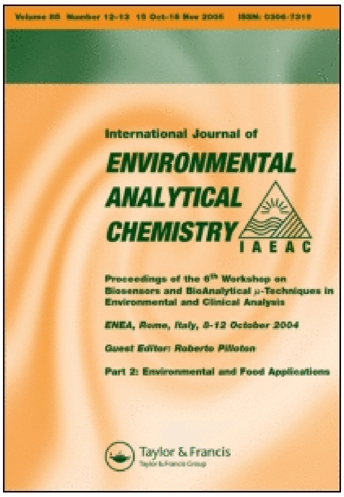

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Identification of atmospheric trace-element sources by passive biomonitoring employing PCA and variogram analysis

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The epiphyte plant *Tillandsia capillaris* was used as a passive biomonitor to study the relationship between elemental accumulation and emission sources in the province of Córdoba, Argentina. The concentrations of As, Ba, Br, Ca, Ce, Co, Cr, Cs, Eu, Fe, Gd, Hf, K, La, Lu, Na, Nd, Rb, Sb, Sc, Se, Sm, Ta, Tb, Th, U, Yb, and Zn were determined in *T. capillaris* leaves by Instrumental Neutron Activation Analysis. A variogram analysis was performed to identify the emission sources of these elements in the study area, obtaining different patterns for each element analysed. A principal-component analysis was subsequently performed to further confirm the different contaminant emission sources and it coincided with the results of the variogram analysis. We observed that the enrichment of most elements was associated with natural sources (soil) and that only some elements showed evidence of enrichement related to sources such as traffic (K, Sb and Zn), industries (Br), and mining activity (Ca).

Keywords: Tillandsia capillaris; Biomonitoring; INNA; Variogram and factor analysis; Córdoba province; Argentina

1. Introduction

The use of living organisms to monitor environmental quality is now widely accepted. Furthermore, the use of corroborative information obtained from biomonitoring surveys is highly recommended in order to support the limited data obtained by physico-chemical measurements [1, 2]. While geobotanical studies do not give information on the plant chemistry, the use of bioindicators in field studies has the great advantage of enabling long-term monitoring studies that do not require a widespread establishment and maintenance of sophisticated and costly equipment. Besides, intensive biomonitoring is a necessary component for any programme aiming to achieve an effective long-term observation of air pollution [2, 3].

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Bioaccumulation monitoring methods can be divided into active and passive. Active monitoring includes the exposure of well-defined species under controlled conditions, whereas passive monitoring refers to the observation or chemical analysis of 'inside' indigenous plants. Active biomonitoring can be divided into transplantation, test plant, and test chamber methods [4].

It should be made clear that although bioindicators reflect atmospheric pollution, their use is more closely related to the concept of atmospheric quality, since the term 'pollution' could be defined as that situation in which concentrations of some elements and compounds are above set values, according to given standards [5]. These values should be measured by instruments on an individual basis. On the other hand, the term 'atmospheric quality' is used almost exclusively to indicate the atmospheric condition that is defined by means of the use of bioindicators and/or biomonitors, for they cannot provide information about concentrations of compounds or elements in air, since about their effects [6].

Epiphytic plants are efficient air pollution biomonitors because they have no functional roots in contact with the soil to obtain their nutrients from the atmosphere. Therefore, the elemental composition of their tissues and their physiological responses largely reflect the atmospheric input of air pollutants, such as toxic gases and heavy metals [7].

In Argentina, studies on the multielemental composition of atmospheric pollutants with bioindicators have been performed mainly with lichens [8–15]. However, over the last years several studies have been carried out using species from the *Tillandsia* genus [16–18].

The object of the present study was to identify emission sources of trace elements in Córdoba, Argentina, using *T. capillaris* as a passive biomonitor, and to explore different techniques to statistically analyse the data obtained through the biomonitoring approach.

2. Experimental

2.1 *Study area and sampling procedure*

A study area of 50 000 km [2], located in the central region of the Argentine Republic, was selected, bounded by a quadrilateral whose extreme points had the following coordinates: to the west, 31° 25′ 21″ S, 65° 24′ W; to the east, 31° 41′ 15″ S, 62° 38′ 34″ W; to the north, 30° 36′ S, 63° 15′ W; to the south, 32° 52′ S, 64° 10′ 12″ W. Land morphology is highly variable, ranging from a mean altitude of about 250 m in the southeast to more than 2500 m to the mid-west. Regarding the geology of the sample area, it can be mentioned that in the high lands of the province of Córdoba, there are metamorphic proteozoic rocks where calcoalkaline granitoids are placed. In the low lands, there are loessic deposits that are alternated with tertiary and quaternary era fluvial sediments [19].

The area is formed by the following phitogeographical regions: Chaco province (West and East Chaco), Del Espinal province and steppe Pampa [20]. Among the most important lakes in the area under study are: San Roque Lake, Los Molinos Lake and Cruz del Eje Lake.

From a demographic point of view, large and medium-sized cities and many small villages are found in the area. Industrial plants (mainly metallurgical, petrochemical, or chemical), food, vegetable oil, and cement factories are mostly located in the centre and south where the highest population density is recorded.

For sampling purposes, the study area was divided into squares, each measuring 25 × 25 km (81 sampling sites in all). *Tillandsia capillaris* samples were collected at each intersection point whenever present (only 52 sites were sampled) from 4 December 2000 to 28 February 2001. The collection sites were located at least 500 m away from main roads and densely populated areas, and at least 300 m from streets with low traffic density (figure 1).

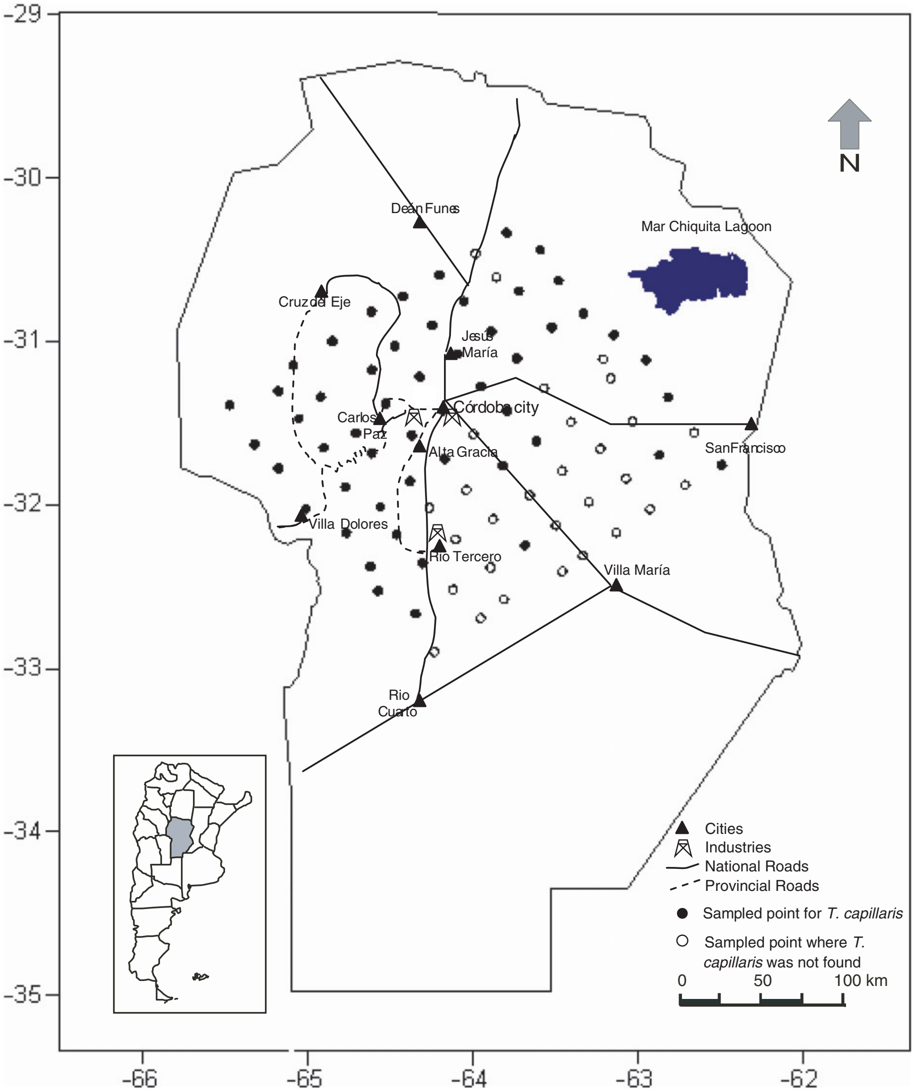

Figure 1. Localization of the study area with sampling sites.

Each sample consisted of 15–20 individuals randomly collected along the four cardinal directions within an area of 100 × 100 m, but no further than 100 m from the geographical reference point. Sampling was only performed when it had not rained in the area during the previous 5 days. Plant samples were collected at a height of 2–3 m using plastic gloves, and all foreign materials were removed in order to avoid the risk of sample contamination [21]. We collected leaves from each individual to form a pool that was later used for the INNA analysis.

2.2 *Neutron activation analysis*

T. capillaris samples were ground in a mortar using liquid nitrogen and freeze-dried for 24 h. About 300 mg of freeze-dried material was pelletised and wrapped-up in aluminium foil for irradiation together with two certified reference materials, NIST 1633b Coal Fly Ash and IAEA V-10 Hay Powder or Lichen 336.

Irradiation was performed for 7 h using the RA-3 reactor (thermal flux $3 \times 10^{13}\,\mathrm{cm}^{-1}\,\mathrm{s}^{-1}$, 5 MW) at the Ezeiza Atomic Centre (CNEA: Argentinian National Atomic Energy Committee). Instrumental Neutron Activation Analysis (INAA) was carried out by taking two measurements after 6 and 30 days of decay with GeHP detectors (30% efficiency, 1.8 keV resolution for the 1332.5 keV ^{60}Co peak), using Gamma Vision software for data collection.

The concentrations of As, Ba, Br, Ca, Ce, Co, Cr, Cs, Eu, Fe, Gd, Hf, K, La, Lu, Na, Nd, Rb, Sb, Sc, Se, Sm, Ta, Tb, Th, U, Yb, and Zn were estimated using a software program developed at the INAA laboratory. Control charts (z-values) were used to inspect normalised concentrations in a series of measurements of one control sample for every element analysed [22]. All values were within the $|z| < 3$ range. NIST SRM 1547 Peach Leaves, 679 Brick Clay, and 2709 San Joaquín Soil were used as control samples.

Three certified reference materials were used as control: IAEA Lichen 336, NIST SRM 1547 Peach Leaves and GBW07105 Rock with the purpose of performing a quality control. The results of the first one are included in Table 1, and they represent the average of two determinations. In general, there is agreement between expected and experimental values.

2.3 *Data analysis*

Twenty-eight elements were selected for principal-component analysis (PCA) and then rotated with Varimax rotation. Keeping the factors with eigenvalues over one, a total of four factors were chosen that accounted for approximately 85% of the total variance, indicating that the results are statistically consistent. The analysis was performed using SPSS version 10.0.

A mapping procedure was used to evaluate the distribution of the elements suspected of having an anthropogenic origin. The contour plots were calculated by means of Kriging estimation using Surfer 8.02. A variogram analysis was performed using spatial modelling (linear model), whereas the interpolation method of Kriging [23] was also performed using Surfer 8.02 software.

Table 1. Instrumental neutron activation analysis of the reference material IAEA Lichen 336 (values expressed in $\mathrm{mg\,kg^{-1}}$ of dry mass).

Element	Certified value	Experimental value	SD (%)	Detection limit (ppm)
As	0.63 ± 0.08	0.646 ± 0.046	7.1	0.1
Ba	6.4 ± 1.1	6.38 ± 0.99	16	4
Br	12.9 ± 1.7	11.48 ± 0.43	3.7	0.19
Ca	NC[b]	2400 ± 230		300
Ce	1.28 ± 0.17	1.18 ± 0.15	13	0.11
Co	0.29 ± 0.05	0.261 ± 0.012	3.8	0.01
Cr	1.06 ± 0.17	1.044 ± 0.016	1.5	0.19
Cs	0.110 ± 0.013	0.1085 ± 0.0077	7.1	0.023
Eu	0.023 ± 0.004	0.0258 ± 0.0004	1.4	0.0022
Fe	430 ± 50	407.1 ± 6.2	3.9	9.9
Gd	NC[b]	< LD[a]		0.18
Hf	NC[b]	0.0562 ± 0.0017		0.014
K	1840 ± 200	1812 ± 52	2.8	95
La	0.66 ± 0.10	0.643 ± 0.039	6	0.0057
Lu	0.0066 ± 0.0024	0.0069 ± 0.0003	4.3	0.0026
Na	320 ± 40	302 ± 26	8.6	2.6
Nd	0.60 ± 0.18	< LD[a]		0.7
Rb	1.76 ± 0.22	1.655 ± 0.078	4.7	0.45
Sb	0.073 ± 0.010	0.0713 ± 0.00035	4.9	0.0089
Sc	0.17 ± 0.02	0.1678 ± 0.0063	3.8	0.0022
Se	0.22 ± 0.04	0.169 ± 0.031	18	0.073
Sm	0.106 ± 0.014	0.1075 ± 0.0085	7.9	0.0021
Ta	NC[b]	0.0173 ± 0.0020		0.0055
Tb	0.014 ± 0.002	< LD[a]		0.019
Th	0.14 ± 0.02	0.1394 ± 0.0077	5.5	0.02
U	NC[b]	< LD[a]		0.056
Yb	0.037 ± 0.0125	0.0448 ± 0.0067	15	0.012
Zn	30.4 ± 3.4	27.0 ± 1.7	6.3	1.5

[a] < LD, concentrations below the detection limits.
[b] NC, not certified for this element; no information value available.

3. Results and discussion

3.1 *Data analysis*

Table 2 shows the mean, minimum, and maximum values and the coefficients of variation for each element measured in *T. capillaris* samples obtained from the study area ($n = 52$). The values of maximum concentration for As, Br, Ca, Ce, Cr, Fe, La, Na, Rb, Sc, Sm, Th, U, and Yb were higher than the values obtained in *Tillandsia usneoides* samples exposed to different metropolitan areas of Sao Paulo for 8 weeks [24]. However, the values for Ba, Co, Eu, Sb, and Nd were within the same order as those observed in the aforementioned study, and the maximum concentrations for Zn were lower.

The concentrations of Br, Co, Fe, and Zn measured in this study were higher compared with previous results for the same species in the same study area [18]. Nonetheless, the differences found might have been caused on the one hand by the way of expressing results, and on the other hand, by the technique that has been used (TXRF) in this procedure, which does not digest the silicates. Therefore, the results reported hereby refer to pseudototal metals. The INNA technique used in this work measures the total content of metals.

When we compare the values found in *R. celastri* [25] with those found in this research work, we observe that, except for As and Zn, the concentrations of all the

Table 2. Mean (mg g^{-1} DW), range, and coefficient of variation (CV) of the elemental concentration found in *T. capillaris* samples from Córdoba, Argentina ($n = 52$).

Element	Mean	Range (min.–max.)	CV
As	1.616	0.565–3.525	0.429
Ba	51.48	22.23–110.89	0.335
Br	14.94	6.61–39.34	0.441
Ca	8062	3928–20003	0.378
Ce	5.989	1.451–11.459	0.394
Co	1.551	0.457–2.901	0.373
Cr	4.108	1.219–7.644	0.351
Cs	0.770	0.265–1.931	0.424
Eu	0.095	0.025–0.161	0.369
Fe	2954.3	851.1–5441.8	0.354
Gd	0.460	0.189–0.877	0.339
Hf	0.469	0.142–0.868	0.370
K	10786	5840–17862	0.253
La	2.950	0.883–6.144	0.408
Lu	0.038	0.008–0.081	0.437
Na	1744.2	753.6–6895.6	0.636
Nd	3.396	1.015–6.882	0.386
Rb	12.19	4.97–22.20	0.325
Sb	0.182	0.069–0.864	0.737
Sc	1.002	0.275–1.987	0.375
Se	0.315	0.131–0.529	0.318
Sm	0.523	0.017–1.201	0.523
Ta	0.092	0.027–0.196	0.389
Tb	0.075	0.039–0.125	0.338
Th	1.016	0.236–2.270	0.448
U	0.279	0.096–0.596	0.442
Yb	0.247	0.084–0.497	0.412
Zn	26.72	11.84–108.38	0.651

elements quantified in *T. capillaris* were higher than the concentrations of the same elements found in *R. celastri*. This fact suggests that *T. capillaris* behaves as a better accumulation biomonitor than *R. celastri* for Ba, Br, Ca, Ce, Co, Cr, Cs, Eu, Fe, Gd, Hf, K, La, Lu, Na, Nd, Rb, Sb, Sc, Se, Sm, Ta, Tb, Th, U, and Yb.

3.2 *Variogram analysis*

The spatial autocorrelation was characterised through the experimental semivariogram. The semivariogram (usually abbreviated as variogram) is the basic tool for the analysis of spatial structure. The variogram is a mathematical description of the relationship (structure) between the variance of pairs of observations (data points) and the distance separating these observations [26].

A variogram slope tending to zero indicates the absence of spatial structure. This is the case of a variable with random distribution [27, 28]. In this research work, the variogram lineal models were applied because the main interest was in having a visual idea of the slope that was formed with each of the variograms modelled.

Figure 2 shows the variograms for As, Ba, Ca, Ce, Co, Cr, Cs, Eu, Fe, Gd, Hf, La, Lu, Nd, Rb, Sb, Sc, Sm, Ta, Tb, Th, U, and Yb, all of which have a horizontal slope. If the value of the tangent to the curve is near 0, it would indicate the absence of emission sources in the study area. It could also be indicating the presence of emission sources with a wide geographical distribution, such as an emission source related to soil. This agrees with an analysis about atmospheric vs. lithogenic contribution to the composition of first- and second-order stream waters in Seoul, where the authors observed that the variograms performed with solutes as Na^+, K^+, and Mg^+ do not show any systematic variation; they simply approach a unity [29]. These trends indicate that sources of these solutes are ubiquitous (mostly lithogenic) in the study area. These authors also observed that the variogram for SO_4^{2-} increased exponentially with increasing distance, due to a source area like Seoul City, unlike regional lithogenic source(s).

On the other hand, the variograms of Br, K, Na, Sb, Se, and Zn have positive slopes (figure 3). These tendencies could be associated with the emission sources of the study area (natural or non-natural).

3.3 *PCA*

PCA on the analytical data was executed in order to obtain a visual representation of the main characteristics. It is an unsupervised multivariate technique in which new variables (called principal components (PCs)) are calculated as linear combinations of the old ones. The combined plot of scores and loadings allows us to recognise groups of

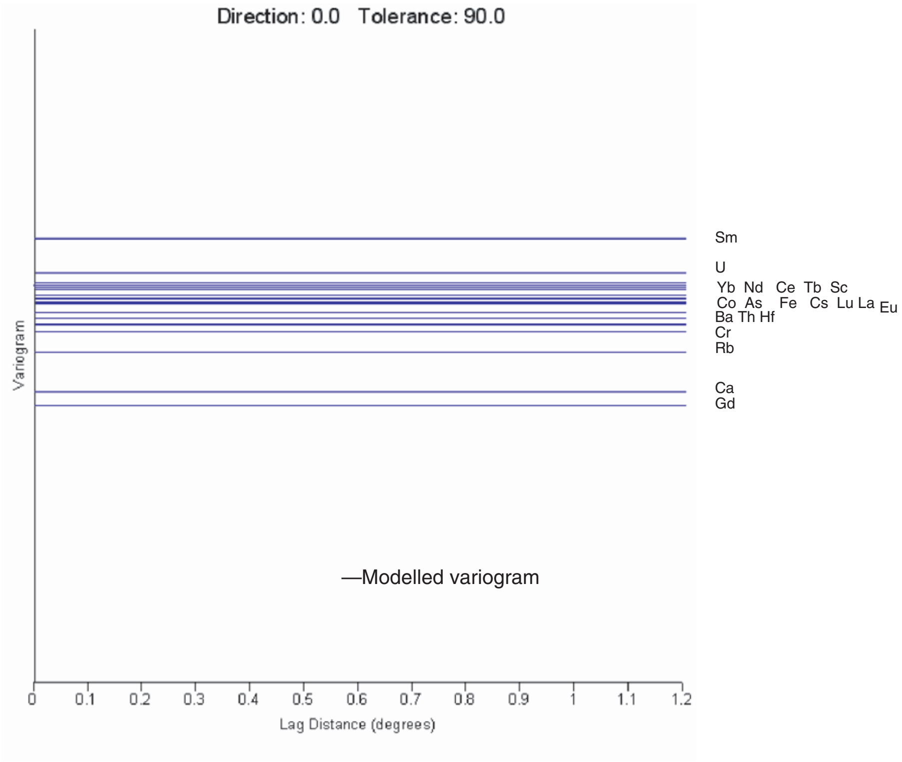

Figure 2. Variogram showing the variance of the diferente elements (As, Ba, Ca, Ce, Co, Cr, Cs, Eu, Fe, Gd, Hf, La, Lu, Nd, Rb, Sb, Sc, Sm, Ta, Tb, Th, U, and Yb) concentrations determined in *T. capillaris* as a function of distance between each sampling.

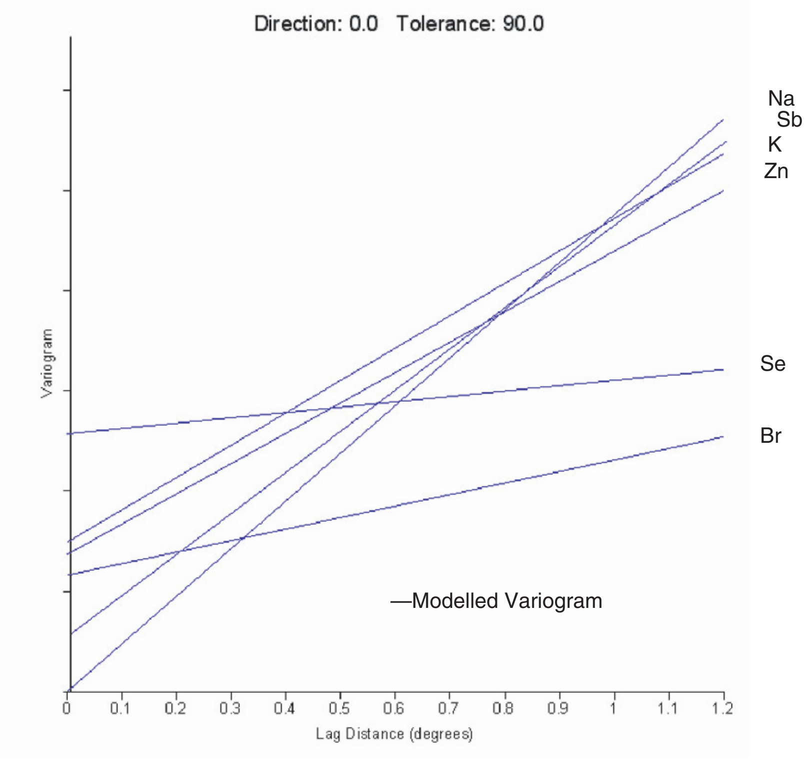

Figure 3. Variogram showing the variance of the diferente elements (Br, K, Na, Sb, Se, and Zn) concentrations determined in *T. capillaris* as a function of distance between each sampling.

samples with similar behaviour and the existing correlation among the original variables [30].

The results of PCA are shown in table 3. Most of the elements appear in the first factor, which can be attributed to soil. In a previous study, performed in the same study area but with another biomonitor [25], it was shown that the concentrations of Ba, Ce, Co, Cr, Cs, Eu, Fe, Hf, La, Lu, Na, Nd, Rb, Sc, Sm, Ta, Tb, Th, and Yb measured in the *Ramalina celastri* lichen can be related to the soil composition. Furthermore, a study using *T. usneoides* as a passive biomonitor in Sao Paulo showed that it was highly probable that soil was the main source of the REE, Fe and Rb [24]. These same elements except Se presented a tangential slope of 0 in the variogram analysis (figure 2). We therefore consider that in this study area, there are no important non-natural emission sources for these elements.

The elements that contribute most to the rest of the components of the analysis are those with a positive slope in the variogram analysis, except for Ca (figure 3). Hence, it is possible to assume that there are different anthropogenic emission sources for these elements within the study area.

The greatest contribution in the second factor is made by K, Sb, and Zn, which is probably related to traffic. In the same sample area, an enrichment of Zn in *R. celastri* was observed, due to vehicular traffic emissions [25].

Table 3. Eigenvectors obtained in the PCA of the elements measured in *T. capillaris* leaves.

	Component			
	1	2	3	4
As	0.798	0.182	−0.159	0.013
Ba	0.904	0.210	0.002	−0.087
Ce	0.973	−0.130	−0.040	0.003
Co	0.946	0.086	0.010	−0.001
Cr	0.815	0.113	−0.260	−0.001
Cs	0.890	−0.052	0.240	0.012
Eu	0.942	0.033	−0.025	0.001
Fe	0.971	0.085	0.006	0.012
Gd	0.808	−0.036	−0.190	0.049
Hf	0.958	−0.034	0.096	−0.004
La	0.960	−0.091	−0.001	0.003
Lu	0.969	0.015	0.099	0.093
Nd	0.763	−0.136	−0.186	−0.081
Rb	0.808	−0.041	0.222	0.017
Sc	0.959	0.089	0.116	0.020
Se	0.765	−0.309	0.036	−0.093
Sm	0.984	−0.034	−0.037	0.097
Ta	0.822	−0.269	0.052	0.020
Tb	0.830	−0.145	−0.401	−0.001
Th	0.931	−0.138	0.117	−0.035
U	0.864	−0.099	0.174	−0.151
Yb	0.961	0.029	0.089	0.093
K	0.244	0.704	0.347	0.319
Sb	0.135	0.801	−0.136	−0.001
Zn	0.290	0.740	0.091	−0.482
Na	−0.043	−0.299	0.673	−0.410
Ca	0.110	0.183	−0.561	0.523
Br	0.028	0.202	0.607	0.678
Total var (%)	64.58	7.97	6.47	5.21
Eigenvalues	17.80	2.23	1.81	1.46

Some authors considered that the concentration of Zn in *T. usneoids* accounted for the presence of vehicular sources [24]. Other authors, on the other hand, emphasised that Ba and Zn are new tracers of vehicle emissions, instead of Pb [31]. It is important to note that rubber tyres contain 58% organic material (polymers and high aromatics), 29% soot (i.e. black carbon), and 13% inorganic material, mainly Zn, Ca, S, Fe, Al, Ti, K, Pb, and Mg [32–34].

The third factor is represented by Na and Ca, but here Ca holds a negative sign, which would indicate a distribution opposite to the Na distribution in the study area. The emission source for Ca in the study area is a lime-producing plant (San Agustín quarries) located 34 km to the north-east of the city of Río Tercero. Na could be related to the Salinas Grandes, a large salt pan in the north-western area of the study area, or Mar Chiquita Lagoon, an extensive hypersaline lake to the north-east.

The only element contributing to the last factor is Br. This element could be associated with traffic, as previously mentioned by other authors [35–37]. Our results are in accordance with what was found using *Ramalina celastri* lichen in the same study area [25]. These authors found high concentrations of Br in an industrial area within the province of Córdoba (Rio Tercero), which were attributed to the presence of heavy chemical (chlor-alkali plants) and petrochemical industries.

3.4 *Mapping*

In order to identify different emission sources within the study area and to geographically integrate the results obtained in the previous analyses, distribution maps were made with the scores obtained for each component on the basis of the PCA. Table 4 shows the

Table 4. Scores for each principal component obtained in the PCA of each sampling site.

Site	CP 1	CP 2	CP 3	CP 4
1	−0.83	0.68	−0.73	0.61
2	−5.09	0.78	−0.96	0.74
4	−2.30	1.43	−0.26	−0.13
5	0.97	0.11	0.22	−0.03
6	−3.01	0.77	−0.54	0.96
7	1.26	1.34	0.00	1.29
8	−1.08	−0.49	−0.36	0.69
9	−1.17	−0.59	−1.24	0.39
10	0.19	2.48	1.64	2.93
11	0.49	0.60	1.20	−0.09
12	−6.03	−0.42	−0.49	0.47
13	2.97	0.08	−1.89	1.77
14	−3.34	−2.14	0.88	−3.83
15	−0.78	−2.09	0.10	−0.35
16	6.01	−2.38	0.66	0.26
17	4.86	−2.14	1.09	0.75
18	−2.52	−2.04	3.77	−0.51
21	−6.35	−1.41	0.22	−0.28
22	−2.42	−0.05	0.41	0.10
23	−0.81	−0.54	−0.98	−0.42
24	−2.96	−0.34	0.02	0.71
25	−2.87	−0.31	−1.45	3.15
30	−1.82	0.33	−0.88	0.43
31	−4.80	−1.29	−1.32	−0.41
32	2.73	−1.81	−2.49	−1.87
33	−0.65	−0.55	0.46	0.11
34	0.97	−0.88	−0.11	−0.74
37	0.36	−0.28	−0.38	−0.66
39	7.23	−2.69	−0.33	0.67
40	6.49	−2.07	−2.06	0.31
41	−6.77	−0.39	1.12	1.12
42	−4.38	−1.55	2.60	−0.04
44	4.11	0.62	2.80	−1.10
48	2.94	−1.61	−1.51	0.16
49	4.53	−0.33	−0.67	0.85
50	3.72	0.08	1.65	0.07
51	−1.86	1.04	1.07	0.82
52	1.49	0.85	−0.96	−0.65
53	2.75	1.25	0.98	−0.70
57	−1.82	−0.28	0.68	0.00
58	−1.33	−0.10	0.14	−0.15
59	−2.57	−0.15	−0.40	0.40
60	5.73	0.50	0.02	−0.18
68	5.61	1.87	−0.36	−1.14
69	−4.50	1.16	0.78	0.42
73	−0.65	1.75	0.36	−1.10
75	5.23	2.93	0.01	−0.37
76	8.74	2.55	1.34	−0.04
77	−6.64	1.63	−1.37	−1.63
78	6.69	0.40	−0.46	−0.64
79	−2.61	3.14	−1.53	−2.97
80	−4.09	0.55	−0.46	−0.14

contribution of each sampling site (score) to each of four components calculated in the PCA.

Figure 4 shows the distribution map for the scores of the first component. The distribution of this component, attributed to soil, coincides with the region with the greatest agricultural activity of the study area, which subsequently produces an increased contribution of soil particles to the atmosphere. Studies on the accumulation of Fe, Mn, and Co in the same species and in the same area attributed the accumulation of these elements to their presence in the soil [16], in accordance with others carried out for atmospheric particulate matter collected in Argentina [38]. These authors reported that together with Al, the source of Fe and Mn in eolic dust samples comes mainly from natural weathered materials. Even though Al and Mn have not been quantified in this study, Fe and Co appear in the first component, which would confirm the hypothesis that this factor corresponds to soil.

The highest values in the map for the second component (figure 5), attributed to traffic, correspond to the region that includes the city of Córdoba and National Route 9

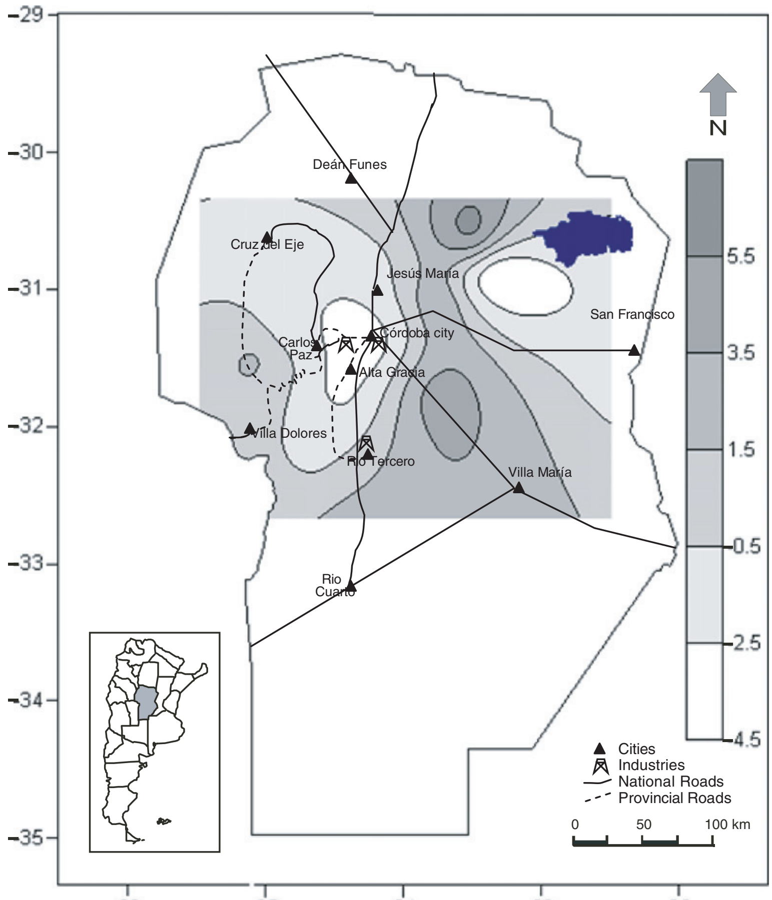

Figure 4. Geographic distribution of the first principal component obtained in the PCA made with the measured elements in *T. capillaris* in the study area.

(the main route accessing the city), confirming previous results. These results are also in accordance with those who reported elevated levels of Zn in a biomonitoring study using *T. capillaris* undertaken in the city of Córdoba and its industrial surroundings [16, 17].

The distribution of the third component (represented by Na and Ca) in the study area (figure 6) shows that the highest values correspond to the north-eastern region. It is important to note that Na could be originated from the region surrounding the Mar Chiquita Lagoon, Argentina's hypersaline lake. On the other hand, Ca, which contributes negatively to the second component, would indicate an enrichment of Ca in places with low Na content and vice versa.

The highest scores for Ca observed for the second component coincide with the location of large limestone San Agustín quarries. Besides, we had already mentioned an enrichment of Ca in lichen *Ramalina celastri* in the same sampling area [25].

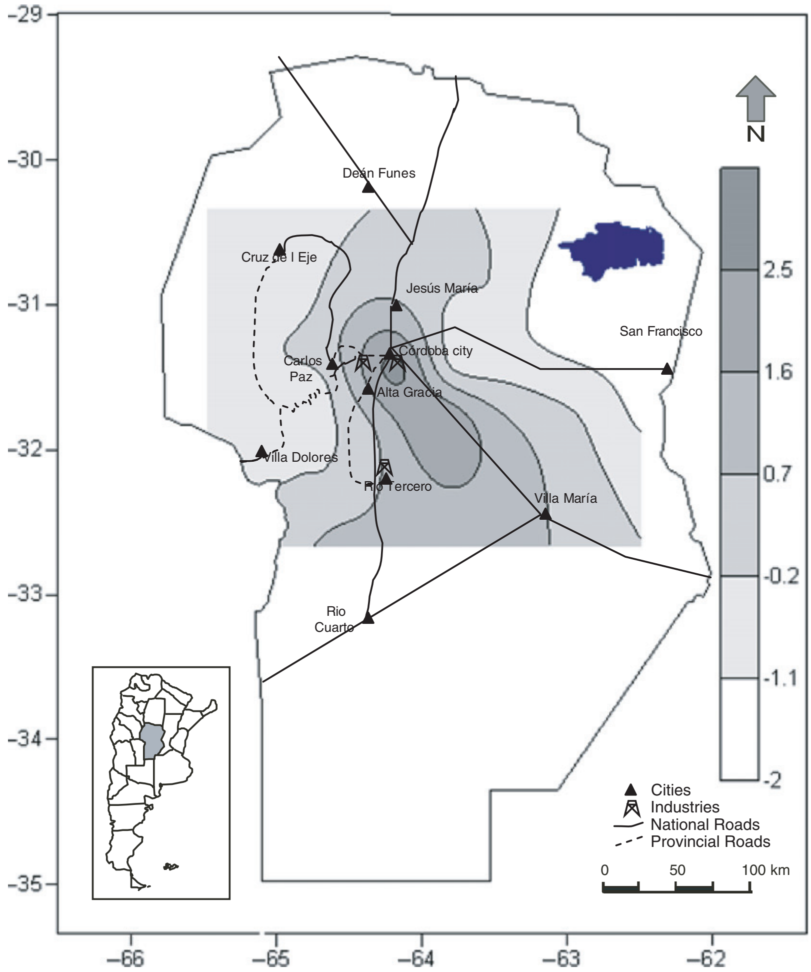

Figure 5. Geographic distribution of the second principal component obtained in the PCA made with the measured elements in *T. capillaris* in the study area.

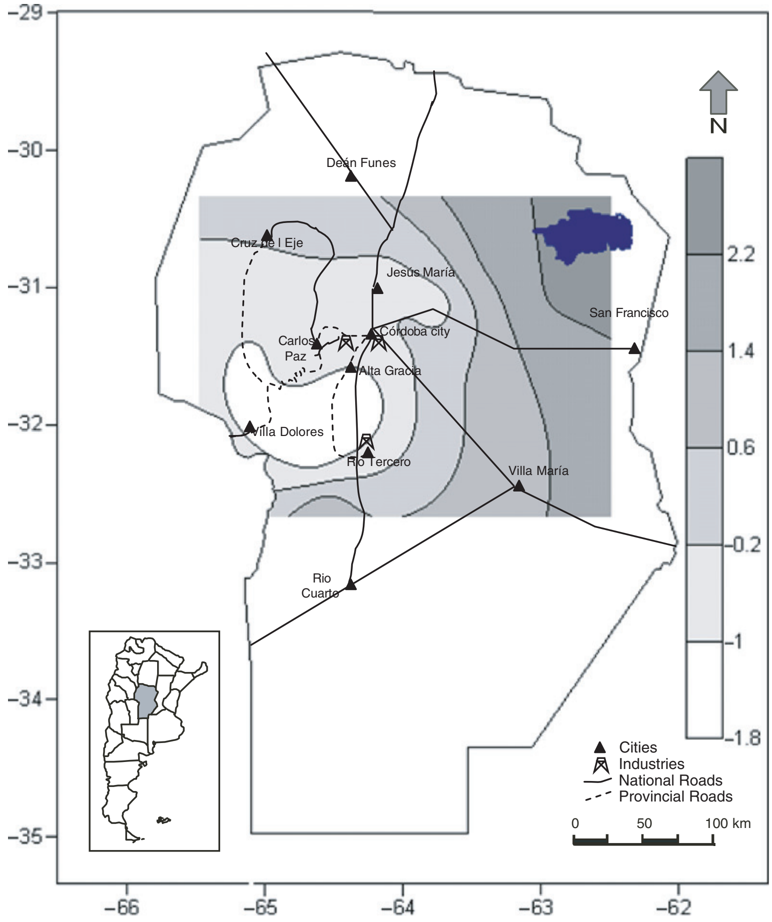

Figure 6. Geographic distribution of the third principal component obtained in the PCA made with the measured elements in *T. capillaris* in the study area.

The highest values of the distribution of the fourth component, represented by Br (figure 7), are found in the southern region of the study area, which corresponds to an industrial sector, suggesting that this element is related to the chemical industries therein. In table 3, it can be seen that the element Ca also contributes, to a lesser extent, to the fourth factor. This could reassert the emission sources that were previously suggested for these elements, since these sources – San Agustín quarries for Ca and chemical industries in Río Tercero for Br – are 34 km away.

According to the results obtained in the PCA and also the results obtained by other authors [25] in the same study area using lichen *R. celastri*, the enrichment of Br can be related to long-range transport.

4. Conclusions

The present study has revealed the potential of *T. capillaris* in detecting emission sources of certain polluting elements on a regional scale. Furthermore, it was observed

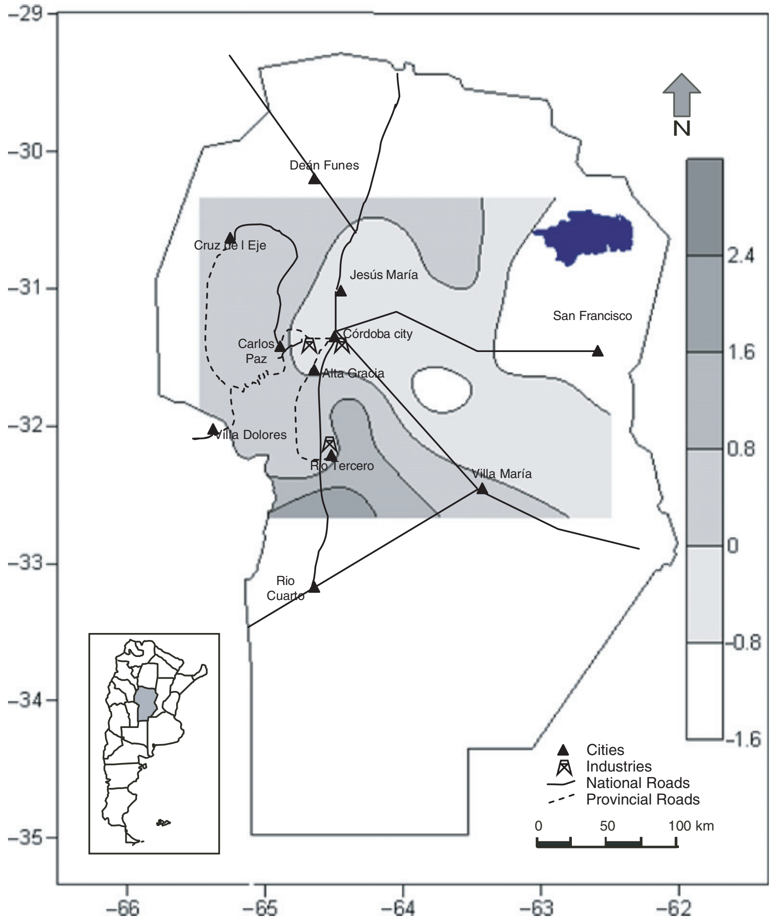

Figure 7. Geographic distribution of the fourth principal component obtained in the PCA made with the measured elements in *T. capillaris* in the study area.

that, among the anthropogenic sources, vehicular traffic causes K, Sb, and Zn biomonitor enrichment, industrial activity produces Br enrichment, and mining activity is reflected in Ca enrichment. Additionally, Na enrichment due to natural sources was also recorded.

As to this potential of *T. capillaris* as a biomonitor, it has been confirmed that variogram analysis can be a very useful tool for establishing the presence of emission sources in a study area.

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