Ecological Indicators 20 (2012) 163–169

Contents lists available at SciVerse ScienceDirect

Ecological Indicators

journal homepage: www.elsevier.com/locate/ecolind

Use of biomonitors for the identification of heavy metals emission sources

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ARTICLE INFO

Article history:
Received 10 August 2011
Received in revised form 15 February 2012
Accepted 20 February 2012

Keywords:
Tillandsia capillaris
Passive biomonitoring
Heavy metals
Air pollution sources
Lead
Dove hunting

ABSTRACT

Heavy metals accumulation by *Tillandsia capillaris* was measured to identify their main emission sources in the province of Córdoba, Argentina. Samples of *T. capillaris* collected over three years at different sites were analysed by flame atomic absorption spectrometry to determine the amounts of Cu, Fe, Ni, Mn, Pb and Zn. The sampling sites were categorized according to land use, anthropic activities and/or distance from the potential heavy metal emission sources. We found that the concentration of heavy metals in the study area is mainly driven by industrial activity while traffic contributed only to the levels of Zn. In addition, we observed a strong relationship between a diffuse emission source and the content of Pb accumulated on the biomonitors which could be attributed to dove hunting activities. Future studies are needed to confirm this hypothesis.

1. Introduction

Epiphytic plants are efficient air pollution biomonitors since they obtain the nutrients from the atmosphere and have no contact with the soil. Therefore, the elemental composition of their tissues largely reflects the atmospheric input of air pollutants such as toxic gases and heavy metals (Figueiredo et al., 2001). The use of biomonitors is important in developing countries because the measurement of atmospheric pollutants requires expensive technical equipment which are often unavailable (Pignata et al., 2002). Biomonitors have several advantages over instrumental equipments regarding the identification of polluting emission sources, such as their low costs, the possibility of monitoring the effects of pollution over longer periods and also at many sites simultaneously (Calasans and Malm, 1997).

In Argentina, studies on the multielemental composition of the environment using bioindicators have mainly been undertaken using lichens (Calvelo et al., 1998, 2002; Carreras and Pignata, 2001, 2002; Jasan et al., 2004; Pignata et al., 2004; Carreras et al., 2005) and epiphytic species of the *Tillandsia* genus (Pignata et al., 2002; Wannaz and Pignata, 2006; Wannaz et al., 2006, 2008; Bermudez et al., 2009). The first biomonitoring study in a large area in the province of Córdoba, Argentina using *Tillandsia capillaris* as a passive biomonitor (Pignata et al., 2002), reported the content of Fe, Mn and Co to have probably originated in the soil; Pb was related to the presence of granitic rocks, Ni to an industrial origin, Zn to agricultural areas and Mn to the employment of pesticides. In our subsequent studies, the number of monitoring sites was increased, which allowed us to detect the enrichment of some metals in relation to precise sources (Wannaz et al., 2006). Thus, an association of the content of Zn and Pb was found with vehicular traffic and the concentrations of V, Co, Ni, Cu and Zn were related to industrial sources. Later, similar results were obtained in an active biomonitoring study using *T. capillaris* by Wannaz and Pignata (2006) and Bermudez et al. (2009). However, several years of measurements are needed to confirm that the concentrations of heavy metals measured are not related to a random episode but to the contribution of the emission sources already identified.

Therefore the objective of the present study was to relate the heavy metals accumulation patterns from three consecutive years in *T. capillaris* with the emissions sources presented in the study area.

2. Materials and methods

2.1. Study area

The sampling points were located in the province of Córdoba, in the centre of Argentina (Fig. 1). The land morphology of this area is highly variable, ranging from a mean elevation of around 100 m.a.s.l. in the southeast to over 2500 m.a.s.l. in the midwest. Agricultural activity is practiced over a wide area of the province, with the main crops being soybean and maize with 70 and 20% of acreage respectively.

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doi:10.1016/j.ecolind.2012.02.022

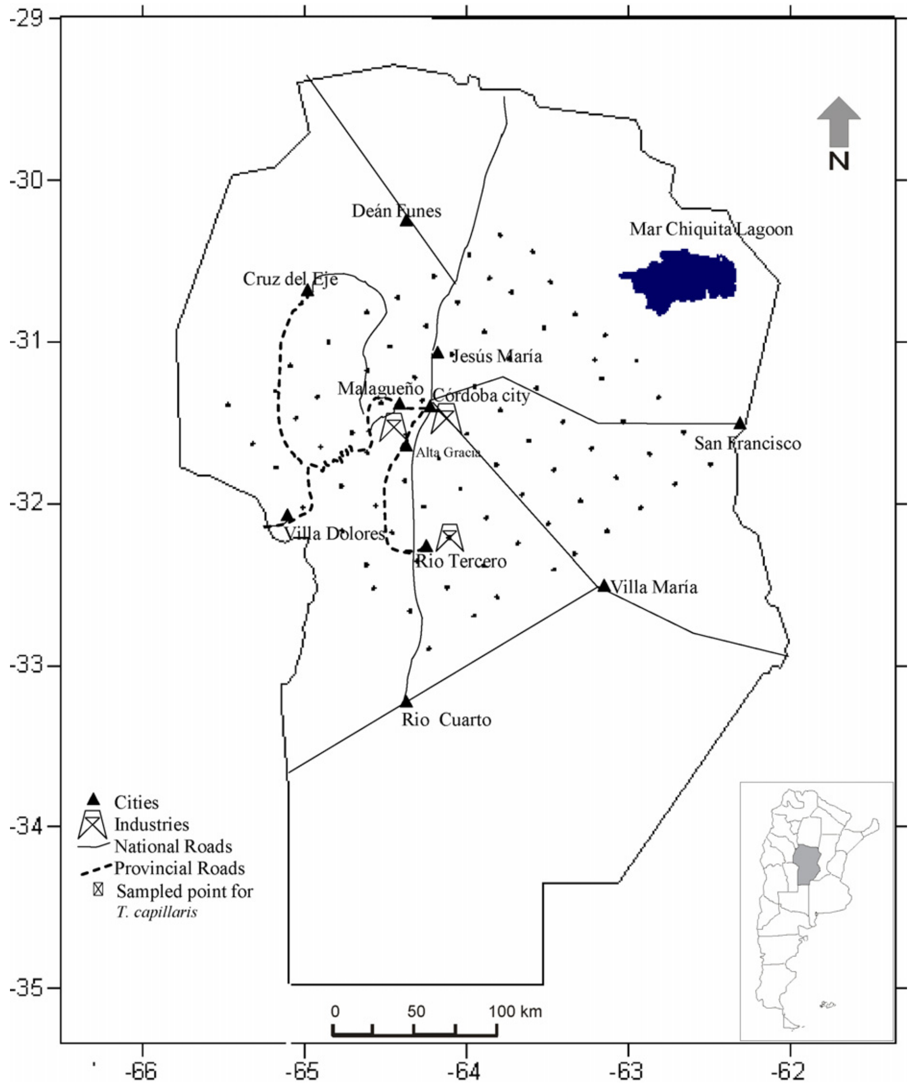

Fig. 1. Localization of the study area in Córdoba province, showing sampling sites and characterizing air pollutant emission sources.

The most important cities closest to the sampling sites are Córdoba (c. 1.3 million inhabitants), Río Cuarto (c. 155,000 inhabitants), Villa María (c. 90,000 inhabitants), San Francisco (c. 60,000 inhabitants), Villa Carlos Paz (c. 56,000 inhabitants), Río Tercero (c. 46,000 inhabitants), Alta Gracia (c. 50,000 inhabitants), Jesús María (c. 37,000 inhabitants), Villa Dolores (c. 28,000 inhabitants) and Cruz de Eje (c. 28,000 inhabitants). The main industrial activities of the city of Córdoba are metallurgic, although there is also a cement factory 18 km SW of the city which uses an industrial waste incinerator. Moreover, the province has important petrochemical and chemical industries situated 110 km south of Córdoba city in Río Tercero. The meteorological data for the whole sampling period were obtained from the weather station located at the center of the study area (31°51′S and 63°44′W). Table 1 presents monthly means of temperature and rainfall during the sampling months, and 2 months before.

2.2. Biological material and sampling procedures

For sampling purposes, the study area was divided into squares, with each square measuring 25 km × 25 km (81 sampling sites in all). Samples of *T. capillaris* Ruiz & Pav. f. *capillaris* were collected at each intersection point whenever present. Three samplings were made during the years 2001, 2002 and 2003 and the biomonitor was found in 52, 53 and 57 sites, respectively. Each sampling period started in November and continued for a period of 2 months,

Table 1
Monthly means of temperatures and rainfall during the study period.

	Year 2001		Year 2002		Year 2003	
	Rainfall (mm)	Mean *T* (°C)	Rainfall (mm)	Mean *T* (°C)	Rainfall (mm)	Mean *T* (°C)
September	110	13.0	26	13.7	4	13.7
October	114	17.2	32	18.9	20	18.8
November	113	19.5	250	21.6	60	21.8
December	84	22.6	117	22.3	123	21.6
Total	421	18.08	425	19.13	207	19.98

sampling was only done if there had been no rain during the previous 5 days, with an average of four sampling sites on each working day. At each sampling site, three pools ($n = 3$) composed of 15–20 individuals of *T. capillaris*, were randomly collected along the four cardinal directions, in a quadrant of 100 m × 100 m. The sample collections were made using plastic gloves, to avoid any sort of contamination, and immediately placed into paper bags according to Sloof (1993). Back in the laboratory, any foreign particles were eliminated manually from the plants in each pool. Also, in order to represent in more detail the most important city of the area under study, another sampling site was incorporated in the vicinity of the city of Córdoba (site 42.1).

2.3. Characterization of sampling sites

The sites were categorized according to Wannaz et al. (2006). Land use, anthropic activities and/or proximity to heavy metal emission sources were characterized at each sampling site in the province of Córdoba. Each category was graded on a scale of 1–3, where 1 represents the condition with the lowest anthropogenic activity and/or absence of known emission sources. The variables taken into consideration to score the areas were:

- *Agricultural*: This variable was chosen due to the fact that in the Córdoba province there are vast areas dedicated to extensive agriculture where pesticides and phosphate fertilizers are used, which can cause the incorporation of toxic substances, such as heavy metals, into the soil (Giuffré de López Camelo et al., 1997). The categories designated were: (1) no agricultural activity, (2) low agricultural activity, and (3) agriculture as the main activity.
- *Urban-Industrial*: In this variable, the presence and/or distance from towns with pollutants emitted by chemical, petrochemical and metallurgic-metallic industries were considered. Category (1) included sites located in areas without industries or in urban centers. Category (2) included the sampling sites close to urban centers (less than 10 km) with a population of 5,000–40,000 inhabitants and with some small industries. Category (3) included the areas close to large industries and cities with a population of over 40,000 inhabitants.
- *Vehicular traffic*: We used this variable to asses the contribution of metals from vehicular traffic, considering that traffic is the main source of urban air pollution in Córdoba city (Olcese and Toselli, 2004), and the study area has many roads with heavy traffic. It was categorized according to the distance of the sampling points to roads with high, medium on low levels of traffic (Fig. 1). Therefore, category (1) represented the absence of nearby roads (more than 3 km), category (2) included sites near secondary roads (within 3 km) with scarce vehicular traffic, and category (3) included the sites near main roads (within 3 km) such as roads with circulation of long distance buses, heavy trucks, vehicles, etc.

On the other hand, a Pearson correlation coefficient was calculated between altitude of each sampling site and the concentration of heavy metals in the biomonitor, to rule out any possible association (data not shown). We did not find any association, which agrees with previous studies that demonstrated that altitude had no influence elemental accumulation in biomonitors (Wannaz et al., 2006).

2.4. Heavy metals quantification

Unwashed *T. capillaris* leaves from each pool ($n = 3$ for site) were dried to constant weight in an oven at 50 ± 2 °C, and 5 g dry weight of this material was taken for elemental analysis by Atomic Absorption Spectrometry (AAS). The material was ground and reduced to ashes at 450 °C for 12 h. Then, the ashes were digested using a mixture of HCl (18%) and concentrated HNO_3 (5:1) v/v, and the solid residue was separated by centrifugation. Finally, the volume was adjusted to 25 mL with Milli-Q water and analyzed by AAS using a Perkin Elmer Spectrophotometer Model AA 3110 in order to determine the concentrations of Co, Cu, Fe, Mn, Ni, Pb and Zn. The certified material IAEA/V-10 Hay Powder was analyzed every 20 samples in order to control the analytical method. Digestion blanks were prepared and analyzed in the same manner as described above (Pfeiffer and Barclay-Estrup, 1992). All these results were expressed in $\mu g\, g^{-1}$ DW.

2.5. Dry weight/fresh weight ratio

The dry weight/fresh weight ratio (DW/FW) of the samples was determined by drying 4 g fresh material at 60 ± 2 °C until reaching constant weight. The results were expressed in g DW/g FW (Table 2).

2.6. Data analysis

Categorical environmental data were standardized to mean zero and variance equal to one. Spearman's coefficient of correlation was calculated in order to study the relationship between the heavy metals accumulated in the biomonitors and categorical variables, while Pearson's correlation coefficient was calculated between altitude and data from biomonitors.

Analysis of variance (ANOVA) was performed to compare the concentration of elements acumulated during the diferent sampling years. Pairwise comparison of means by least significant difference (LSD) was carried out whenever the ANOVA indicated significant differences between means ($p < 0.05$).

Principal component analysis (PCA) was used to analyze data from the three years of study in order to reduce the dimension of the data set. Only factors with eigenvalues over one were considered.

Kriging method was used to interpolate heavy metals concentration values in the study area. The kriging and contour plot derivation were performed using the software Surfer 8.02.

Finally, a variogram analysis was carried out to further corroborate the results from the multivariate analysis, with variogram models (spherical, exponential, linear and gaussian) being obtained with the software package GS$^+$ (Gamma Design).

3. Results and discussion

3.1. Descriptive statistics

Table 2 shows the mean values of heavy metals quantified in *T. capillaris* on each sampling year. These values are similar to those found in a passive biomonitoring study conducted with this species in the province of Córdoba, where the metals were measured by Total Reflection X-ray Fluorescence (TXRF) (Wannaz et al., 2006), but are lower than those reported by Zambrano García et al. (2009) in a study conducted with *Tillandsia recurvata* in an agricultural and an industrial region of Mexico.

The highest accumulation of Fe, Co and Ni was observed during the first sampling year. These results could be due to the different weather conditions of the mentioned year, i.e. the relatively low temperature and high rainfall could had favored the uptake of atmospheric nutrients. On the contrary, during the last study year rainfall was particularly low on the months before the sampling, therefore the water content of the biomonitors was low (Table 3).

3.2. Correlation analysis

The correlation coefficients (Spearman) among the categorical variables and the heavy metal quantified in the biomonitors for the three sampling years of the study are shown in Table 4. Most of the

Table 2
Mean values, variation coefficient (C.V.) and results of the analysis of variance (ANOVA) of the heavy metals measured in *T. capillaris* in Córdoba, Argentina, during three sampling years.

Heavy metals ($\mu g\,g^{-1}$ DW)	Sampling year						ANOVA
	2001 (sites = 52)		2002 (sites = 57)		2003 (sites = 53)		
	Mean	C.V.	Mean	C.V.	Mean	C.V.	*p*-value
Fe	581.4a	0.32	485.4b	0.61	441.7b	0.63	0.016
Mn	317.4	0.92	319.1	1.53	293.7	1.40	0.962
Co	0.39a	0.35	0.30b	0.68	0.33b	0.61	0.019
Ni	1.29a	0.43	0.97b	0.94	0.91b	0.66	0.020
Cu	12.9	0.35	11.1	0.97	10.5	0.75	0.225
Zn	25.5	0.66	18.7	1.10	24.8	1.04	0.138
Pb	1.02	0.57	0.84	1.18	0.81	1.09	0.362

Note: values followed by the same letter do not differ significantly at $p < 0.05$ (test a posteriori: least significant differency – LSD). ANOVA among sampling years.

Table 3
Mean values ± standard deviation (SD) of DW/FW ($g\,g^{-1}$) measured in *T. capillaris* leaves.

Year	Mean	SD
2001	0.212b	0.030
2002	0.212b	0.026
2003	0.233a	0.038
ANOVA (*p*-value)	0.007	

Note: values followed by the same letter do not differ significantly at $p < 0.05$ (test a posteriori: LSD). ANOVA among sampling years.

elements quantified in leaves of *T. capillaris* (Fe, Co, Ni, Cu and Zn) showed significant correlations with the Urban-Industrial variable during the three sampling years, with the exception of Co that did not correlate in the last sampling year.

It has been demonstrated that in industrial areas the concentration of heavy metals in the atmosphere depends mainly on the type and size of industries. Thus, Cd, Cu, Ni, Pb, Sr, Zn and Mn are emitted by metal industries (Asami, 1975); Pb, Ni and Cd are emitted by battery factories (Tyler, 1970) while Cu, Co, Cd, Cr, Ni, Se, V, Zn, Be, Pb, Fe and Ti are emitted by chemical industries (Severson and Gouth, 1976) and cement plants (Schuhmacher et al., 2004; Isikli et al., 2006). In our study the concentrations of heavy metals measured in the biomonitors were associated to metal-mechanic factories located in Córdoba city, chemical industries in Río Tercero and cement plant incinerators in Malagueño.

In relation to vehicular traffic, our results indicated an important association of this emission source with Zn, showing a significant correlation during the three sampling years. Previous biomonitoring studies with *T. capillaris* also showed a Zn enrichment in areas with high vehicular traffic (Wannaz et al., 2006; Wannaz and Pignata, 2006; Rodriguez et al., 2011a) and chemical industries (Rodriguez et al., 2011b). Similarly, in another biomonitoring study using *Tillandsia usneoides* in the city of Sao Paulo, Brasil, Ba and Ca as well as Zn enrichment was perceived in areas with heavy traffic (Figueiredo et al., 2007). Indeed Zinc has been mentioned as one of the main elements released by brake shoes, therefore it can be used as an indicator of vehicular traffic (Davis and Williams, 1975).

The Agricultural variable was correlated with Mn content in all sampling years and with Pb in the last year of sampling. Previously, Pignata et al. (2002) in a study performed with the same species, observed Mn enrichment in agricultural areas, which was attributed to the use of pesticides. In the last decade, there was a huge increase in the use of agrochemicals in Argentina, which is nowadays one of the major producers of soybean worldwide (Giuffré de López Camelo et al., 1997; Ghida Daza, 2005). Our results are also supported by the results of Bermudez et al. (2009) in an active biomonitoring study, that demonstrated Mn enrichment in agricultural areas.

Table 4
Correlation coefficients (Spearman) between categorical environmental variables and heavy metals measured in *T. capillaris* in Córdoba, Argentina.

Year	Variables	Urban industrial	Vehicular traffic	Agricultural
2001	Mn			0.37**
	Fe	0.35**		
	Co	0.33*		
	Ni	0.38**		
	Cu	0.29*		
	Zn	0.41***	0.28*	
	Pb			
2002	Mn			0.32*
	Fe	0.27*		
	Co	0.38**		
	Ni	0.45***		
	Cu	0.41***		
	Zn	0.47***	0.33*	
	Pb			
2003	Mn			0.38**
	Fe	0.36**		
	Co			
	Ni	0.36*		
	Cu	0.33**		
	Zn	0.38**	0.35**	
	Pb			0.39**

* $p < 0.05$.
** $p < 0.01$.
*** $p < 0.001$.

3.3. Principal component analysis (PCA)

The results of the PCA are reported in Table 5. According to Qishlaqi et al. (2009), the association of different metals in the same component may indicate a common source (litogenic, anthropogenic or mixed). In our study, the heavy metals that contributed to the first component (Zn, Co, Ni, Fe and Cu) may be related to Urban Industrial and Vehicular Traffic emissions sources (Table 4). The second component was driven by Mn, associated to agriculture and the third one was related only to Pb.

Table 5
Eigenvectors obtained from a principal components analysis of heavy metals measured in *T. capillaris* in Córdoba, Argentina.

Heavy metals	Component		
	1	2	3
Zn	0.73	−0.17	−0.02
Ni	0.71	−0.02	−0.03
Fe	0.69	0.13	0.06
Cu	0.57	0.22	0.04
Co	0.55	−0.47	−0.51
Mn	0.38	0.75	0.14
Pb	0.24	−0.43	0.84
Eigenvalues	2.34	1.07	1.00
Accumulated variance (%)	33.4	48.8	63.1

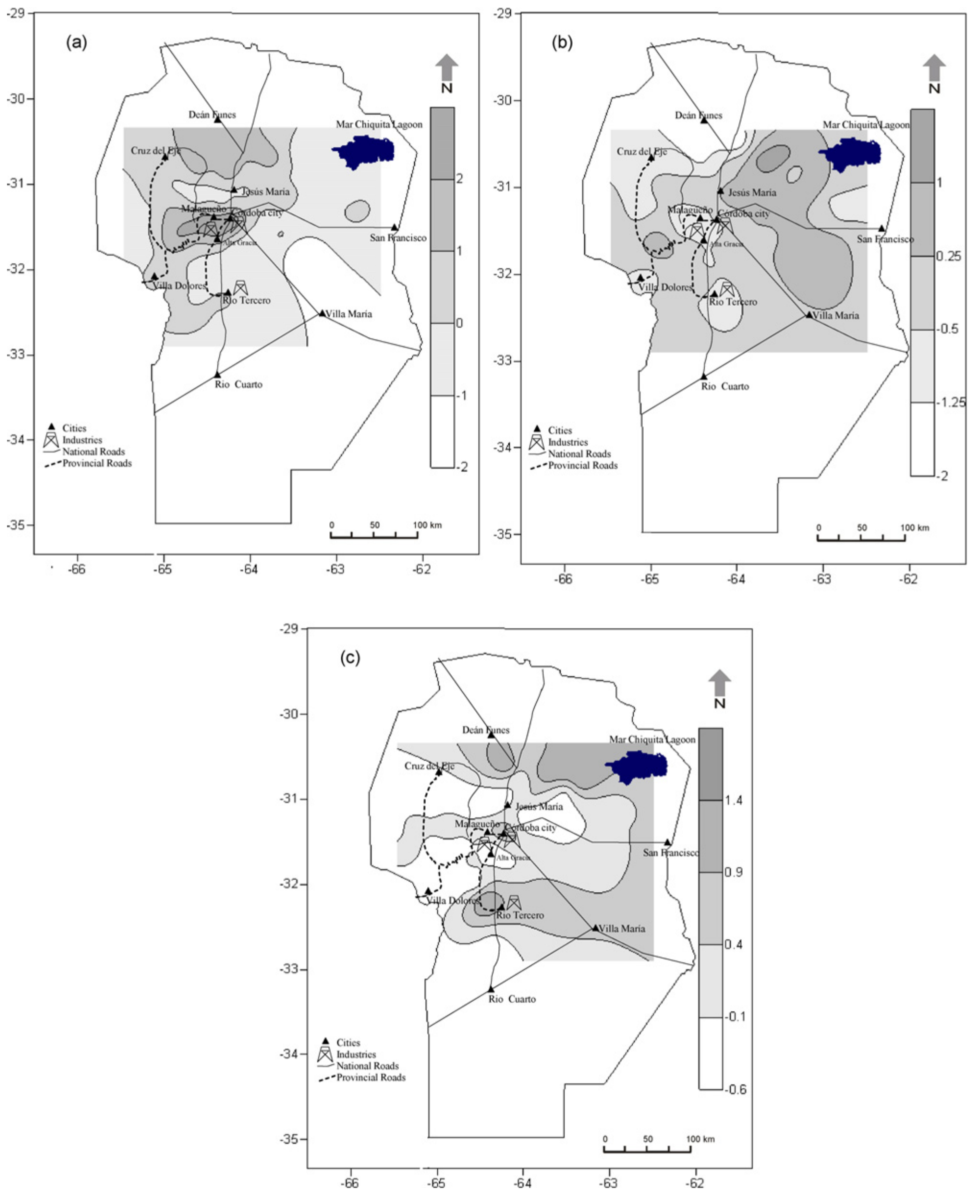

Fig. 2. Geographic distribution of the first (a), second (b) and third (c) principal component obtained from the PCA made with the measured elements in *T. capillaris*.

The results of the PCA analysis agree with those obtained with correlation analysis confirming the classification of emission sources in the study area.

In order to identify the main emission sources and to geographically integrate the results obtained in the previous analyses, we made distribution maps with the scores obtained for each component on the basis of the PCA (Fig. 2). The first component highlights the area surrounding Córdoba city, suggesting that concentrations of Zn, Ni, Fe, Cu, Co in *T. capillaris* are affected by urban emissions sources. The distribution of the second component, attributed

Table 6
Semivariogram models for the first three principal components and their parameters.

Component	Model	Nugget	Sill	Range	NRS	R^2	RSS
1	Spherical	0.001	1.620	0.333	0.0053	0.725	0.158
	Exponential	0.001	1.637	0.393	0.0051	0.604	0.230
	Linear	1.320	1.680	1.164	0.4772	0.142	0.479
	Gaussian	0.001	1.625	0.268	0.0006	0.727	0.153
2	Spherical	0.001	0.778	0.421	0.0012	0.880	0.039
	Exponential	0.001	0.788	0.510	0.0013	0.714	0.083
	Linear	0.558	0.823	1.195	0.6780	0.193	0.204
	Gaussian	0.001	0.781	0.336	0.0012	0.893	0.029
3	Spherical	0.008	0.589	0.583	0.0135	0.921	0.008
	Exponential	0.001	0.604	0.660	0.0016	0.897	0.011
	Linear	0.346	0.653	1.164	0.5298	0.567	0.044
	Gaussian	0.135	0.586	0.457	0.2303	0.921	0.008

to agricultural activities, agrees with the agricultural area in the province. The map of the third component revealed high Pb concentrations to the south, near the city of Río Tercero where several petrochemical industries are located, but also to the northeast area of Córdoba province, which could be attributed to dove hunting activities based on similar findings reported by Bermudez et al. (2010) who found an enrichment of Pb in top soils from that area which they attributed to dove hunting activities. Similarly, Manninen and Tanskanen (1993) in Finland and Chrastný and Komárek (2010) in the Czech Republic, informed Pb contamination in top soils from different shooting ranges. In the last 15 years sport hunting and particularly dove hunting was greatly benefited from the expansion of agriculture in the province of Cordoba. Therefore, the soil of the hunting areas can be enriched with Pb contained in the bullets used by the hunters. After that, Pb containing particles can reach the biomonitors due to mobilization processes and transportation of soil by the wind. Moreover, the incineration of wastes is a common practice after the hunt, which would contribute to the lead dispersion in the atmosphere. The sampling design of the present study was not made to evaluate this particular Pb emission source. However, considering that Pb contamination of soils used for agriculture is a major concern for human health (Ma, 1996) and the fact that there is no information on the hunting influence in this area, we decided to perform an exploratory analysis. We did an ANOVA to compare these potential hunting places (sites 57, 58, 29, 66 and 67) with the rest of the sites with no emission sources nearby. We found that Pb accumulation was higher in the dove hunting areas, although the differences were significant only for the first year. Lead is known as reproductive toxicants for humans and other mammals. In addition to direct toxicity, Pb can interfere with the metabolism of certain essential elements including copper, zinc and selenium by affecting their absorption, distribution, and bioavailability (Nordberg et al., 2007). Despite the fact that these are preliminary results, they highlight the need to perform further studies, moreover if we consider the high number of pellets deposited on the soil and the high number of hunters that come annually to this area of Cordoba.

3.4. Geostatistical analysis

Geostatistics is based on the theory of a regionalized variable (Matheron, 1963), which is distributed in space (with spatial coordinates) and shows spatial autocorrelation, therefore samples close together in space are more alike than those that are further apart (McGrath et al., 2004). The scores obtained for each component on the basis of the PCA were used to determine the autocorrelation value and to produce a minimum unbiased variance estimate, calculated as a function of a semivariogram. The variogram is a mathematical description of the relationship (structure) between the variance of pairs of observations (data points) and the distance separating them (Isaaks and Srivastava, 1989). According to the sampling grid, no anisotropy was evident in the directional semivariograms, thus isotropic semivariogram models (spherical, exponential, Gaussian and linear) could be fitted to the data. The attributes of the semivariogram for the PC1, PC2 and PC3 data are shown in Table 5. PC1 and PC2 were fitted to the Gaussian model, and PC3 was fitted to the spherical model, with high coefficients of determination (R^2) and a low residual sum of squares (RRS) being observed. The values of the nugget to sill ratio can be used as a criterion for determining the spatial dependence of variables. If the ratio is less than 25%, then the variable has strong spatial dependence. Values between 25% and 75%, indicate moderate spatial dependence, and ratios greater than 75%, show only weak spatial dependence (Lui et al., 2004). This study had a strong spatial dependence of all principal components (PC), which could indicate the presence of emission sources in the study area or that the distribution of heavy metals in the study area is not random. Another parameter to consider in the analysis of the variogram is the range, and Table 5 shows that the range values were 0.268, 0.336 and 0.583 for PC1, PC2 and PC3, respectively. The range is a measure of spatial dependence, with the rate of change of this variable being independent of the separation of the observations. By transforming the values of the range into kilometers (assuming that 1° is about 111 km), we calculated the range values for PC1: 30 km, PC2: 37 km and PC3: 65 km, thus producing information on the type of source for the metals associated to these components. For example, Zn, Co, Ni, Fe and Cu presented emission sources with an influence of up to 30 km, which coincides with the presence of urban centers and industries. The variogram for PC3 showed a range of about 65 km, suggesting the presence of a diffuse source for this component distributed over a large part of the study area. This result reinforces the hypothesis that dove hunting is a strong Pb emission source in the study area (Table 6).

4. Conclusions

The statistical analysis employed in the present study, showed a similar pattern of accumulation of heavy metals in *T. capillaris* during the three sampling years, which may indicate the same type and intensity of emissions. The results revealed that the industrial activity in Córdoba produced the biggest input of heavy metals into the atmosphere, vehicular traffic contributed mainly with Zn while agricultural activities influenced Mn enrichment in the *T. capillaris* leaves. The accumulation of Pb in *T. capillaris* demonstrated the significant contribution of industrial activity and dove hunting activities, indicating a serious health risk for the people living there. However, further studies are needed to confirm the Pb increase in soil, water and crops and to assess the magnitude and impact of this activity on human health.

Acknowledgments

This work was partially supported by the Secretaría de Ciencia y Técnica de la Universidad Nacional de Córdoba (SECYT-UNC) and the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET). Special thanks to Dr. P. Hobson (native speaker) for language revision.

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