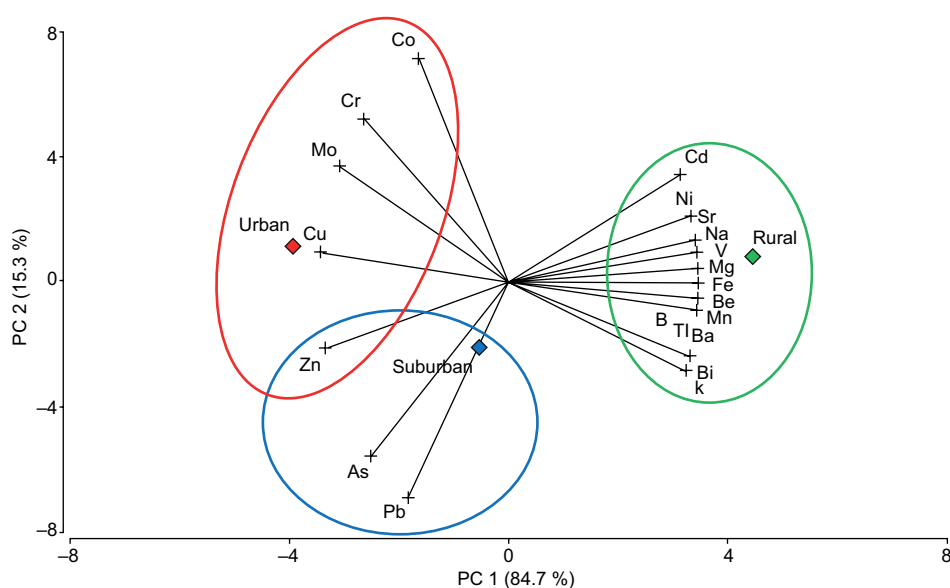
suggesting a predominant anthropogenic origin—especially in urban areas—while elements like Mg, Fe, K, V, Na, Mn, and Ba showed values consistent with a natural origin. Additionally, some elements such as Be, Co, and Ni displayed intermediate behavior, indicating potential contributions from both natural and anthropogenic sources depending on the zone (**Fig. 4**).

Overall, the combined use of PCA and EF analyses provided a more comprehensive understanding of the potential sources of the elements identified in indoor environments. It is important to note that some elements may have multiple origins, and the interpretation of their sources must consider both the statistical associations and the geochemical context. The integration of both approaches allowed for a more nuanced source apportionment.

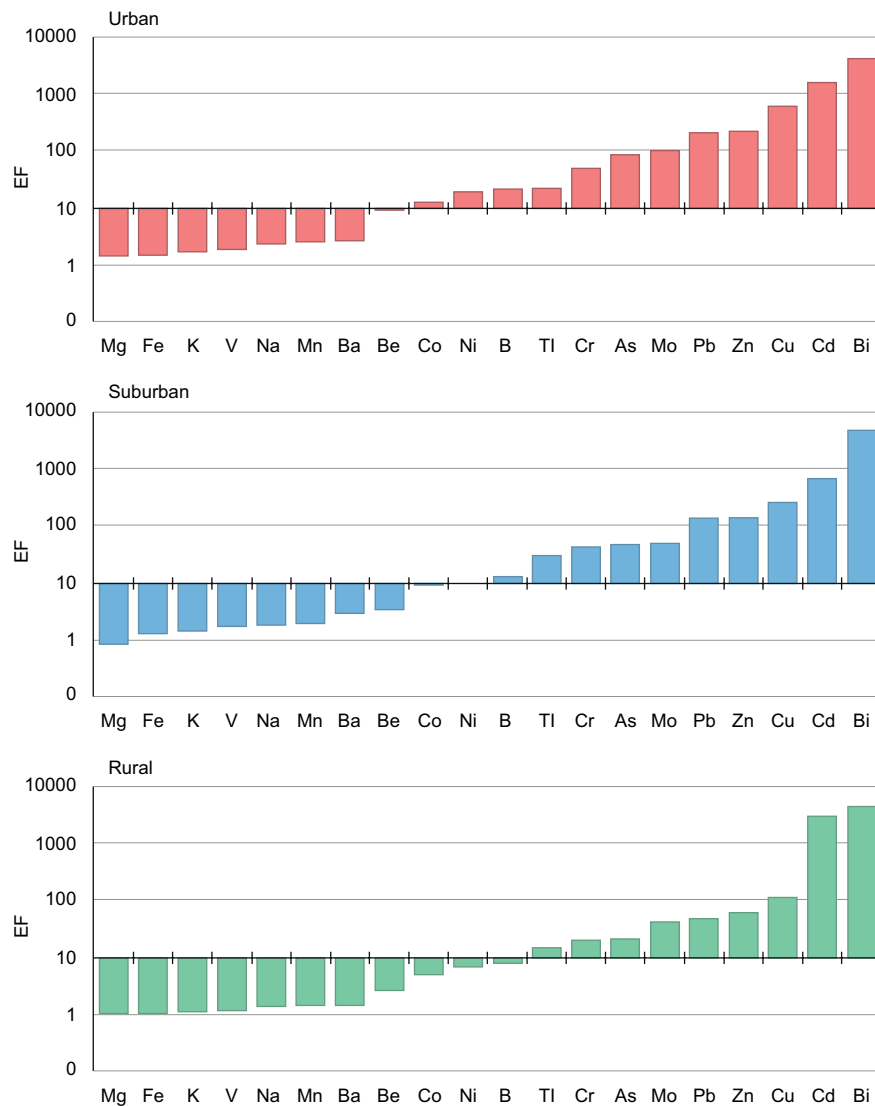
### Health risk assessment

**Table III** shows the mean cancer risk resulting from exposure to metals determined in PM<sub>2.5</sub>, for each analyzed sampling zone and period, along with the percentage contribution to total risk by zone and season. The carcinogenic risk corresponding to different age groups is presented in **table IV**.

We found that As is the element that contributes most to the total risk, both by study area and by season analyzed. Furthermore, as expected, the total



**Fig. 3.** Associations between sampling zones and PM<sub>2.5</sub> elemental composition concentrations. PC 1: Principal Component 1; PC 2: Principal Component 2.



**Fig. 4.** Enrichment factor (EF) obtained for the elemental composition of PM<sub>2.5</sub> for urban, suburban, and rural areas.

cancer risk from exposure to the elements determined increases with age.

## DISCUSSION

### PM<sub>2.5</sub> concentration

The seasonal and spatial variations in PM<sub>2.5</sub> concentrations are shown in **figure 2** and are discussed in detail below. The PM<sub>2.5</sub> concentration was higher in the rural area (**Fig. 2.A**), which can be attributed to two main factors associated with land use. Firstly, agricultural practices generate airborne PM by increasing the dispersion of soil particles. These

particles can be easily resuspended by wind, and subsequently find their way into homes through open windows and gaps or even carried on the clothing of residents (Tong and Lam 2000, Hassanvand et al. 2015, Li et al. 2017).

On the other hand, there is a grain elevator facility (**Fig. 1**) situated in the rural area under study. Such establishments are facilities where grains (in this case, soybeans, wheat, and corn) are received, stored, and subsequently distributed (Potapova et al. 2020). Grain elevators are known to be significant sources of PM, which is one of the primary air pollutants associated with these facilities (Mclouth and Paulus 1961, Boac et al. 2009, Pattey and Qiu

**TABLE III.** MEAN CANCER RISK ( $R_i$ ) FROM EXPOSURE TO METALS DETERMINED IN  $PM_{2.5}$ , FOR EACH SAMPLING ZONE AND PERIOD ANALYZED, AND PERCENTAGE (%) CONTRIBUTION TO TOTAL RISK BY ZONE AND SEASON.

Metal		Urban		Suburban		Rural	
		Summer	Winter	Summer	Winter	Summer	Winter
As	Ri	$1.37 \cdot 10^{-6}$	$7.56 \cdot 10^{-7}$	$1.43 \cdot 10^{-6}$	$5.09 \cdot 10^{-7}$	$9.49 \cdot 10^{-7}$	$4.80 \cdot 10^{-7}$
	%	60.62	61.97	86.67	56.56	82.52	53.39
Be	Ri	$2.12 \cdot 10^{-8}$	$2.49 \cdot 10^{-8}$	$2.48 \cdot 10^{-8}$	$2.51 \cdot 10^{-8}$	$2.34 \cdot 10^{-8}$	$2.97 \cdot 10^{-8}$
	%	0.94	2.04	1.50	2.79	2.03	3.30
Cd	Ri	$9.90 \cdot 10^{-8}$	$1.17 \cdot 10^{-7}$	$1.10 \cdot 10^{-7}$	$6.08 \cdot 10^{-8}$	$1.03 \cdot 10^{-7}$	$6.75 \cdot 10^{-8}$
	%	4.38	9.59	6.67	6.76	8.96	7.51
Co	Ri	$7.37 \cdot 10^{-7}$	$2.89 \cdot 10^{-7}$	$6.04 \cdot 10^{-8}$	$2.80 \cdot 10^{-7}$	$4.64 \cdot 10^{-8}$	$2.90 \cdot 10^{-7}$
	%	32.61	23.69	3.66	31.11	4.03	32.26
Ni	Ri	$1.76 \cdot 10^{-8}$	$2.18 \cdot 10^{-8}$	$1.35 \cdot 10^{-8}$	$1.63 \cdot 10^{-8}$	$1.39 \cdot 10^{-8}$	$2.21 \cdot 10^{-8}$
	%	0.78	1.79	0.82	1.81	1.21	2.46
Pb	Ri	$1.06 \cdot 10^{-8}$	$1.34 \cdot 10^{-8}$	$1.23 \cdot 10^{-8}$	$8.36 \cdot 10^{-9}$	$1.06 \cdot 10^{-8}$	$9.23 \cdot 10^{-9}$
	%	0.47	1.10	0.75	0.93	0.92	1.03
$\Sigma$ Risks		$2.26 \cdot 10^{-6}$	$1.22 \cdot 10^{-6}$	$1.65 \cdot 10^{-6}$	$9.00 \cdot 10^{-7}$	$1.15 \cdot 10^{-6}$	$10^{-7}$

**TABLE IV.** TOTAL CANCER RISK FROM EXPOSURE TO METALS DETERMINED IN  $PM_{2.5}$  IN DIFFERENT AGE GROUPS.

Age groups (years old)	Cancer risk
< 1	$4.43 \cdot 10^{-9}$
1 to < 6	$2.72 \cdot 10^{-8}$
6 to < 11	$5.94 \cdot 10^{-8}$
11 to < 16	$9.35 \cdot 10^{-8}$
16 to < 21	$1.21 \cdot 10^{-7}$
21 to < 61	$3.05 \cdot 10^{-7}$
61 to < 71	$6.05 \cdot 10^{-7}$
71 to < 81	$7.02 \cdot 10^{-7}$
$\geq 81$	$7.94 \cdot 10^{-7}$

2012). Previous studies have shown a significant contribution of both fine and coarse PM from outdoor sources to indoor environments, including homes, offices, schools, restaurants, etc., located in rural and urban zones (Thatcher 1995, Jones et al. 2000, Chao and Wong 2002, Madureira et al. 2012, Qian et al. 2014, Morawska et al. 2017). It should be noted that indoor  $PM_{2.5}$  levels exhibit high variability, as they are strongly influenced by outdoor conditions,

making it challenging to establishing a regular pattern (Fernández-Agüera et al. 2019). In addition, the lower concentrations of  $PM_{2.5}$  observed in homes situated in proximity to green areas can be attributed to the filtering effects of foliage, as reported by Kocić et al. (2014). Furthermore, consistent with the findings of Madureira et al. (2020) and Jorquera et al. (2018), higher PM concentrations were observed in homes with pets (**Table E1, Appendix E, SM**), suggesting that pets may contribute to PM resuspension. The results obtained here were compared with studies conducted outdoors in Córdoba city and indoor studies from other cities (**Table F1, Appendix F, SM**). It is noteworthy that all values are within the same order of magnitude, although some variations are observed due to the distinct characteristics of each environment. Specifically, the comparison of the measured  $PM_{2.5}$  values in the present study with those presented by López et al. (2011) and Tavera Busso et al. (2017) for outdoor environments in Córdoba city reveals that indoor concentrations are up to an order of magnitude lower. Moreover,  $PM_{2.5}$  levels were found to be lower in urban and suburban areas compared to rural areas, likely due to reduced ventilation in urbanized regions where windows are not opened as frequently resulting

in decreased outdoor PM contribution. Additionally, it is necessary to consider that most of the homes in the urban area were in high-rise buildings where the contribution of PM is significantly lower than in ground-level homes. The vertical distribution of PM is influenced by both the meteorological conditions of the sampling area and the characteristics of the house. Previous studies reported a decrease in PM pollutants concentration with increasing altitude, attributed to the higher concentration of vehicular emissions at ground level (Li et al. 2005, Menichini et al. 2007, Tao et al. 2007, Zhang et al. 2021).

In all sampling zones, the highest PM<sub>2.5</sub> levels were found in samples collected during the summer (**Fig. 2.B**). This result agrees with findings reported for homes in Lodi, Italy (Cattaneo et al. 2016). The differences can only be attributed to individual characteristics of the sampling environments (Chao and Wong 2002). Hence, PM values may be influenced not only by the outdoor PM levels but also by specific characteristics of indoor environments, such as the number of occupants in each room of the home, cooking and cleaning practices, all of which contribute to the generation and resuspension of particles (Escobedo et al. 2014).

In previous studies conducted in Córdoba city, higher outdoor PM concentrations were reported during winter compared to summer (Amarillo and Carreras 2016), which disagrees with our observations. This difference could be attributed to the reduced ventilation in houses during winter, leading to a limited entry of outdoor PM (Perrino et al. 2016). Some authors have estimated that PM infiltration in naturally ventilated homes contributes up to 70% to internal particulate levels (Fernández-Agüera et al. 2019).

Based on the effects of PM on human health, the World Health Organization (WHO) has established maximum values of 15 µg/m<sup>3</sup> 24-h mean and 5 µg/m<sup>3</sup> annual mean PM<sub>2.5</sub> in outdoor environments (WHO 2021). These guidelines should also be applied to indoor environments, except for work environments (WHO 2010). Particularly, Córdoba province established a regional maximum value of 35 µg/m<sup>3</sup> 24-h mean (GC 2017). On average, PM<sub>2.5</sub> concentrations found in homes in Córdoba city did not exceed the values of these regulations, both for the urban and suburban zones, whereas in Las Higueras this limit was exceeded in summer only (**Fig. 2**).

### Elemental composition and EF

PM elemental composition can be divided into two major groups: earth-crust elements derived from soil (natural sources) and introduced elements

derived from human activities (anthropogenic sources; Zhang et al. 2021). Also, there is a third possibility, which is that there are elements that combine natural and anthropogenic sources. In line with this, the interpretation of the elemental sources in PM<sub>2.5</sub> was based on an integrative analysis that combines the results from the PCA, EF and relevant literature. This approach allows us to identify natural and anthropogenic sources, as well as potential mixed origins or indirect processes –such as the resuspension of previously deposited particles– particularly in environments influenced by both indoor and outdoor emissions.

Fe is the most important metal and one of the major constituents of the earth's lithosphere. Consequently, its soil concentration is typically high (Kabata-Pendias and Mukherjee 2007). Along with Ni, Mg, K, Na and V, this element was found in elevated concentrations in the rural zone, suggesting that their main source of emission is soil resuspension. This is related to the high proportion of exposed soil in rural zones, favoring the resuspension of particles by wind. The calculated EF for these elements supports this hypothesis (**Fig. 4**).

Besides being a constituent element of the soil, Ni is frequently used in industry (McGranahan and Murray 2012, Srithawirat et al. 2016). Similarly, Mn finds various applications, such as in the production of steel and nonferrous alloys, as well as in the manufacturing of products like porcelains, ceramics, dyes, fungicides, disinfectants, and food additives (Satsangi et al. 2014). The EF value suggests a natural origin for all the studied zones. In indoor environments, trace amounts of Mn were attributed to dust resuspension from human or pet movement inside homes (Chao and Wong 2002). Furthermore, the EF values for Ba and Be suggest that soil resuspension is their primary source of origin (ATSDR 2007, 2023).

Regarding Co and B, they may have diverse origins. Co is used in the manufacturing of colored glass, ceramics, paints, batteries, and metal alloys, as well as in the use of phosphate fertilizers, incinerators, and fossil fuels (Kabata-Pendias and Mukherjee 2007). However, its EF values suggest a natural origin for the suburban and rural areas, indicating a potential infiltration of resuspended PM from outdoor sources. Similarly, the highest Co levels found in summer suggest that this element likely originates from external emission sources. It is worth noting that natural processes such as resuspension of soil or dust can act as secondary emission pathways for anthropogenic elements, especially in areas with a history of contamination or long-term atmospheric

deposition. On the other hand, B could be released by glass and ceramic articles in indoor environments (Kabata-Pendias and Mukherjee 2007). However, the EF results indicate an anthropogenic origin in urban and suburban zones, likely due to a simultaneous contribution from natural sources (such as dust resuspension) and human activities. In contrast, in the rural zone, B is likely of natural origin.

The principal atmospheric emission sources of Cd, Tl and Cu are industrial activities, like fossil coal and fuel combustion, non-ferrous metal production, waste incineration, iron and steel production, cement production, industries manufacturing batteries and photovoltaic devices, pigments, paints, coatings, and plastic stabilizers manufacturing units (ATSDR 1992, Chao and Wong 2002, Kabata-Pendias and Mukherjee 2007, ATSDR 2012, Bermudez et al. 2012, McGranahan and Murray 2012). Cu can also originate from the use and abrasion of kitchen utensils, ceramic products, and electric appliances equipped with brush motors (Chao and Wong 2002, Jellesen et al. 2006, Taner et al. 2013, Satsangi et al. 2014, Tofful et al. 2021). However, forest fires and soil and rock erosion by wind can also contribute to its levels in the air (Alloway and Steinnes 1999).

Finally, the EF values of Cr, As, Zn, and Pb suggest mainly anthropogenic origins, such as combustion and solid waste incineration, cement industries and energy generation, smelting and traffic emissions, usage and abrasion of kitchen utensils, meat and oil cooking processes, paints, and because they are also used in various industrial processes like tanning of animal hides, production of alloys, electroplating and as a water corrosion inhibitor (Chao and Wong 2002, ATSDR 2005, Satsangi et al. 2014, Sah et al. 2017, Niu et al. 2021). Pb was traditionally considered as a marker of vehicle emissions (Cai et al. 2019) since it was used as an additive in fossil fuels. Although Pb-added fuel has no longer been used in Argentina since 1999, it is still detected in trace levels in urban environments due to the contribution of soil resuspension and from lubricating oil and by-products of engine wear that enter the combustion chamber (Giordano et al. 2010). In this sense, although resuspension is a natural process, it may contribute to the re-emission of anthropogenic pollutants previously deposited in the environment, serving as a secondary source. Chattopadhyay et al. (2003) found that, although air Pb levels have dramatically decreased over the last decade in Sydney (Australia), Pb concentrations in household dust remain unchanged, possibly due to the accumulation of lead from old paints and almost 80 years of leaded gasoline use.

Specifically in Argentina, As is a characteristic contaminant of soils and groundwater in the Pampas plains (Bermudez 2011). Until the 1970s, it was also used in the large-scale production of pesticides, and although its use has decreased in recent years, it is still employed for wood preservation, photoelectric elements, and in acid Pb batteries (Taner et al. 2013). Therefore, the EF values could be affected by the high levels of As present in the soils of the analyzed zones.

The presence of Mo and Bi in the air has been scarcely studied. It is known that Mo is released into the atmosphere through coal incineration, biomass burning, and is also used in the production of metal alloys, in the electronics industry, and as a chemical catalyst (ATSDR 2020). On the other hand, Bi is emitted from metal mines, chemical or metallurgical plants, coal combustion and waste incineration (Kabata-Pendias and Mukherjee 2007). EF values suggest an anthropogenic origin of Mo in all the analyzed zones, while Bi shows a mixed emission source.

In general, PM<sub>2.5</sub> collected in urban and suburban zones showed a higher abundance of elements originating from anthropogenic sources (e.g., Mo, Cr, Zn, As). In contrast, samples collected in rural zones contained elements released from both natural and anthropogenic sources (e.g., Cd, Ni, Fe, Tl, K). Additionally, certain elements (Mn, Ba, Cd, B, Tl, Zn) exhibited higher concentrations during the winter, suggesting a potential contribution from an unidentified internal emission source. Regarding the rural zone, it is possible that there is an anthropogenic contribution from fertilizer use associated with soil particles, and this cannot be ruled out (Kabata-Pendias and Mukherjee 2007, Bermudez et al. 2012). This hypothesis is supported by the enrichment of Be and Cd observed in PM<sub>2.5</sub> samples collected in this area. Further investigations are required to better understand and identify the specific sources and dynamics of these elements in the different zones under study.

### Health risk assessment

Our findings indicate that the cancer risks associated with exposure to heavy metals in indoor environments of Córdoba city are a matter of concern, as it is likely that one person or more per 1 000 000 may develop cancer in their lifetime, thereby potentially reducing the population's life expectancy. Nevertheless, these values were comparatively lower than those reported by Mateos et al. (2018), who conducted daily (24-hour) total suspended particles sampling to analyze cancer risk levels associated with metal inhalation in outdoor environments in Córdoba. This suggests that people are exposed to

lower levels of metals inside their homes compared to outdoor environments. In addition, they found higher risk values for Cr followed by Co, As and Ni, while we found higher risks for As, followed by Co and Cd. These differences suggest that, although outdoor PM infiltration influences indoor air quality, there are also internal emission sources that require further investigation. Understanding these internal sources is vital for effectively addressing and mitigating the health risks associated with exposure to heavy metals in indoor environments.

To the best of our knowledge, no studies have been conducted in Argentina investigating indoor residential environments like the present. However, our results indicate lower cancer risks compared to those reported by Colman Lerner et al. (2018), who analyzed cancer risks associated with metal inhalation in indoor air in industries from La Plata (Buenos Aires, Argentina). Generally, in indoor environments, the higher carcinogenic risk is due to anthropogenic activities rather than natural sources (Sah et al. 2017).

Despite Pb being the element with the highest contribution to the total concentration of elements in each zone and season (**Table I**), it contributed the least to the overall risk (**Table IV**). In contrast, As was the metal that most significantly contributed to the total risk in each zone and season analyzed. This difference is due to the relative weight of each metal in the risk calculation, with As being categorized as Group 1 according to IARC, indicating it is carcinogenic to humans, while Pb is classified as Group 2A, meaning it is possibly carcinogenic to humans (IARC 2014).

Regarding vulnerability based on age, we observed a higher risk in the elder group (**Table IV**), which aligns with the understanding that toxicological risk increases with exposure to pollutants (Mateos et al. 2018, Zhang et al. 2021). However, it is worth noting that none of the resulting risk values exceeded acceptable levels set by the USEPA ( $1 \times 10^{-4}$ ; USEPA 2011).

## CONCLUSIONS

The results obtained in the present study indicate that, although the levels of particulate matter (PM) found in indoor air in homes in Córdoba did not exceed the standard values established by governmental and international agencies, they are still detectable, suggesting a potential risk due to chronic exposure. This situation highlights the importance of considering PM exposure in indoor environments,

as even at low concentrations, PM has been shown to have adverse health effects (Adam et al. 2015). Typically, studies on the elemental composition of indoor PM focus on a limited number of elements, restricting comprehensive conclusions about all the elements to which individuals are exposed, given that numerous elements and their interactions can occur simultaneously. To the best of our knowledge, there are relatively few studies like the present one, where the composition of a high number of elements and their possible origin is simultaneously analyzed. Our findings suggest that indoor pollution has a combined origin, including both external sources such as vehicular traffic (Co, Cr, As, Zn, and Pb) and internal sources like cooking (Co and Cu), paints (Mn, Cr, and Pb), plastics (Zn), and electronic elements (Mo), among others.

While the carcinogenic risk values did not exceed the limits proposed by the USEPA in any case, the results provide a significant contribution to human health risk assessments, as PM exposure is identified as one of the main suspected causes of cancer. These values should be considered when calculating total exposure risks for humans, encompassing occupational, indoor, and outdoor environments.

Several limitations were encountered during this study. One notable limitation pertains to the sample size, which, although sufficient for the study's scope, was constrained to a specific geographic location (Córdoba province, Argentina), potentially limiting the broader applicability of the findings to a more diverse geography. Consequently, while the results offer preliminary insights into the possible emission sources of elements in indoor environments, these trends should be verified by extending this research to other areas or by increasing the number of samples collected. Moreover, the study's duration was relatively short, potentially overlooking long-term trends or fluctuations in the observed variables. It should also be noted that the calculated risk values might be underestimated, as only inhalation was considered for the analysis, and exposures through ingestion and dermal contact could increase the reported values. Additionally, possible synergies between compounds that may enhance carcinogenicity levels were not considered. Finally, this study did not account for non-carcinogenic risk indices, as well as concentrations of other airborne compounds (e.g., polycyclic aromatic hydrocarbons, black carbon, etc.), which may be equally or more hazardous to health than the elements presented here. Furthermore, since no outdoor PM measurements were conducted, the infiltration factor could not be estimated; future studies

should include both indoor and outdoor monitoring to allow for its calculation and a better understanding of particle dynamics in indoor environments.

Nevertheless, it is expected that the data obtained in the present study will contribute to estimating the exposure risk of inhabitants in urban and rural areas with similar geographical and climatological characteristics to those in Córdoba province.

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## SUPPLEMENTAL MATERIAL (SM)

### Appendix A: Survey for collecting the characteristics of the selected households

a. Environment:

- Home type: House (presence of backyard / presence of garage) / apartment (floor number: ..... / street view / balcony presence)
- Room in which the samplers are left: living room / living-dining room / kitchen-dining room / living-kitchen-dining room / other, which one?.....
- Main type of pollution emitting source: vehicular traffic / crops / industries
- Distance to the main source identified as a possible pollution emitting: ..... m
- Emission level of the pollution emitting source: low / medium / high
- Distance to green areas: ..... m

b. Home occupation:

- Number of occupants: .....
- Presence of children (0 - 5 years old): no / yes
- Presence of pets: no / yes (which one?.....; how many? .....
- Presence of occasional smokers: no / yes (How many people? .....; how many cigarettes per day? low < 10 per day / moderate = 11 to 19 per day / high > 20 per day)
- Presence of plants: no / some / various / several
- Main home activities: .....

c. Building characteristics:

- Type of fuel used for cooking: electric / natural gas / gas cylinder / firewood / other, which one? .....
- Type of heating: electric / natural gas / gas cylinder / firewood / kerosene / other, which one? .....
- Home structure: wood / concrete / Durlock / other, which one? .....
- Presence of air conditioning: no / yes (how many hours is it used x day? .....; what type of air is it? cold / hot-cold)
- Presence of extractor fan in the kitchen: no / yes
- Presence of window in the kitchen: no / yes
- Approximate age of the building: .....
- Type of housing floor: ceramic / tile / other, which one? .....
- Home surface: ..... m<sup>2</sup>
- Presence of garage / motorcycle storage inside the home.

d. Activities at home

- Main types of cooking: frying / baking / roasting / stewing / grilling / boiling / other, which ones? .....
- Hours per day in which the inhabitants are circulating in the home: ..... h
- Appliances: computer / printer / microwave / refrigerator / television / washing machine / hair dryer / other, which ones? .....
- Use of: essential oils / aromatic candles / incense / aromatic vaporization / other, which one? .....

.....  
How many hours per week? ..... h

e. Cleaning and ventilation

- Cleaning frequency: monthly / weekly / daily
- Ventilation frequency: how many hours per week? ..... h
- Windows orientation: .....
- Products used for cleaning: .....
- Use of aerosols: insecticide / air sanitizer / other, which ones? .....

**Appendix B: LOD and LOQ of elements****TABLE B1.** ANALYTICAL BLANKS (AB), FILTER BLANKS (FB), LIMITS OF DETECTION (LOD) AND OF QUANTIFICATION (LOQ) (ppb) OF THE MEASURED ELEMENTS.

Element	AB	FB	LOD	LOQ
As	0.8337	0.0075	0.0021	0.0829
B	6.7517	1.0335	0.2140	2.2508
Ba	0.1478	1.1174	0.0198	0.0493
Be	0.0830	0.1945	0.0037	0.0047
Bi	2.5500	2.6418	0.0126	0.1152
Cd	0.0146	0.1224	0.0045	0.0061
Co	3.9503	0.0111	0.0016	0.0545
Cr	0.3227	0.9246	0.0101	0.0575
Cu	11.4753	1.6898	0.0293	0.2603
Fe	3.4537	49.9581	0.3795	2.3873
K	258.2333	15.5300	1.9023	32.4550
Mg	75.0967	6.5150	0.2123	17.1775
Mn	4.5070	0.5468	0.0129	0.1240
Mo	0.4126	0.0421	0.0101	0.0310
Na	273.7000	47.3790	1.3427	27.3100
Ni	2.2713	0.0576	0.0077	0.1212
Pb	2.5893	1.5122	0.0599	0.1710
Sr	0.9361	0.2884	0.0113	0.0398
Tl	1.1149	0.2839	0.0202	0.0459
V	1.0409	0.0196	0.0016	0.0246
Zn	6.2723	17.1292	0.1406	1.0698

Ref.: Values correspond to the concentrations in the final digest solutions analyzed by ICP and represent the mean of replicate measurements.

**Appendix C: Enrichment Factor****TABLE C1.** ELEMENT CONCENTRATIONS IN EARTH'S CRUST. SOURCES: BERMUDEZ (2011), KABATA-PENDIAS AND MUKHERJEE (2007), AND RUDNICK AND GAO (2005).

Element	Earth's crust concentration (ppm)
As	7.4
B	17
Ba	518
Be	3.1
Bi	0.123
Cd	0.102
Co	11
Cr	41.1
Cu	7.94
Fe	33,000
K	28,650
Mg	13,510
Mn	395
Mo	1.4
Na	18,000
Ni	8.38
Pb	10
Sr	316
Tl	0.75
V	53
Zn	106

## Appendix D: Health Risk Assessment

**Equations used to calculate the Health Risk Assessment.** Source: USEPA (2011).

$$R = \text{LADD} \times \text{SF} \quad \text{(Equation D1)}$$

R: Health Risk Assessment.

LADD: average daily dose (mg/(kg day)).

SF: Slope factor (kg/day)/mg

$$\text{LADD} = \text{CC} \times \text{IF} \quad \text{(Equation D2)}$$

CC: concentration of each compound (mg/m<sup>3</sup>).

IF: intake factor (m<sup>3</sup>/(kg day))

$$\text{IF} = \text{IR}_a \quad \text{(Equation D3)}$$

BW: average body weight (kg).

IR<sub>a</sub>: breathing rate (m<sup>3</sup>/h).

EF: exposure frequency (number of exposures per year).

ED: duration of exposure (years).

ET: exposure time (number of hours per exposure).

AT: average time, obtained from the average exposure time over a lifetime of 70 years (28,489.5 days).

$$\text{SF} = \text{IUR} \times \text{BW} \times 1000 / \text{IR}_b \quad \text{(Equation D4)}$$

IUR: inhalation unit risks.

IR<sub>b</sub>: breathing rate (m<sup>3</sup>/day)

$$R_{\text{cum}} = \sum R_i \quad \text{(Equation D5)}$$

R<sub>cum</sub>: total carcinogenic risk for each sampling site and for each age group

R<sub>i</sub>: partial risks of the individual pollutants.

**TABLE D1.** CANCER POTENCY FACTOR EXPRESSED AS INHALATION UNIT RISK FOR METALS (IUR, µg/m<sup>3</sup>). SOURCE: USEPA (2011).

Metal	IUR
As	0.0043
Be	0.0024
Cd	0.0018
Co	0.009
Ni	0.00026
Pb	0.000012

**TABLE D2.** PARAMETERS EMPLOYED FOR RISK EXPOSURE ASSESSMENT. SOURCE: USEPA (2011).

Age groups (years old)	BW (kg)	IR <sub>a</sub> (m <sup>3</sup> /h)	IR <sub>b</sub> (m <sup>3</sup> /day)	EF (exposures per year)	ET (hours per exposure)
<1	7.7	0.23	5.4	365	18.47
1 - <6	16.2	0.39	9.44	365	16.66
6 - <11	31.8	0.5	12.0	365	14.87
11 - <16	56.8	0.63	15.2	365	14.82
16 - <21	71.6	0.68	16.3	365	13.87
21 - <61	80.0	0.66	15.8	365	15.8
61 - <71	80.0	0.59	14.2	365	19.58
71 - <81	80.0	0.54	12.9	365	19.58
≥81	80.0	0.51	12.2	365	19.58

**Appendix E: PM<sub>2.5</sub> and households' characteristics****TABLE E1.** PM<sub>2.5</sub> CONCENTRATION ( $\mu\text{g}/\text{m}^3$ ) IN EACH ZONE AND SAMPLING PERIOD RESPECTIVELY, ACCORDING TO THE CHARACTERISTICS OF EACH HOUSEHOLD.

Households' characteristics		Urban (n=20)		Suburban (n=20)		Rural (n=20)	
		Summer	Winter	Summer	Winter	Summer	Winter
House type	House	-	-	10.52±1.90	11.32±1.55	40.23±26.65	19.97±4.39
	Apartment	7.00±1.08	7.99±1.20	-	-	-	-
Distance to high traffic roads	Very close (0-130 m)	7.00±1.08	7.99±1.20	7.03±2.37	13.50±1.41	54.43±43.12	10.97±2.60
	Close (131-250 m)	-	-	1.21±0.52	1.57±0.57	17.16±4.73	33.46±8.45
	Away (251-375 m)	-	-	20.46±1.65	10.68±3.57	-	-
	Far away (376-500 m)	-	-	16.89±1.35	17.33±2.57	-	-
Distance to green areas	Very close (0-250 m)	7.00±1.08	7.99±1.20	12.85±2.61	9.86±2.36	-	-
	Close (251-500 m)	-	-	7.03±2.37	13.50±1.41	-	-
	Away (501-750 m)	-	-	-	-	3.96±1.67	5.61±1.73
	Far away (751-1000 m)	-	-	-	-	51.56±34.73	23.56±5.10
Height above ground	Low (0-10 m, or 0-3 floors)	7.79±2.02	9.09±2.27	10.52±1.90	11.32±1.55	40.23±26.65	19.97±4.39
	Medium (11-22 m, or 4-7 floors)	8.04±2.22	11.52±1.55	-	-	-	-
	High (23-33 m, or 8-10 floors)	5.55±1.27	3.91±1.43	-	-	-	-
N° of occupants	1 to 2	7.00±1.08	7.99±1.20	10.31±2.12	14.78±1.32	46.26±32.93	15.90±4.60
	3 to 4	-	-	10.83±3.72	6.13±2.40	14.59±3.06	36.24±8.72
Children under five years old	Yes	-	-	-	-	-	7.67±5.67
	No	7.00±1.08	7.99±1.20	10.52±1.90	11.32±1.55	14.95±2.94	23.04±5.07
Pets	Yes	7.99±2.18	5.92±2.52	12.51±2.07	10.81±1.89	62.18±46.31	21.18±4.73
	No	6.33±1.11	9.37±1.01	2.57±1.53	13.34±1.70	10.96±4.86	18.15±8.78
Occasional Smokers	Yes	7.79±2.02	9.09±2.27	20.46±1.65	10.68±3.57	54.43±43.12	10.97±2.60
	No	6.80±1.28	7.72±1.41	8.04±1.88	11.48±1.77	17.16±4.73	33.46±8.45
Type of fuel used for cooking	Natural Gas	7.00±1.08	7.99±1.20	12.85±1.98	13.75±1.34	40.23±26.65	19.97±4.39
	Gas cylinder	-	-	1.21±0.52	1.57±0.57	-	-
Type of heating	Natural Gas	6.14±1.66	7.83±1.87	12.85±1.98	13.75±1.34	40.23±26.65	19.97±4.39
	Electric	7.79±2.02	9.09±2.27	1.21±0.52	1.57±0.57	-	-
	Radiant ceramics	8.78±0.72	7.39±1.9	-	-	-	-
Air conditioning	Yes	5.61±1.34	9.51±1.14	11.05±2.62	8.64±2.04	83.70±69.78	19.18±8.93
	No	7.92±1.55	6.98±1.83	9.73±2.87	15.34±1.61	13.48±2.70	20.49±4.64
Extractor fan in the kitchen	Yes	8.78±0.72	7.39±1.19	18.67±1.19	14.00±2.39	54.43±43.12	10.97±2.60
	No	6.55±1.32	8.14±1.48	5.09±1.76	9.53±1.94	17.16±4.73	33.46±8.45
Window in the kitchen	Yes	5.33±0.94	7.14±1.25	12.85±1.98	13.75±1.34	40.23±26.65	19.97±4.39
	No	13.65±0.92	11.41±3.08	1.21±0.52	1.57±0.57	-	-
Cleaning frequency	Daily	-	-	9.86±2.24	10.85±2.31	51.56±34.73	23.56±5.10
	Weekly	7.00±1.08	7.99±1.20	11.51±3.54	12.01±1.90	3.96±1.67	5.61±1.73
Use of aromatizers	Yes	7.00±1.08	7.99±1.20	10.52±1.90	11.32±1.55	81.13±70.00	21.95±7.23
	No	-	-	-	-	15.06±3.79	18.64±5.73
Aerosols	Yes	5.06±1.40	4.76±1.95	10.52±1.90	11.32±1.55	46.26±32.93	15.90±4.60
	No	8.29±1.47	10.14±1.22	-	-	14.59±3.06	36.24±8.72

**Appendix F: Comparison of results from this study with others****TABLE F1.** COMPARISON OF PM<sub>2.5</sub> CONCENTRATIONS INDOORS AND OUTDOORS AT DIFFERENT LOCATIONS.

Origin	City, Country	Sample year	PM <sub>2.5</sub> (µg/m <sup>3</sup> )		Reference
			Summer	Winter	
Indoor (homes) - Urban	Córdoba, Argentina	2015	7.9	8.4	This study
Indoor (homes) - Suburban	Córdoba, Argentina		6.3	11.3	
Indoor (homes) - Rural	Las Higueras, Argentina		41.8	21	
Outdoor - Urban	Córdoba, Argentina	2009 - 2010	71		López et al. 2011
Outdoor - Suburban	Córdoba, Argentina		67		
Indoor (homes) - Urban	Boston, EEUU	1996	13.9		Abt et al. 2000
Indoor (homes) - Urban	Hong Kong, China	1999 - 2000	42.7		Chao and Wong 2002
Indoor (homes) - Urban	Lodi, Italy	2007 - 2008	14	39	Cattaneo et al. 2016
Indoor (homes) - Urban	Boulder, Colorado (USA)	2012	7.0	-	Escobedo et al. 2014
Indoor (homes) - Urban	Temuco, Chile	2014	-	55.7	Jorquera et al. 2018
Indoor (homes) - Urban	Krakow, Poland	2013 - 2015	20.1		Ścibor et al. 2019

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