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Land use and air quality in urban environments: Human health risk assessment due to inhalation of airborne particles

A.C. Mateos*, A.C. Amarillo, H.A. Carreras, C.M. González

Instituto Multidisciplinario de Biología Vegetal (IMBIV-CONICET) and Chemistry Department, FCEFyN, Universidad Nacional de Córdoba, Av. Vélez Sarsfield 1611, X5016 GCA Córdoba, Argentina

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ABSTRACT

Particle matter (PM) and its associated compounds are a serious problem for urban air quality and a threat to human health. In the present study, we assessed the intraurban variation of PM, and characterized the human health risk associated to the inhalation of particles measured on PM filters, considering different land use areas in the urban area of Cordoba city (Argentina) and different age groups. To assess the intraurban variation of PM, a biomonitoring network of *T. capillaris* was established in 15 sampling sites with different land use and the bioaccumulation of Co, Cu, Fe, Mn, Ni, Pb and Zn was quantified. After that, particles were collected by instrumental monitors placed at the most representative sampling sites of each land use category and an inhalation risk was calculated. A remarkable intraurban difference in the heavy metals content measured in the biomonitors was observed, in relation with the sampling site land use. The higher content was detected at industrial areas as well as in sites with intense vehicular traffic. Mean PM_{10} levels exceeded the standard suggested by the U.S. EPA in all land use areas, except for the downtown. Hazard Index values were below EPA's safe limit in all land use areas and in the different age groups. In contrast, the carcinogenic risk analysis showed that all urban areas exceeded the acceptable limit (1×10^{-6}), while the industrial sampling sites and the elder group presented a carcinogenic risk higher that the unacceptable limit. These findings validate the use of *T. capillaris* to assess intraurban air quality and also show there is an important intraurban variation in human health risk associated to different land use.

1. Introduction

Air pollution is considered one of the biggest environmental problems, particularly in urban environments where the population is constantly growing and the air quality decreases proportionally to this population increase (WHO, 2013). Since the 90's, quantification of particle matter (PM), either PM_{10} or $PM_{2.5}$, increased exponentially due to many studies showing that high PM concentrations were associated to adverse human health outcomes (Pirani et al., 2015). Particles consist of a core whose composition depends on their emission source and a large number of adsorbed substances, such as heavy metals, organic compounds, biological material, ions, reactive gases and mineral components (Valavanidis et al., 2006). In urban environments, the presence of metals in the inorganic fraction of airborne particles comes mainly from metal processing activities, road dust, cement production, soil resuspension, waste incinerators and sometimes coal burning (Mugica et al., 2002; He et al., 2016; Izhar et al., 2016). Vehicles are another major emission source of metal particles through combustion processes, transportation, corrosion of metallic parts and motor vehicle exhaust (Karagulian et al., 2015; Pernigotti et al., 2016).

Several studies confirmed the relationship between human exposure to particles and increased mortality rate (WHO, 2016). In addition, toxicological and epidemiological studies over the last years presented strong evidence of an association between particles bound metals and potential toxicological health effects (Castillo, 2016; Izhar et al., 2016; Li et al., 2016). Indeed, PM bound metals were associated to adverse health effects such as lung cancer (Chen et al., 2016), cardiovascular damage (Zhang et al., 2016), arteriosclerosis, hypertension (Fang and Zheng, 2014), among others. Therefore, in urban environments it is important to perform a careful monitoring of particle bound metals in order to get information related to population exposure. Thus, for the preliminary assessment of potential health effects of this pollutants, risk assessment strategies are an interesting approach (Romanazzi et al., 2014), considering pollutants toxicity as well as different exposure routes. Indeed, risk assessment strategies have been extensively used by government authorities to define guideline values in developed countries (Ferreira-Baptista and De Miguel, 2005).

World population is concentrated in urban areas suggesting the

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* Corresponding author.
E-mail address: ac.mateos@unc.edu.ar (A.C. Mateos).

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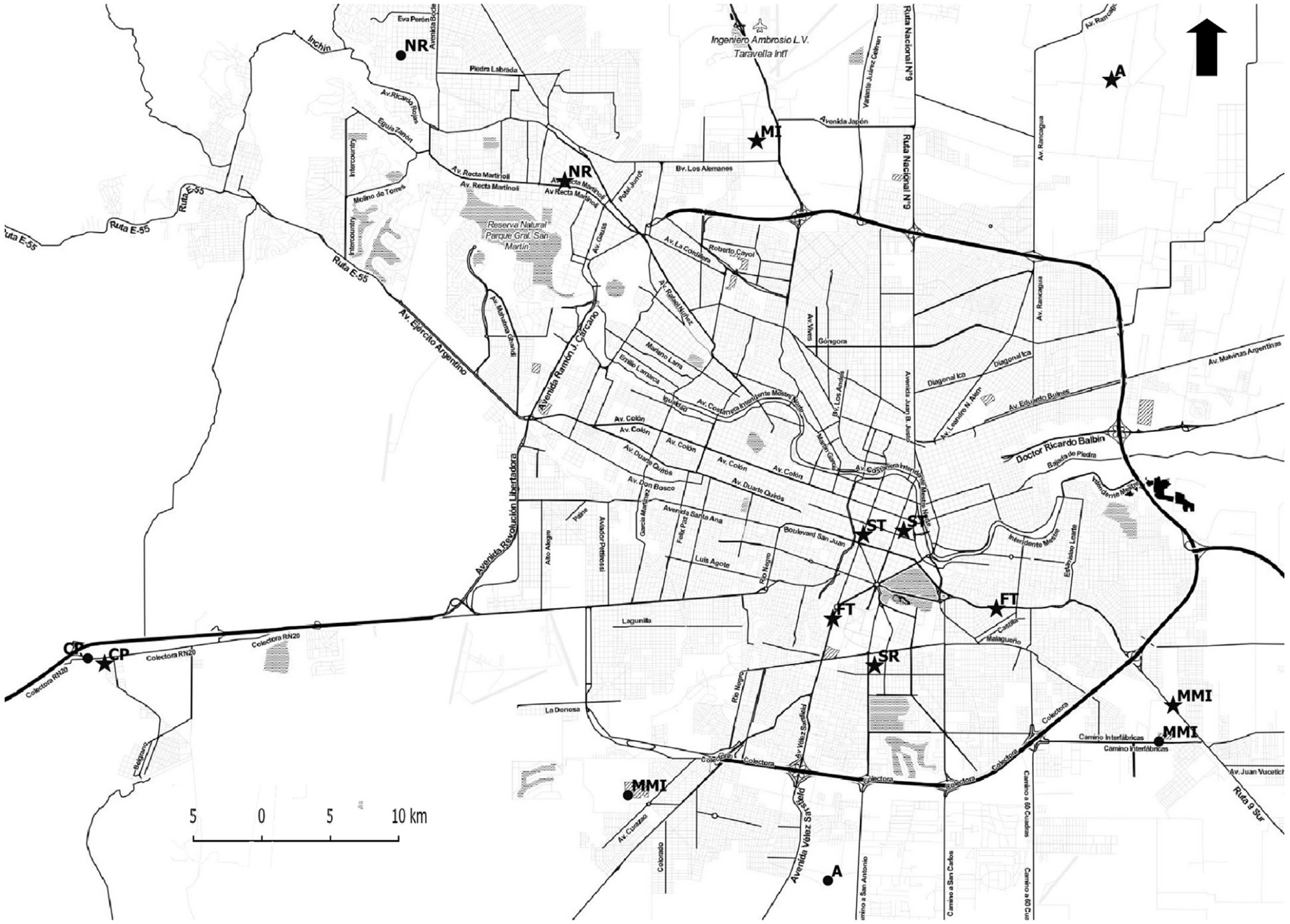

Fig. 1. Location of sampling sites (n = 15 sites) in the city of Córdoba, Argentina. Sites with ★ are biomonitoring and instrumental monitors sampling sites, and sites with • only biomonitors sites.

Table 1

Reference Dose expressed as Reference Concentration (RfC) and Cancer Potency Factor expressed as Inhalation Unit Risk (IUR) for elements determined in PM_{10}. *Ferreira-Baptista and De Miguel (2005); **Zhou et al. (2014).

Element	RfC [ppm/day]	IUR [$m^3/\mu g$]
Cr	2.86×10^{-5}*	3.36×10^{-2}*
Mn	1.43×10^{-5}*	
Co	5.71×10^{-6}*	7.84×10^{-3}*
Ni		6.72×10^{-4}*
Cu	4.02×10^{-2}**	
Zn	3×10^{-1}**	
As		1.21×10^{-4}*
Ba	1.43×10^{-4}*	
Pb	3.52×10^{-3}**	

Table 2

Parameters employed for non-cancer and cancer risk assessment in different age groups.

Age group	IRa (m^3/h)	IRb (m^3/day)	ET (h/day)	EF (days/year)	ED (years)	BW (kg)	AT (days)
Children	0.43	10.3	1.81	365.25[a]	5.7	23.15	28,489.5[b]
Youth	0.66	15.8	1.68		16	64.2	
Adults	0.66	15.8	4.68		41	80	
Elder	0.56	13.6	4.90		71	80	

Ira,b: inhalation rate; ET: time of exposure; EF: frequency of exposure; ED: duration of exposure; BW: body weight; AT: Average exposure time throughout life.

[a] It is considered that people are exposed to air pollutants every day of the year.

[b] Average life expectancy for men and women.

need to monitor air pollutants in such environments. However, the availability of instrumental monitors in developing countries is sometimes scarce, due mainly to their high cost (Monaci et al., 2000; Olcese and Toselli, 2004; Mateos and González, 2016). An alternative to instrumental monitoring is the use of biomonitors, that is, to get information on pollutants levels and their effects using living organisms (Nimis et al., 2000; González et al., 2003; Smodis, 2008; Van Dijk et al., 2015). Moreover, the use of active biomonitoring and the identification of efficient biomarkers have been suggested as a necessary complementary tool for instrumental monitoring (EuroBionet, 2000). In addition, biomonitoring has many advantages compared to instrumental monitoring: it is possible to assess many different sampling sites simultaneously, biomonitors are extremely low-cost and they provide information about pollutant effects on a living organism (Augusto et al., 2010; Wannaz et al., 2013; de Paula et al., 2015; Capozzi et al., 2016; Giampaoli et al., 2016). Epiphytic plants are one of the most frequently used atmospheric biomonitors, since they obtain their nutrients from the atmosphere, avoiding the influence of soil pollutants. Particularly, species from the *Tillandsia* genus demonstrated to be suitable biomonitors of heavy metals associated to airborne particles over vast areas in Argentina (Pignata et al., 2002; Wannaz et al., 2006, 2012; Bermudez et al., 2009; Abril et al., 2014), however these biomonitors have never been employed on a local scale.

Despite the fact that vehicle exhausts have been acknowledged as

Table 3
Meteorological conditions during the biomonitoring and instrumental monitoring period.

	Biomonitoring period June-December 2013				Instrumental monitoring period June-September 2014			
	Mean	SD	Min	Max	Mean	SD	Min	Max
Temperature (°C)	17.5	8.0	− 4.0	40.6	12.8	6.8	− 4.2	33.0
Relative humidity (%)	56.5	19.8	15.0	99.0	60.4	23.9	10.0	100.0
Atmospheric pressure (h Pa)	965.7	6.3	947.8	983.8	959.2	5.6	944.4	973.4
Wind speed (km h^{-1})	7.9	6.2	0.0	44.0	14.1	9.3	0.0	52.0
Rainfall (mm/exposure period)	7.4	12.4	0.0	69.0	7.3	7.8	0.0	20.0

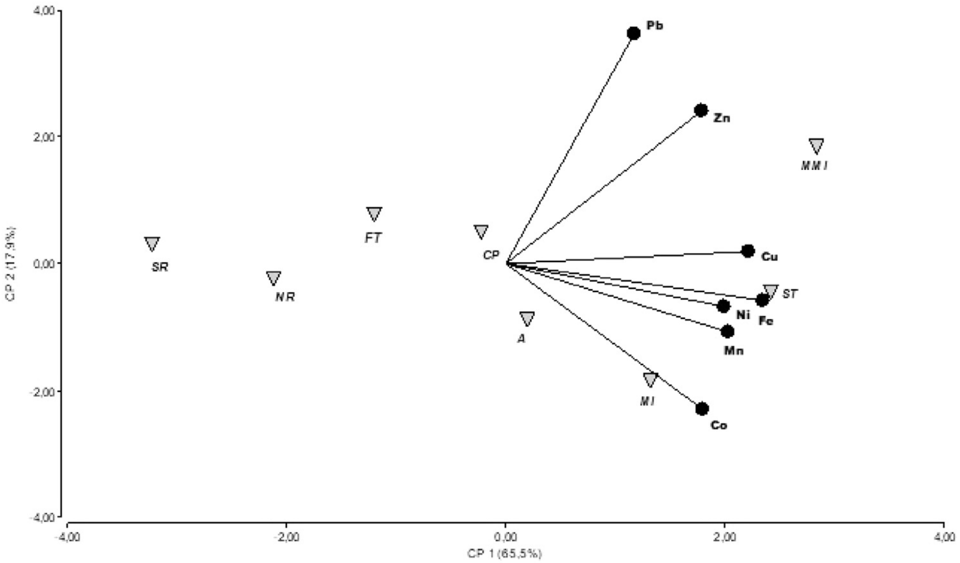

Fig. 2. Bi-plot representing associations between heavy metals accumulated in *Tillandsia capillaris* and sampling sites categories (MMI: metal-mechanic industry; MI: metallurgical industry; CP: cement plant; ST: slow traffic in downtown; FT: fluid traffic in avenues; NR: north residential; SR: south residential; A: agricultural).

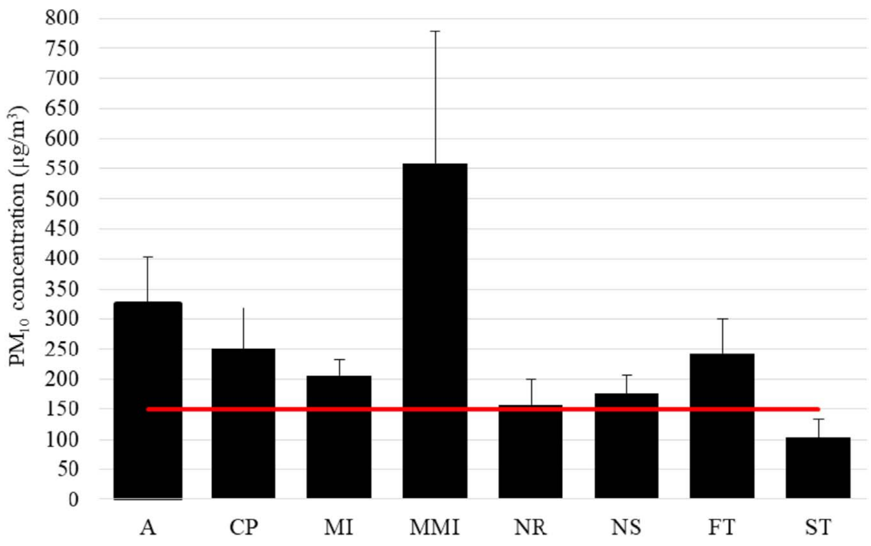

Fig. 3. Daily PM_{10} mean (n = 6) concentration (µg/m^3) in different land use areas. (A: agricultural CP: cement plant MI: metallurgical industry; MMI: metal-mechanic industry; NR: north residential; SR: south residential FT: fluid traffic in avenues; ST: slow traffic in downtown). The red line is the primary standard for PM_{10} (150 µg/m^3) established in the NAAQS (USEPA).

the main emission source of airborne particles in Cordoba city (Argentina) (Olcese and Toselli, 2002; Amarillo et al., 2017) and that their number had risen exponentially in recent years (Lazić et al., 2016) their emissions are not continuously monitored (Mateos and González, 2016). A previous study (Amarillo et al., 2014) already assessed the influence of PM organic fraction on human health in Cordoba city, but the risk due to PM bound metals is still unknown. Thus, the aim of the present study was to estimate the intraurban variation of PM associated to different land use areas, employing both biological and instrumental monitors, as well as to calculate the human non-carcinogenic (or toxicological) and carcinogenic risk related with the inhalation of PM bound heavy metals. In addition, we aimed to validate *Tillandsia capillaris* as a biomonitor to capture intraurban air quality differences.

2. Materials and methods

2.1. Study area and sampling sites

The study was conducted in Cordoba city, which is the second largest city in Argentina located in the central area (31°25′S, 64°11′W)

Table 4
PM_{10} composition (μg/m^3) ± standard deviations (S.D.) (n = 6) in different land use categories (A: agricultural CP: cement plant MI: metallurgical industry; MMI: metal-mechanic industry; NR: north residential; SR: south residential FT: fluid traffic in avenues; ST: slow traffic in downtown) and ANOVA results (*p*-values)* $p < 0.05$, ** $p < 0.01$ and *** $p < 0.001$, *ns* not significant and *nd* no data available.

	Mean ± S.D.								
Categories	**As**	**Ba**	**Co**	**Cr**	**Cu**	**Mn**	**Ni**	**Pb**	**Zn**
A	24.32 ± 3.55	636.02 ± 212.26	6.18 ± 4.2 BCE	4.83 ± 1.52 D	16.24 ± 11.24 B	151.56 ± 44.49 AB	nd	20.17 ± 2.09 C	616.66 ± 95.82
CP	10.57 ± 0.61	923.94 ± 521.54	15.41 ± 4 A	32.33 ± 2.82 A	13.87 ± 8.21 B	104.2 ± 60.81 ABC	nd	201.94 ± 16.83 A	673.87 ± 46.88
MI	nd	454.22 ± 245.69	6.53 ± 0.9 BCE	7.23 ± 2.11 CD	15.02 ± 7.82 B	86.37 ± 11.16 BCE	2.12 ± 0.26	87.79 ± 31.04 B	684.38 ± 40.35
MMI	20.05 ± 2.66	558.99 ± 329.43	12.76 ± 5.77 A	17.97 ± 8.46 B	29.65 ± 12.91 B	183.32 ± 66.42 A	nd	76.28 ± 7.17 B	686.91 ± 95.03
NR	nd	684.35 ± 187.23	1.82 ± 0.58 C	13.16 ± 8.75 BCE	18.21 ± 9.46 B	72.69 ± 23.51 BCE	nd	32.35 ± 20.36 C	667.96 ± 74.58
SR	21.92 ± 1.77	575.09 ± 194.36	4.13 ± 1.87 BCE	7.32 ± 2.59 CD	18.35 ± 9.31 B	75.32 ± 15.43 BCE	nd	24.26 ± 3.48 C	757.35 ± 36.67
FT	nd	487.27 ± 203.72	7.52 ± 3.42 B	7.23 ± 0.87 CD	192.76 ± 92.71 A	94.42 ± 38.13 BCE	nd	76.6 ± 18.89 B	631.76 ± 97.9
ST	nd	722.88 ± 203.42	5.79 ± 3.24 BCE	6.17 ± 0.98 D	89.25 ± 32.52 B	50.96 ± 22.77 C	nd	73.07 ± 10.55 B	694.73 ± 66.74
ANOVA	*nd*	*Ns*	**	***	*	*	*nd*	***	*ns*

with a population of 1.3 million (INDEC, 2010). The city lies in a depression causing a reduction of air circulation, therefore intense thermal inversions frequently occur in both autumn and winter when the highest air pollution episodes are registered (Stein and Toselli, 1996). The climate is sub-humid, with an average annual rainfall of 790 mm that is concentrated mainly in summer. The mean annual temperature is 17.4 °C with prevailing winds coming from the NE, S and SE (Olcese and Toselli, 2002). During the cold season, June 21 to December 21, 2013, a biomonitoring network was established in 15 urban sampling sites classified according to their land use in Agricultural (A), Industrial (I), Residential (R) and urban with intense traffic (T). Then, a more detailed classification was derived according to the location of the residential sites and the type of industries and vehicular traffic. Thus, we monitored four sites with heavy traffic, two of them located in large avenues with fluid and intense traffic (FT), and the other two located in the downtown area with slow and intense traffic (ST); another sampling site was located near an agricultural area (A); three industrial sites located close to metallurgical industries (MI), metal-mechanic industries (MMI) and a cement plant (CP); and two sampling sites located in residential areas to the north (NR) and to the south (SR) of the city (Fig. 1). Instrumental monitors were located from June 21 to September 21, 2014, in 10 out of the 15 sampling sites that were the most representative of each land use category and also were safe enough to avoid vandalism. We acknowledged that in urban environments is very common the overlapping between land use areas, therefore to avoid this effect we selected only sampling sites that were surrounded by the same land use categories.

2.2. *Biomonitoring*

2.2.1. *Biological material, sample preparation and active biomonitoring*

Plants of *Tillandsia capillaris* Ruiz & Pav. *form capillaris* (Fig. S1 – Supplementary material) were collected from tree trunks in a natural area, La Quebrada, located 38 km NW from the city. This area (hydric natural reserve) is considered a non-polluted spot (Abril et al., 2014). Sampling was conducted only when a condition of 5 days without rain was fulfilled. The collection was done using plastic gloves to prevent any risk of sample contamination (Pignata et al., 2002). At the laboratory, part of the plant material was separated, dried to constant weight and kept at − 15 °C in the dark until analyses. These samples were used as controls (baseline).

The rest of the material was placed in net bags (30 cm × 15 cm) with 10–12 plants each (approximately 200 g per plant bag) and transplanted to the different sampling sites (n = 3 bags/site) according to Wannaz and Pignata (2006) and Abril et al. (2014). The bags were placed 3 m above ground level in trees branches exposed for 6 months. After this period plants were collected, placed in paper bags and dried to constant weight.

2.2.2. *Heavy metal quantification*

Unwashed leaf samples (2.5 g DW) of *T. capillaris* were ground and reduced to ashes at 450 °C for 4 h and then digested with concentrated HNO_3 (65% Merck, Germany), during 24 h in the dark (Wannaz and Pignata, 2006). Next, samples were filtered and the acid solutions were analyzed by Atomic Absorption Spectroscopy (AAS) using a Perkin Elmer Spectrophotometer Model AA3110 (Wannaz et al., 2012) to quantify the content of Co, Cu, Fe, Mn, Ni, Pb and Zn. All these results were expressed in μg g^{-1} DW.

2.2.3. *Quality control*

In order to validate the precision of this process, digestion blanks and two replicate samples of Certified Reference Material of oriental tobacco leaves ("CTA-OTL-1" - Institute of Nuclear Chemistry and Technology) were prepared following the same treatment and run every ten samples in order to control the analytical method (Pfeiffer and Barclay-Estrup, 1992). Values for all blank samples were below the

Table 5
Hazard Quotients (HQ) and Hazard Index (HI) for non-carcinogenic metals measured in PM_{10} samples collected at different land use categories in Córdoba city, according to age groups.

			Land use						
	Element	**Age group**	[a]**R**	**FT**	**ST**	**A**	**CP**	**MMI**	**MI**
HQ	Mn	Children	1.58E−02	1.69E−02	1.20E−02	3.25E−02	2.23E−02	3.93E−02	1.85E−02
		Youth	2.20E−02	2.35E−02	1.67E−02	4.50E−02	3.10E−02	5.45E−02	2.57E−02
		Adults	1.26E−01	1.35E−01	9.58E−02	2.58E−01	1.78E−01	3.12E−01	1.47E−01
		Elder	1.96E−01	2.09E−01	1.49E−01	4.01E−01	2.76E−01	4.85E−01	2.28E−01
	Ba	Children	1.35E−02	1.04E−02	1.50E−02	1.36E−02	1.98E−02	1.20E−02	9.73E−03
		Youth	1.87E−02	1.45E−02	2.09E−02	1.89E−02	2.74E−02	1.66E−02	1.35E−02
		Adults	1.07E−01	8.29E−02	1.20E−01	1.08E−01	1.57E−01	9.52E−02	7.74E−02
		Elder	1.67E−01	1.29E−01	1.86E−01	1.68E−01	2.44E−01	1.48E−01	1.20E−01
	Co	Children	1.57E−03	3.53E−03	3.10E−03	3.31E−03	6.05E−03	6.85E−03	3.38E−03
		Youth	2.17E−03	4.89E−03	4.30E−03	4.59E−03	8.40E−03	9.50E−03	4.69E−03
		Adults	1.25E−02	2.80E−02	2.46E−02	2.63E−02	4.82E−02	5.45E−02	2.69E−02
		Elder	1.94E−02	4.35E−02	3.83E−02	4.09E−02	7.48E−02	8.46E−02	4.18E−02
	Cr	Children	1.44E−03	7.97E−04	5.48E−04	4.54E−04	3.80E−03	1.92E−03	7.73E−04
		Youth	2.00E−03	1.11E−03	7.60E−04	6.30E−04	5.28E−03	2.67E−03	1.07E−03
		Adults	1.15E−02	6.34E−03	4.36E−03	3.61E−03	3.03E−02	1.53E−02	6.15E−03
		Elder	1.78E−02	9.85E−03	6.77E−03	5.61E−03	4.70E−02	2.38E−02	9.55E−03
	Cu	Children	1.39E−06	2.36E−05	6.99E−06	1.24E−06	1.06E−06	2.26E−06	1.14E−06
		Youth	1.93E−06	3.27E−05	9.70E−06	1.72E−06	1.46E−06	3.13E−06	1.59E−06
		Adults	1.11E−05	1.88E−04	5.56E−05	9.84E−06	8.40E−06	1.80E−05	9.10E−06
		Elder	1.72E−05	2.91E−04	8.64E−05	1.53E−05	1.30E−05	2.79E−05	1.41E−05
	Pb	Children	2.80E−05	nd	5.53E−05	1.73E−05	1.92E−04	nd	7.00E−05
		Youth	3.89E−05	nd	7.66E−05	2.41E−05	2.66E−04	nd	9.71E−05
		Adults	2.23E−04	nd	4.40E−04	1.38E−04	1.52E−03	nd	5.57E−04
		Elder	3.46E−04	nd	6.83E−04	2.14E−04	2.37E−03	nd	8.65E−04
	Zn	Children	7.27E−06	6.84E−06	7.12E−06	6.29E−06	6.88E−06	7.01E−06	6.98E−06
		Youth	1.01E−05	9.49E−06	9.88E−06	8.73E−06	9.54E−06	9.73E−06	9.69E−06
		Adults	5.79E−05	5.44E−05	5.67E−05	5.01E−05	5.47E−05	5.58E−05	5.56E−05
		Elder	8.99E−05	8.45E−05	8.80E−05	7.78E−05	8.50E−05	8.66E−05	8.63E−05
HI		Children	3.23E−02	3.17E−02	3.07E−02	4.99E−02	5.21E−02	6.01E−02	3.25E−02
		Youth	4.49E−02	4.40E−02	4.28E−02	6.92E−02	7.24E−02	8.33E−02	4.51E−02
		Adults	2.57E−01	2.52E−01	2.45E−01	3.96E−01	4.15E−01	4.77E−01	2.58E−01
		Elder	4.01E−01	3.92E−01	3.81E−01	6.16E−01	6.44E−01	7.42E−01	4.00E−01

[a] R: residential; FT: fluid traffic in avenues; ST: slow traffic downtown; A: agricultural; CP: cement plant; MMI: metal-mechanic industry; MI: metallurgical industry. nd: no data.

detection limits of AAS, with recovery percentages varying between 85.18% (Cu) and 97.33% (Mn) (Table S2).

2.3. Instrumental monitoring

2.3.1. PM measurements

Particles were collected during 24 h, three consecutive days (with no rain during the sampling period and at least one rainless day before the beginning of the monitoring) at each sampling site, twice along the winter period (June 21 to August 30, 2014), using a Handi-Vol medium volume samplers for total suspended particles (TSP, Energetica, Brazil) equipped with glass fiber filters (0.6 µm pore size and 10 cm diameter). The sampler was located 7 m high above ground level, at each sampling site and operated at a flow rate of 0.2 $m^3\ min^{-1}$ to obtain a total volume sample higher than 300 m^3 over the 24 h period. All freshly exposed filters were conditioned in a desiccator for 24 h to remove moisture. Exposed filters were then folded and wrapped in aluminum foil and stored in sealed plastic bags until analysis. The concentration of TSP ($\mu g\ m^{-3}$) was determined gravimetrically using an electronic microbalance with a resolution of 0.01 mg, considering the filtered air volume (Amarillo et al., 2014). The TSP data was transformed in PM_{10} using the conversion factor ($PM_{10} = 0.83 \times TSP$) suggested by the 1999 Council Directive of European Commission (Directive, 1999).

2.3.2. Meteorological data

Weather data were obtained from the meteorological station of the National Meteorological Service located at the Cordoba Airport, 9.5 km north from the city center (31°18′56.56″ S, 64°12′44.84″ W, altitude 484 masl), which is considered the most reliable data source in the area. For the present study, we assessed the influence of mean temperature (°C), relative humidity (%), atmospheric pressure (hPa), Pa), wind speed ($km\ h^{-1}$), and rainfall (mm).

2.3.3. Inorganic composition of PM

Inorganic composition (As, Ba, Co, Cr, Cu, Mn, Ni, Pb and Zn) of particles collected on filters was analyzed by Total Reflection X-Ray Fluorescence (TXRF). Each sample was digested with 25 mL of HNO_3 (20%) and centrifuged for 15 min at 3000 rpm. An aliquot of 0.9 mL of the supernatant was taken and 0.1 mL of a 10 ppm Ge solution was added as internal standard. Finally, aliquots of 5 µl were taken from this solution and dried in an oven at 60 ± 2 °C on acrylic support (Wannaz et al., 2011). Samples were measured for 200 s, using the total reflection setup mounted at the X-ray fluorescence beamline of the National Synchrotron Light Laboratory (LNLS), Campinas, SP, Brazil. A polychromatic beam approximately 5 mm wide and 0.1 mm high was used for excitation. For the X-ray detection, a Si (Li) detector was used with an energy resolution of 165 eV at 5.9 keV. Standard solutions with known concentrations of all elements to be determined (with Ge as an internal standard) were prepared for the calibration of the system.

2.4. Risk assessment

A human health risk assessment is an estimation of the nature and probability of adverse health effects in humans that may be exposed to chemicals, now or in the future (USEPA, 2011). This risk can be classified in either cancer risk or non-cancer risk assessment, according to the effect of chemicals on human health. Cancer risk is treated as a stochastic response, meaning that the increase in the dose does not necessarily means an increase in the severity of the response, but the occurrence probability. On the other hand, non-cancer risk assessments are treated as deterministic, i.e., when increasing the dose, a more severe response is expected (Evans, 2003).

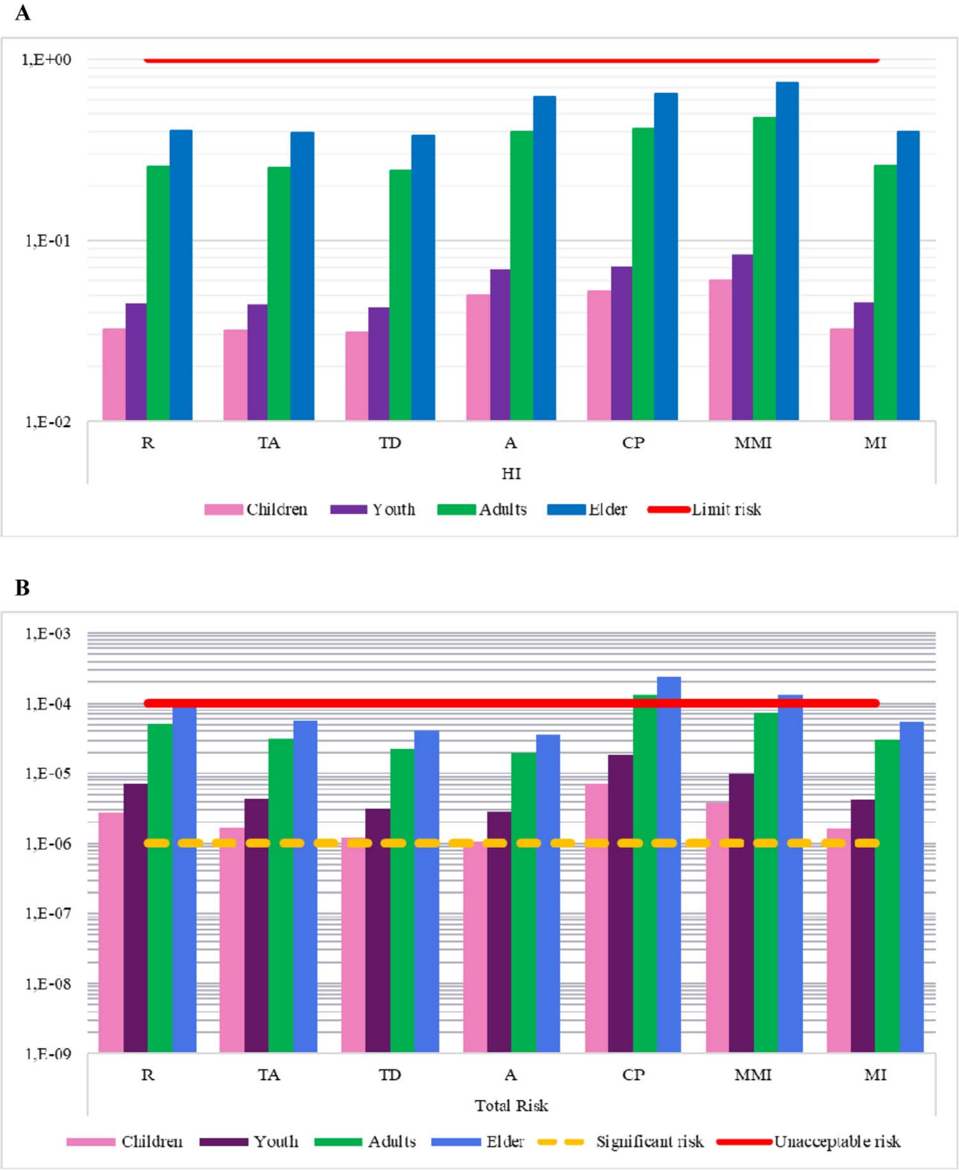

Fig. 4. A) Hazard Index and B) Total carcinogenic risk for the different land use categories and age groups.

Risk estimations from exposure to particles via inhalation is a tool that contributes to air quality management, particularly in developing countries where there is scarce information on the composition and concentration of particles (Romanazzi et al., 2014). In addition, a large number of studies already demonstrated that some age groups may be more susceptible to air pollutants than others (Kan et al., 2008). This study attempts to evaluate a non-carcinogenic health risk based on the concentrations of seven heavy metals (Ba, Co, Cr, Cu, Mn, Pb and Zn) and also a carcinogenic risk due to exposure to carcinogenic metals (Co, Cr, Ni and As) through inhalation on different age groups using standard Environmental Protection Agency of United State (EPA) methods (USEPA, 2011). The metals classification into carcinogenic or non-carcinogenic was obtained from the Integrated Risk Information System (IRIS) of the USEPA.

The metal-specific carcinogenic risks were calculated considering the Life Averaged Daily Dose (LADD, mg $(\text{kg day})^{-1}$) and the Slope Factor (SF, (kg day^{-1}) mg^{-1}) (Eq. (1)).

$$\text{Metal–specific carcinogenic Risk} = [\text{LADD}] \times \text{SF} \tag{1}$$

$$\text{Metal–specific carcinogenic Risk} = [\text{CA} \times \text{IF}] \times \text{SF} \tag{2}$$

$$\text{Metal} - \text{specific carcinogenic Risk} = \left[\text{CA x}\left(\frac{\text{IRa x EF x ED x ET}}{\text{BW x AT}}\right)\right]\text{x}\left(\frac{\text{IUR x BW x1000}}{\text{IRb}}\right) \tag{3}$$

The LADD is the chronic daily intake of carcinogenic substances and can be calculated as shown in Eq. (2) using the compound concentration (CA, mg m^{-3}) and the intake factor (IF, m^{-3} $\text{kg}-^{1}$ day^{-1}) where LADD = [CA × IF]. The IF was calculated from age specific physiological and exposure parameters (Eq. (3)), where IR_a is the breathing rate expressed as m^3 h^{-1}; exposure frequency (EF) is the number of exposures per year; exposure duration (ED) is the duration of exposure in years; exposure time (ET) is the number of hours per exposure; Body weight (BW) is the default weight of the receptor body (kg) and averaging time (AT) is the average exposure extent over a lifetime (28,489.5 days of carcinogenic exposure). The Slope Factor is an estimate of the upper-bound probability of a person to develop a cancer as a result of the lifetime exposure to certain level of potential carcinogen (USEPA, 2011). It was calculated considering the inhalation unit risks (IUR), derived from cancer potency factors for inhalation exposure (USEPA, 1998), the Body Weight (BW) per 1000 (conversion factor, µg mg^{-1}) and the breathing rate IR_b expressed as m^3 day^{-1}. The IUR values used are presented in Table 1 and expressed as m^3 μg^{-1}. Several studies

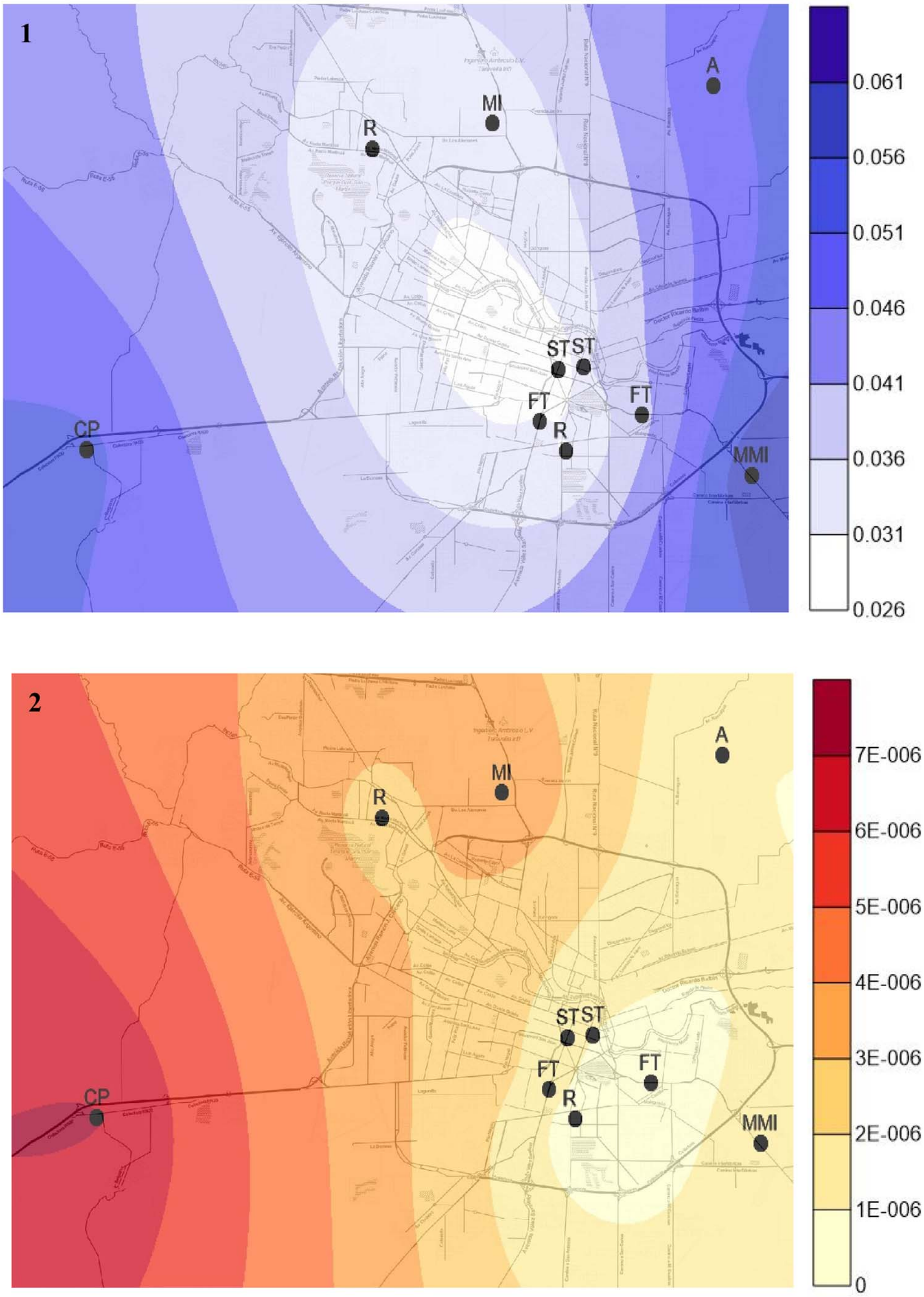

Fig. 5. Spatial distribution by Kriging of total non-carcinogenic risk (HI) (1) and carcinogenic risk (2) in the city of Córdoba (Argentina).

indicate that some segments of the population may be more susceptible to air pollutants than others (Kan et al., 2008). Therefore, we compared the health risk in four age categories: children (0 to < 11 years), youth (11 to < 21 years), adults (21 to < 61 years) and elder (> 61 years). All the parameters used for each age group are shown in Table 2. The carcinogenic benchmark level used represents an exposure that poses an upper-bound lifetime excess cancer risk of 1×10^{-6} (USEPA, 2003). Exposure for which the risk factor exceeded 1×10^{-6} (i.e. one occurrence over 1 million people) was scored as significant (Amarillo et al., 2014).

To assess the non-carcinogenic risk due to exposure to particles inhalation we calculated a Hazard Quotient (HQ) according to Eq. (4) that estimate the risk of a single contaminant using the LADD and a specific reference concentration (RfC) that is the estimated maximum permissible risk to humans through daily exposure. The goal of this analysis is to determine if the exposure to a particular pollutant overcome a limit representing an environmental concern (Evans, 2003).

$$HQ = LADD / RfC \qquad (4)$$

The RfC is analogous to the reference dose inhalation (RfDinh) and is based on the assumption that there is a threshold for certain toxic effects. It is an estimate of daily exposure by inhalation that human population is able to tolerate over a lifetime without deleterious effects appear. The RfC (mg kg^{-1} day^{-1}) used are shown in Table 2 which are the values recommended by the IRIS EPA Program (USEPA, 2003). A HQ ≤ 1 is generally considered an acceptable risk, whereas a HQ greater than 1 is often considered as an indicator of a potential risk for some exposed individuals to experience adverse health effects (Cao et al., 2015). Then, to assess the entire potential non-carcinogenic effects posed by all metals (e.g., i), the HQ values corresponding to every

Table 6
Carcinogenic Risk for As, Co, Cr and Ni measured PM_{10} samples collected at different land use categories in Córdoba city, according to age groups.

Element	Age group	Land use						
		[a]R	FT	ST	A	CP	MMI	MI
Cr	Children	2.49E−06	1.38E−06	9.46E−07	7.84E−07	6.57E−06	3.32E−06	1.33E−06
	Youth	6.51E−06	3.60E−06	2.47E−06	2.05E−06	1.72E−05	8.69E−06	3.49E−06
	Adults	4.64E−05	2.57E−05	1.76E−05	1.46E−05	1.22E−04	6.19E−05	2.49E−05
	Elder	8.40E−05	4.65E−05	3.19E−05	2.65E−05	2.22E−04	1.12E−04	4.51E−05
Co	Children	2.21E−07	2.83E−07	2.49E−07	2.66E−07	4.87E−07	5.50E−07	2.72E−07
	Youth	5.79E−07	7.41E−07	6.52E−07	6.97E−07	1.27E−06	1.44E−06	7.11E−07
	Adults	4.13E−06	5.29E−06	4.65E−06	4.97E−06	9.08E−06	1.03E−05	5.07E−06
	Elder	7.47E−06	9.57E−06	8.41E−06	8.99E−06	1.64E−05	1.86E−05	9.18E−06
Ni	Children	nd	nd	nd	nd	nd	nd	6.81E−09
	Youth							1.78E−08
	Adults							1.27E−07
	Elder							2.30E−07
As	Children	1.58E−08	nd	nd	1.81E−08	6.70E−09	1.15E−08	nd
	Youth	4.14E−08			4.73E−08	1.75E−08	3.00E−08	
	Adults	2.95E−07			3.37E−07	1.25E−07	2.14E−07	
	Elder	5.35E−07			6.11E−07	2.26E−07	3.87E−07	
Total Risk	Children	2.73E−06	1.66E−06	1.20E−06	1.07E−06	7.06E−06	3.88E−06	1.61E−06
	Youth	7.13E−06	4.34E−06	3.12E−06	2.79E−06	1.85E−05	1.02E−05	4.22E−06
	Adults	5.08E−05	3.10E−05	2.23E−05	1.99E−05	1.31E−04	7.24E−05	3.01E−05
	Elder	9.20E−05	5.61E−05	4.03E−05	3.61E−05	2.39E−04	1.31E−04	5.45E−05

[a] R: residential; HT: fluid traffic in avenues; ST: slow traffic downtown; A: agricultural; CP: cement plant; MMI: metal-mechanic industry; MI: metallurgical industry. nd: no data.

metals were summed and expressed as a Hazard Index (HI):

$$HI = \sum_{1}^{i} HQ \tag{5}$$

If HI is smaller than 1, then an adverse health effect is not expected. But, when HI > 1, the individual chemicals and their HQs are examined to determine if HQs for all chemicals that act through a common pathway (equal toxicodynamics) add to greater than 1. If not, then the prediction remains that no effects are expected on health (Valberg, 2004).

2.5. Statistical analysis

Assumptions of normality were tested using the Shapiro Wilk test, and non-normal distributed variables were LOG_{10} transformed; the homogeneity of variance was checked with Levene's test. Descriptive statistics were calculated for the determinations of heavy metals content in the biomonitor (*T. capillaris*), the concentration of the metals determined in the filters collected by instrumental monitoring networks and PM mass. In addition, a Pearson correlation analysis was performed between all these variables. The differences in the levels of heavy metals between sampling sites were assessed with a one way analysis of variance (ANOVA). When the ANOVA null hypothesis was rejected (significance level < 0.05), post-hoc comparisons were performed to investigate differences between pairs of means (Least Significant Difference, LSD). A multivariate analysis (Principal Component Analysis - PCA) was performed using sampling sites as classification criterion in order to assess the association between heavy metal content in the biomonitor with the main emission sources. Furthermore, risk estimations were mapped with Surfer 11.6.

3. Results and discussion

Meteorological parameters during biomonitors exposition and instrumental monitoring are presented in Table 3. No significant differences were observed between both sampling periods (data not shown).

3.1. Biomonitoring: heavy metal content in T. capillaris

The heavy metal content accumulated in samples of *T. capillaris* showed significant differences between land use categories, indicating a remarkable intraurban air quality variation (Table S1 – Supplementary material). The PCA run with heavy metals as dependent variables and land use categories as classification criterion, showed that the first and second component (CP1 and CP2) explained 83.4% of the total variance (Fig. 2).

The number of principal components was determined with eigenvalues higher than 1 and explaining more than 75% of the variance (Pires et al., 2008). The first component was represented by Cu, Ni, Fe and Mn, with a strong association with traffic in the downtown area and sampling sites located close to metal-mechanic industries. All these elements indicated the presence of anthropogenic sources, both vehicles and industries (Bermudez et al., 2012); while Fe and Cu could also indicate soil resuspension (Karanasiou et al., 2009). The second factor was conformed by Pb, Co and Zn, emitted mainly by vehicle exhausts which can be deposited and then re-suspended in the form of dust, or could originate from other vehicle parts such as tires, brakes, wheels and bitumen abrasion (Kabata-Pendias and Mukherjee, 2007; Fuga et al., 2008; Bermudez et al., 2009; Wannaz et al., 2011; Iodice et al., 2016). It is noteworthy that all these elements have recognized adverse health effects, which raises the need to analyze population health risk.

3.2. Instrumental monitoring

Fig. 3 shows mean PM_{10} concentration ($\mu g/m^3$). Except for traffic in downtown, mean PM_{10} levels in all land use categories exceeded the USEPA primary standard ($\leq 150\ \mu g/m^3$) and the 24-h WHO standard ($50\ \mu g/m^3$). The comparison with PM values registered in other cities with similar topographies, demonstrate that the levels registered in Córdoba city are really high. For example, Perez and Reyes (2002) measured maximum values of $220\ \mu g/m^3$ during wintertime in the surrounding of Santiago, Chile; in Bogotá, the highest registered PM_{10} values did not reach $100\ \mu g/m^3$ (Vargas et al., 2012) and in Mexico city values near $130\ \mu g/m^3$ were registered only for the cold-dry season (Valle-Hernández et al., 2010).

Considering PM_{10} levels in Cordoba city over the last years, Olcese and Toselli (2002) measured $80\ \mu g/m^3$ in the city center and $120\ \mu g/m^3$ in the suburban area during 1995–1996; the USEPA standard was exceeded only a few times during this period. López et al. (2011) studied two sampling points within the city during 2009–2010 and registered $107\ \mu g/m^3$ and $101\ \mu g/m^3$ in an industrial and semi-urban sampling sites, respectively. Our results indicate a remarkable increase in PM_{10} concentration during the last years, which can be partially attributable to a huge increase in the number of public transport and private vehicles (Castro Rivera, 2013).

The comparison between categories (Table 4) showed that the metal-mechanical industries were the sampling sites with the highest concentrations of PM_{10} while the lowest values were observed in the downtown area. This result could be partially explained by the lower proportion of soil resuspension in the downtown area compared to the city borders, as already observed by Olcese and Toselli (2002). The levels of Ba and Zn were similar in all sampling sites while significant differences were found in the levels of Co, Cr, Cu, Mn and Pb. The highest levels of Co and Cr were observed near the cement plant and metal-mechanic industries that were also the main sources of Cu and Mn along with traffic in main avenues and agricultural areas. High concentrations of Co, Cr and Cu were already observed in industrial areas and in sites with high vehicular traffic (Carreras and Pignata, 2002; Wannaz and Pignata, 2006; Bergamaschi et al., 2007; Fuga et al., 2008; Bermudez et al., 2009). Despite being located in different areas of the city, the residential sites showed similar concentration and composition of PM_{10}.

High levels of Mn were observed near the cement plant, metal-mechanic industries and agricultural sites. This element is one of the main soil component in Argentina (Gaiero et al., 2003; Bermudez et al., 2009), therefore the presence of Mn in air samples could be a result of soil erosion due to agricultural practices as well as the frequent use of fertilizers and pesticides in agricultural zones whose composition also include Mn (Pignata et al., 2007). This metal is present in industrial emissions related with smelting and steel production, as well (Wannaz and Pignata, 2006). The levels of Pb were one order of magnitude higher near the cement plant which is in good agreement with the previous findings of Abril et al. (2014) and Baldantoni et al. (2014) who found high Pb levels in the vicinity of a cement plant in Córdoba (Argentina) and in Salerno (Italy), respectively. Sampling sites with high vehicular traffic and industries also had high Pb levels compared to residential or agricultural areas. Although this metal is no longer used in fuels since the 90 s, vehicular traffic could be partially still a source due to combustion-related emissions that include lead plating of fuel tanks and Pb in vulcanised fuel hoses, piston coatings, valve seats and spark plugs (Maher et al., 2008). In addition, street dust resuspension could be another possible emission source in urban environments (Pandey et al., 2014). Regarding industrial areas, Pb had been recognized as a good marker of industrial sources due to coal and oil combustion (Kabata-Pendias and Mukherjee, 2007).

3.3. Health risk assessment

In this subsection, since both residential sampling areas did not show significant differences neither in particles concentration nor in metal levels, they were grouped under a single category (R). Results of the HQ and HI for the non-carcinogenic risk analysis of each metal, age group and land use are shown in Table 5. Mean HQs of particle bound metals were ordered as follows: Mn > Ba > Co > Cr > Pb > Zn > Cu. These results are consistent with the fact that Ba, Mn and Zn were the most abundant metals in samples collected in filters, Mn was one of the most abundant element in *T. capillaris,* as well. Considering the land use categories, the highest HI corresponded to metal-mechanic industries, followed by the cement plant, agricultural areas, metallurgical industries and residential areas. Although nor the HQ neither the HI exceeded the value of 1 in any category, population living near the cement plant has the highest probability of non-carcinogenic risk since this site showed values closer to 1 (Fig. 5A). Considering vulnerability due to age, we found a higher risk in the elder group (Fig. 4A), which is consistent with the fact that the toxicological risk increases with exposure to pollutants (Amarillo and Carreras, 2012).

Regarding the carcinogenic health risk assessment, the higher values were found for Cr followed by Co, As and Ni (Table 6), which is in good agreement with several studies (Hu et al., 2012; Jiang et al., 2016; Li et al., 2017). The total carcinogenic risk was above the safe value ($> 1 \times 10^{-6}$) in all land use categories, with higher values at the cement and metal-mechanic industries sampling sites (Fig. 5B). Regarding age groups, adults and elder presented unacceptable values in the mentioned categories and in the residential areas (Fig. 4B). Considering these results, we can confirm a higher risk for the population living near industrial sites due to inhalation of particles. On the other hand, it is worrisome that we observed unacceptable risk values in residential sampling sites, where most urban population is concentrated.

4. Conclusions

In the present study we present a combination of biological monitoring and instrumental measurements that allowed not only the identification of hot spots within the urban area of Cordoba but also the estimation of population health risk due to exposure to airborne particles. We found that even within the city there are significant differences in air quality. On the other hand, we found that land use categories with a high proportion of exposed soil had the highest particles number, but not necessarily the highest concentration of toxic metals.

The employment of *T. capillaris* allowed the detection of intraurban air quality differences, i.e. they reveal that industrial areas had the worse air quality, which was further confirm with instrumental monitors. This fact suggests that *T. capillaris* is a valuable tool to be used in cities devoid of instrumental monitoring systems.

It is already known that population from developing countries is considered more vulnerable to the occurrence of extreme events. However, risk assessment studies are not as much frequent as in developed countries. In the present study we perform a preliminary risk assessment in a medium sized city from a developing country, that reveal areas within the city with unacceptable risk levels, considering exposition to non-carcinogenic and carcinogenic elements. We also found unacceptable levels of cancer risk in densely populated residential areas reinforcing the need to continue monitoring these areas. As expected, we found that adults and elder citizens are the most susceptible groups affected by particle inhalation due to their longer exposure. Thus, we demonstrated that the risk assessment analysis is a valuable tool to get information about human exposure, which is particularly useful in urban environments devoid of air quality monitoring networks or emission inventories. Although carcinogenic and non-carcinogenic risk assessments within urban areas are not conclusive, they are the best tool to help policymakers make rational decisions when there is no other information available about air quality. In addition, by characterizing human health risk according to land use, we are considering two very frequent phenomena occurring in developing countries. The first one is that working hours are very long and people spend most of their lifetime at work instead of at home; the second phenomena is that a large proportion of the population works in the same place where they live, mainly due to the fairly high percentage of unemployment.

The fact we measured metal concentrations in the air above the standards, suggests that there is a real risk for city population therefore, more studies are needed to assess if these are rare events or if they occur frequently, more than once a year. This data will help to better understand the human health problems derived from air quality in Cordoba city.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.envres.2017.11.035.

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