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Characterization of atmospheric emission sources of heavy metals and trace elements through a local-scale monitoring network using *T. capillaris*

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A B S T R A C T

This research work presents new insights regarding biomonitoring studies, source apportionment at a local scale, and influence of wind and topography on dispersion of atmospheric pollutants in a complex scenario. The monitoring network consisted of transplanted *Tillandsia capillaris* biomonitors throughout 3 sampling periods in order to assess the effects of the different emission sources and their atmospheric dispersions in a region from the province of Córdoba, Argentina. The elements Mn, Fe, Co, Ni, Cu, Zn, Cd and Pb, were analyzed by Flame Atomic Absorption Spectrometry (FAAS, pseudo-total metal content) and As, Ba, Ca, Ce, Cr, Cs, Eu, Fe, Hf, La, Lu, Na, Rb, Sb, Sc, Se, Sm, Ta, Tb, Th, U, Yb and Zn, by Neutron Activation Analysis (NAA, total metal content). The following atmospheric emission sources were characterized in the study area: cement plant, with emissions of Cd, Pb, Co_{FAAS}, Ni and Ca; waste dumping site fires, with emissions of the elements Sm, Yb, Ba, La, Zn_{NAA}, Ce, Th and Hf; brick kilns with emissions of the elements Na, Ba, As, Se, Cr, Tb, Sc, Fe_{NAA}, Co_{NAA}, Ta; vehicular traffic with emissions of Zn_{FAAS} and Sb and soil re-suspension with emissions of Ni, Zn_{FAAS}, Br, U, Mn, Rb and Eu. It was noticeable that topography played an important role in the dispersion of the pollutants in the study area and this was reflected in the biomonitors. Our results provide a step forward in the application field of this biomonitoring species for characterizing emission sources in a complex scenario at a local scale.

1. Introduction

The purpose of air quality studies conducted locally is to recognize and characterize the emission sources responsible for the greatest inputs of certain pollutants and to assess air quality at a given location. This is essential at places where there are no air monitoring studies, nor control of the operation of industries, thereby increasing the degree of uncertainty present (WHO, 2010). In developing countries, atmospheric studies are expensive and difficult to implement, being necessary to focus on those sites where industrial parks are located, in order to be able to estimate the atmospheric conditions in nearby residential areas.

Studies on atmospheric pollution have frequently been limited by the high cost of classical analytical methods and difficulties in carrying out extensive monitoring in time and space. Therefore, using alternative monitoring tools appears to be a suitable alternative (Aničić et al., 2009), with there being increasing interest in setting up monitoring networks using organisms that can act as bioaccumulators. Biomonitoring studies employing mosses, lichens and epiphytic plants are now widely used for monitoring air quality in both regional and local scale surveys. In large scale surveys, they are used in establishing sampling networks to evaluate patterns of pollution by large foci, including cross-border pollution over large areas (i.e. regions and/or countries) (Carreras and Pignata, 2002; Pignata et al., 2002; Wannaz et al., 2006, 2012). In smaller-scale surveys, they are used to study pollution in the surroundings of particular industrial facilities (e.g., geothermal plants, chlor-alkali plants, thermal power plants, steel works, metal smelters, cement works, etc.), with the aim of describing the extent and intensity of pollution, as well as the small scale spatial patterns generated (Türkan et al., 1995; Ceburnis et al., 2002; Fernández et al., 2007).

Species from the *Tillandsia* genus (epiphytic plants, usually found in the Southern Hemisphere) are biomonitors that have been used in studying the distribution of heavy metals in the air due to their particular morphological and physiological characteristics

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(Pignata et al., 2002; Vianna et al., 2011; Wannaz et al., 2011). The morphology of most species of *Tillandsia* consists of trichomes in the epidermal leaf surfaces, which allow the efficient absorption of scarce nutrients and liquid water directly from the atmosphere into the leaf (Benz and Martin, 2006). Furthermore, a recent study from Papini et al. (2010) on the ultrastructure of *Tillandsia* trichomes, described apoptotic mechanisms at maturity acting as a passive pump and thus achieving an important function in the absorption mechanism.

A challenge in monitoring studies is the complex scenario when trying to identify pollution sources and the chemical characterization of the emissions produced by multiple foci that generate small scale patterns of pollution within an irregular topography that affects wind dynamics and consequent dispersion of pollutants. This situation exists in the town of Malagueño in the province of Córdoba, Argentina, where the concentration of various pollutants in the region depends on the presence of different emission sources as well as on the local topography. Considering this, the main objectives of this study were: (1) to analyze the spatial variability of pollutants on a local scale, given by multiple atmospheric sources of heavy metals and trace elements using *T. capillaris* transplants, and assessing the influence of meteorological and topographical variables in the town of Malagueño at the province of Córdoba, Argentina; (2) to characterize these atmospheric emission sources and their effects on the air quality of the region by means of biomonitor accumulation.

2. Materials and methods

2.1. Monitoring network

A monitoring network, consisting of transplanted biomonitors throughout 3 sampling periods, was designed in order to assess the effects of the different emission sources and their atmospheric dispersions in the locality of Malagueño, located 18 km SW of Cordoba city in Argentina (Fig. 1). In the study area, a cement plant was considered to be the main anthropogenic source of atmospheric pollutants, given the analysis from previous studies undertaken in the area (Carreras and Pignata, 2002; Wannaz et al., 2008; Bermudez et al., 2010; Rodríguez et al., 2011). Different sub-areas within the study area were selected, centering on the vicinities of the cement plant and covering a total area of approximately 400 km^2 (Fig. S1a – Supplementary material):

a) C (Cement Plant): In the town of Malagueño (6404 inhabitants), a private enterprise specializes in the production of cement and ready-mixed concrete. It possesses two plants located a few kilometers away (Yocsina and Malagueño), with the main raw material of these plants being the limestone extracted from two quarries. In 1994, the Yocsina Plant adopted a technology called "blending", a physico-chemical conditioning technique for processing certain wastes of industrial activities, with the aim of using them as alternative fuels and thus significantly reducing the costs incurred from the use of gas (Abril et al., 2014). Currently, this plant uses 75% gas and 25% alternative fuel (Bermudez et al., 2010). Both plants are of great importance with regard to the contribution of particulate matter (cement dust) generated by direct and fugitive emissions. However, this study focused on the Yocsina Plant, due to the use of industrial waste (such as waste oil, waste tyres, oil contaminated soils, polymeric plastics, tars, solvents, mixtures and emulsions of hydrocarbons and water, waste paints, latex, photo products, etc.) as alternative fuels in the cement manufacturing process (Carreras and Pignata, 2002).
b) E (transect toward East): East of the study area (E) in relation to "C" is one of the main entrances to the city of Córdoba. The purpose of this transect was to evaluate the effects of the emissions from the cement plant on the city of Córdoba (1330,023 inhabitants).
c) NE (transect toward Northeast, in relation to "C"): In the northeast direction from the cement plant (NE), farming is developed, with soybeans and wheat being the main crops cultivated in this area. The transect ends at another of the entrances to the city of Cordoba, which also has intense vehicular traffic.
d) SW (transect toward Southwest): The southwest direction from the cement plant (SW) leads to the limestone quarries, beyond

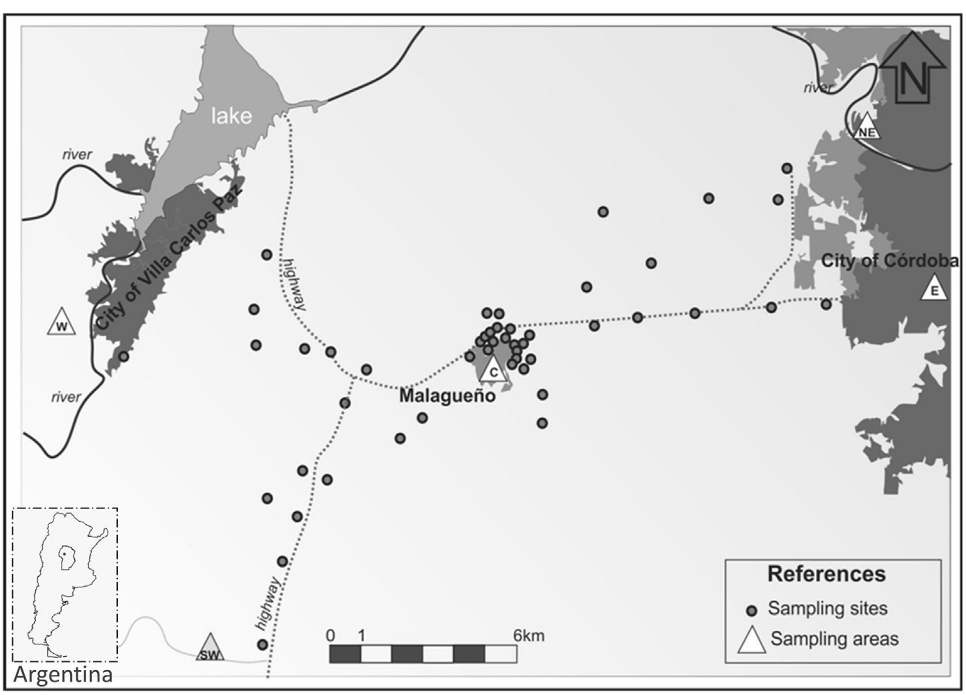

Fig. 1. Location of the study area and identification of the sampling areas (NE, SW, E, W, C) in the town of Malagueño, province of Córdoba, Argentina.

which are found residential areas, agricultural fields and brick kilns.

e) W (transect toward West): West of the cement plant (W) is the waste dumping site of the City of Villa Carlos Paz, located at the top of a geological formation (Sierras Chicas) and which may represent a topographic barrier in the study area (Fig. S1b).

The above sampling sites were chosen with radial distributions surrounding the Yocsina cement plant (designated in this study as C) and also with linear distributions in order to assess the effects of the prevalent winds from Northeast (NE) to Southwest (SW) as well as the influence of the study area on the cities of Cordoba and Villa Carlos Paz (E and W, respectively).

2.2. Biomonitors

Plants of *T. capillaris* Ruíz & Pav. f. *capillaris* were collected from standing trees at Dique la Quebrada, a natural reserve in the province of Córdoba which is located 38 km NW from the capital city. This area is considered to be unpolluted, where the baseline compositions of these plants have remained practically unchanged over the years. *T. capillaris* has been previously employed in other biomonitoring studies carried out by our research group and has been shown to act as a good biomonitor of response and accumulation in the assessment of atmospheric quality (Pignata et al., 2002; Wannaz et al., 2008, 2012; Bermudez et al., 2009; Abril et al., 2014). The plants were collected using plastic gloves in order to avoid any sort of contamination, with samples being immediately placed in paper bags (Sloof, 1993).

2.3. Active biomonitoring and exposure periods

Net bags, containing 8–10 plants, were prepared according to Wannaz and Pignata (2006) and transplanted to the study area ($n = 3$ bags/site). These were placed 3 m above ground level and exposed for three periods of 6 consecutive months each, from September 2009 to March 2011, (Table S1 – Supplementary material). Once the exposure periods had been concluded, plants were collected, placed in paper bags and dried to constant weight in an oven at 50 ± 2 °C for heavy metal and trace element content determinations (Wannaz et al., 2006). In order to establish the initial state of the samples before transplantation, basal samples from the original collection site were analyzed following the same procedures (Wannaz and Pignata, 2006).

2.4. Determination of heavy metals and trace elements

For the determination of heavy metals, 2.5 g of dry weight (DW) of *T. capillaris* leaf samples were ground and reduced to ashes at 450 °C for 4 h (Wannaz and Pignata, 2006), which were then digested with concentrated HNO_3 (65% Merck, Germany), with the samples being kept for 24 h in the dark. Next, the samples were filtered twice, and the acid solutions were analyzed by Flame Atomic Absorption Spectrometry (FAAS, Perkin-Elmer AA3110) to determine the concentrations of Mn, Fe, Co, Ni, Cu, Zn, Cd and Pb, which were expressed as $\mu g\, g^{-1}$ DW. Considering that this technique does not digest silicates, the results reported henceforth refer to "pseudo-total metals" or "FAAS".

For trace element determinations, 0.25 g of dry weight of *T. capillaris* leaf samples were irradiated for 5 h in the RA-3 reactor (thermal flux 3×10^{13} cm^{-2} s^{-1}, 8 Mw) of the Ezeiza Atomic Center (CNEA – Argentinean National Atomic Energy Commission), and the concentrations of As, Ba, Ca, Ce, Co, Cr, Cs, Eu, Fe, Hf, La, Lu, Na, Rb, Sb, Sc, Se, Sm, Ta, Tb, Th, U, Yb and Zn in plants were analyzed by Neutron Activation Analysis (NAA), with the results being expressed as $\mu g\, g^{-1}$ DW. This technique measures the total content of metals, thus the results reported henceforth refer to "total content of metals" or "NAA".

2.5. Quality control

In order to assess the digestion procedure and to check the accuracy of the determination process of the pseudo-total fraction of the metals Mn, Fe, Co, Ni, Cu, Zn, Cd and Pb, laboratory blanks and two replicate samples of Certified Reference Material (CRM) of oriental tobacco leaves "CTA-OTL-1" (Institute of Nuclear Chemistry and Technology) were prepared and ran every ten samples following the same treatment. Values for all blank samples were near to or below than the detection limits of FAAS, with the results being between 87.6% (Fe) and 104% (Pb) of the certified values (Table S2). Table S3 summarizes the total content of metals determined by NAA in CRM "IAEA-336 Lichen" as the calibration standard and "IAEA-392 Lichen" for control purposes. The data obtained were consistent with those mentioned in previous studies (Wannaz et al., 2008; Bermudez et al., 2010, 2011).

2.6. Statistical analysis

Assumptions for normality were tested using the Shapiro–Wilk test, and non-normal distributed variables were LOG_{10} transformed before carrying out parametric statistics. An analysis of variance (ANOVA) was performed for each parameter considering the different areas (C, NE, E, W and SW). 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). In order to analyze comparatively the accumulation of each metal, the elements accumulated in the biomonitors were assessed regarding the content of these elements in the basal samples ("Exposed-to-basal ratio, EB ratio") as described by Frati et al. (2005). Furthermore, a Principal Component Analysis (PCA) was performed, which is generally considered to be able to identify potential sources of air pollution in a study area.

2.7. Meteorological and topographical variables in the study area

Wind roses were elaborated to illustrate flow vectors (wind blowing to) for the three sampling periods from data provided by the National Weather Service (2012) from Córdoba airport station (Fig. S2). It can be seen that for the three sampling periods the main flowing vectors were toward S and SW, indicating that winds mainly blew from the N and NE directions, although there were also winds blowing from S, W and NW. The topography of the area presents a heterogeneous display, ranging from 420 to 1020 m.a.s.l and rising toward the W and SW directions (Fig. S1b). This irregular topography implies a complex scenario, since topography can act in a dispersive manner or as a barrier, according to the location of each source and the influence of the prevalent winds (Abril et al., 2014).

3. Results and discussion

3.1. Descriptive statistics

The mean, minimum and maximum values of the metal concentrations ($\mu g\, g^{-1}$ DW) measured by FAAS and NAA in *T. capillaris* samples transplanted to the study area for sampling periods I, II and III (Table 1) were compared with similar scenarios and presented in Table S4, with the basal values being presented in Table S5. The maximum values found for As, Cu, Fe, Co_{NAA}, La, Ce, Sm,

Table 1
Descriptive statistics of the concentration of heavy metals and trace elements measured in *T. capillaris* leaves (μg g^{-1} DW) by FAAS and NAA (sampling periods I, II and III) in the town of Malagueño, province of Córdoba.

Variable	Sampling period I: September–March 2009–2010						Sampling period II: March–September 2010						Sampling period III: September–March 2010–2011					
	n	Mean	S.E.	% C.V.	Min.	Max.	n	Mean	S.E.	% C.V.	Min.	Max.	n	Mean	S.E.	% C.V.	Min.	Max.
Cu[a]	54	14.69	0.56	28.14	8.33	29.70	52	5.55	0.16	20.15	4.09	9.39	58	6.29	0.14	17.45	4.41	9.50
Ni[a]	54	6.23	0.24	28.68	3.67	12.40	52	5.71	0.12	15.37	4.15	7.58	58	8.66	0.57	50.54	4.23	23.89
Pb[a]	54	6.89	0.48	51.24	2.55	22.7	52	4.63	0.26	41.26	1.15	8.75	58	5.10	0.35	51.88	0.32	12.25
Mn[a]	54	118.1	2.98	18.53	73.90	160.9	52	95.78	3.48	26.19	40.98	153.9	58	105.8	7.59	54.67	28.97	236.8
Co[a]	54	0.94	0.03	24.83	0.59	1.86	52	0.76	0.03	30.30	0.29	1.25	58	0.74	0.03	29.84	0.40	1.53
Cd[a]	54	0.31	0.04	97.59	0.03	1.64	52	0.80	0.03	26.98	0.37	1.28	42	1.04	0.03	18.84	0.57	1.35
Zn[a]	54	29.21	0.89	22.41	20.50	44.50	52	17.66	0.33	13.60	12.00	24.88	58	21.01	0.69	25.10	2.55	35.95
Fe[a]	54	2728	95.2	25.63	1447	4971	52	1947	75.92	28.11	1238	3478	58	3382	208.0	46.83	1122	8116
Ca	54	25207	2540	74.06	10131	116290	56	15091	647.4	32.11	9507	33164	58	21919	1989	65.45	10665	95686
Br	54	8.20	0.17	15.04	6.11	12.75	56	8.92	0.22	18.32	6.30	13.28	58	7.61	0.21	20.92	5.25	11.44
Na	54	3711	118.5	23.46	2237	5154	56	1928	73.91	28.69	1184	4364	58	2276	83.44	27.92	866.8	4283
Sm	54	2.28	0.10	32.57	1.01	3.83	56	0.63	0.04	53.07	0.01	1.76	58	1.04	0.03	24.16	0.41	1.56
Lu	54	0.10	0.004	29.02	0.05	0.15	56	0.03	0.002	48.67	0.00	0.09	58	0.06	0.002	23.78	0.02	0.08
U	50	0.65	0.03	28.75	0.32	1.12	56	0.24	0.02	57.14	0.08	0.73	57	0.35	0.01	25.75	0.14	0.54
Yb	54	0.65	0.02	27.69	0.31	0.96	56	0.22	0.01	49.31	0.08	0.60	58	0.35	0.01	24.37	0.11	0.54
Ba	54	108.6	3.79	25.63	50.99	177.7	56	45.80	1.83	29.97	25.42	84.10	58	64.25	1.70	20.10	37.59	103.4
As	54	2.16	0.06	21.41	1.32	2.84	56	1.26	0.15	88.37	0.53	6.76	58	1.47	0.10	53.33	0.64	5.12
Sb	54	0.36	0.02	36.34	0.17	0.74	56	0.17	0.01	30.97	0.10	0.34	58	0.24	0.01	28.31	0.09	0.43
La	54	13.70	0.65	34.93	6.77	26.10	56	3.92	0.30	57.37	1.61	12.89	58	6.11	0.22	27.50	2.14	8.90
Zn	54	44.66	1.90	31.19	21.78	76.68	56	22.28	0.61	20.33	14.47	35.52	58	26.79	0.81	23.07	9.85	39.17
Se	52	0.96	0.05	36.07	0.19	1.78	56	0.36	0.03	55.33	0.08	1.24	56	0.50	0.02	33.82	0.07	0.96
Ce	54	26.46	1.29	35.80	11.39	51.84	56	7.64	0.57	55.88	2.88	26.08	58	11.72	0.47	30.61	3.15	19.16
Th	54	4.19	0.20	35.29	1.89	8.01	56	1.17	0.09	55.86	0.44	3.89	58	1.81	0.07	29.27	0.56	2.95
Cr	54	33.20	1.35	29.93	15.01	52.83	56	19.59	0.95	36.29	4.86	40.19	58	27.29	1.17	32.68	7.37	52.17
Hf	54	1.72	0.08	32.43	0.77	3.19	56	0.52	0.04	61.32	0.16	1.71	58	0.81	0.03	31.26	0.18	1.26
Cs	54	1.95	0.08	29.92	0.95	3.70	56	0.78	0.04	35.04	0.43	1.68	58	1.20	0.07	42.54	0.58	3.55
Tb	54	0.24	0.01	34.08	0.12	0.56	56	0.08	0.004	41.96	0.04	0.22	58	0.13	0.01	33.41	0.06	0.25
Sc	54	2.89	0.10	25.96	1.49	4.15	56	1.01	0.06	44.17	0.42	2.38	58	1.57	0.05	25.74	0.49	2.53
Rb	54	27.62	0.94	25.09	15.06	40.48	56	14.76	0.66	33.45	8.05	34.95	58	16.99	0.64	28.79	10.02	37.37
Fe	54	9228	361.8	28.81	4895	15061	56	3423	240.1	52.49	1309	9563	58	5135	171.6	25.45	1624	8145
Co	54	3.70	0.11	22.68	1.89	5.39	56	1.78	0.09	39.00	0.93	4.58	58	2.31	0.06	20.83	1.11	3.42
Ta	54	0.24	0.01	29.12	0.12	0.38	56	0.10	0.01	55.06	0.04	0.28	58	0.13	0.005	28.66	0.04	0.21
Eu	54	0.38	0.02	31.91	0.16	0.67	56	0.13	0.01	56.37	0.06	0.37	58	0.19	0.01	25.33	0.07	0.29

[a] Elements extracted with HNO_3 (pseudo-total metals) measured by FAAS; S.E.: Standard Error; C.V.%: Percentage of Variation Coefficient.

Eu, Tb, Yb, Lu, U, Th, Se, Cs, Hf, Na, Rb, Sc and Ta were higher than those found in transplants of the lichen *Usnea amblyoclada* exposed in the region of Yocsina-Malagueño (Bermudez, 2011) and also greater than the values found in *T. capillaris* collected in the province of Cordoba in the years 2001–2003 (Wannaz et al., 2008). Furthermore, the Cu values were higher than transplants of the lichen *U. amblyoclada* (Bermudez, 2011) yet similar to the values informed by Rodríguez et al. (2011) in *T. capillaris* both exposed at the town of Malagueño. The Fe_{NAA} values were higher than *T. capillaris* transplanted for 6 months at an industrial site in the Province of Córdoba (Bermudez et al., 2009) and the Ba values were higher than transplants of the lichen *U. amblyoclada* exposed in the region of Yocsina-Malagueño (Bermudez, 2011). The Zn_{FAAS} concentration values were lower than results found in Bermudez et al. (2009) for the same species yet similar to those found in Rodríguez et al. (2011). With respect to Cd concentration values, these were higher than others reported in woody plant species (Princewill and Adanma, 2011) or in grass around cement factories in Vallcarca, Spain (Schuhmacher et al., 2009). The Ca accumulation values were higher than *Tillandsia usneoides* samples transplanted in Sao Pablo (Figueiredo et al., 2006) and also than those values detected in the lichen *Xanthoria parietina* transplanted to the vicinities of a cement plant (Branquinho et al., 2008). In agreement with the Egyptian Environmental Affairs Agency (EEAA, 2005) and the North American Environmental Protection Agency (EPA, 1995), Cd, along with other heavy metals (such as Pb, Hg, Co, Cu), alumina, silica, metallic oxides and clay, trace amounts of organic chemicals (dioxins and furans) and radio nuclides, were the major constituents in dust from cement manufacturing plants.

3.2. One-way analysis of variance

The results of the ANOVA analysis using the sampling areas as the classification criterion for heavy metal and trace element accumulation ($\mu g\, g^{-1}$ DW) in *T. capillaris* leaves (in the three sampling periods) are presented in Table S6. Substantial differences were found between total and pseudo-total element concentrations regarding emission sources, being the first indicative of geochemical matrices, and the second, of anthropogenic sources. The pseudo-total element content (exchangeable fraction), excludes the determination of metals strongly bound in silicate structure (stable fraction), being considered this fraction not very important for pollution assessment, since elements of anthropogenic origin are usually rather in more mobile forms (Boruvka and Vacha, 2006; Vittori Antisari et al., 2009). Most of the heavy metals (pseudo-total fraction) were associated with the cement plant (C), with Pb, Co and Cd, being significantly higher at (C) sites for the three sampling periods. Additionally, Ca values were also significantly higher at (C). The rest of the elements (total metal content) were significantly higher at sites located at the W and SW. At sampling periods I and II, most of the trace metals were enriched toward the W, whereas at the third sampling period, these were enriched in the SW area. At both W and SW areas, activities related to soil combustion (with emissions of lithogenic elements) were found; toward the W, fires at the waste dumping site were identified at all the sampling periods, according to the records from the local fire station, and at SW brick kilns are located, with both involving biomass burning with emissions of CO_x, NO_x, SO_x, hydrocarbons, and particulates (dust) containing trace metals from soil composition (Ismail et al., 2012). Sb was the element associated with the E and NE directions (toward the city of Cordoba), and is a known marker of vehicle emissions (Huang et al., 1994; Gómez et al., 2005; Smichowski et al., 2005; Wannaz et al., 2008).

Considering the elements Fe, Co and Zn, which were determined by both, pseudo-total and total metal content methods, Co_{FAAS} was mainly found at the vicinities of the cement plant with significant differences, whereas Fe_{FAAS} and Zn_{FAAS} had practically no differences between sampling areas. Regarding total metal content, Co_{NAA} and Fe_{NAA} showed similar behaviors being significantly higher at W and SW for sampling periods I and III (spring-summer seasons), indicating that were mainly emitted from combustion sources (fires at the dumpsite and brick kiln production with emission of lithogenic elements).

3.3. EB ratios

The calculation of the heavy metals and trace elements exposed-to-basal ratios (EB ratio) has been used to evaluate emission sources of metals (natural or anthropogenic). The values obtained from this equation were assessed according to the scale used by Frati et al. (2005), where values between 0.75 and 1.25 indicate normal EB ratios; 1.25–1.75 indicate accumulation, and EB >1.75 indicate greater accumulation that demonstrates the presence of anthropogenic emission sources. Fig. S3–S5 illustrates the mean EB ratios for heavy metals and trace elements for the sampling periods I, II and III. By considering the scale proposed by Frati et al. (2005), the EB ratios revealed a greater accumulation for most of the heavy metals (pseudo-total fraction, Cd, Ni, Pb, Co, Mn, Cu, Fe in the three sampling periods), with Cd values being noticeably higher than the values found for the rest of the elements analyzed in this study (15.97; 22.82 and 24.18 at the sampling periods I, II and III, respectively). Moreover, the Cd values were highly enriched in the vicinities of the cement plant and had an atmospheric dispersion mostly toward the SW (data not shown). The lithogenic elements found in the air were originated from fires at the waste dumping site and from the combustion process at the brick kilns (anthropogenic origin), being some elements more enriched than others: the elements, Lu, Sm, Cr, Sb, Yb, and Zn_{NAA} showed severe accumulation, with highest EB ratios at SW and W, and lowest EB ratios at C.

3.4. Principal Component Analysis and factor assignment

In Table 2 are presented the results of a Principal Component Analysis (PCA) of the metal concentrations to try to identify possible atmospheric pollution sources and the associations between the different sites, with varimax rotation being applied to improve the differentiation between sources. Figs. 2–4 show the spatial mapping of the Principal Component value patterns for each sampling site for factor assignment to each source of pollution identified.

For sampling period I (September–March, 2009–2010) 85% of the variance was explained by 4 factors. Factor 1 was mainly represented by most of the elements analyzed by NAA (Na, Sm, Lu, U, Yb, Ba, As, Sb, La, Zn, Se, Ce, Th, Hf, Cs, Tb, Sc, Rb, Fe, Co, Ta and Eu) with coefficients > 0.70. By observing the distribution map for PC1 (Fig. 2), the highest values were found toward the W direction, where the waste dumping site is located. Factor 2 was mainly represented by the pseudo-total metals (Cu, Ni, Pb, Co, Cd) and Ca, with coefficients > 0.70, thus associating these elements to the cement plant emissions (Fig. 2). Factor 3 was represented by Cr and Mn, possibly related to soil re-suspension. Factor 4 was mainly represented by Zn and Sb with coefficients > 0.70, thus associating these elements with vehicular traffic emissions (Huang et al., 1994; Smichowski et al., 2005; Gómez et al., 2005; Wannaz et al., 2008). In addition, as the distribution map shows in Fig. 2, the highest values of PC4 were found toward E and NE, the areas with the highest intensity of vehicular traffic in close proximity to the city of Córdoba.

For sampling period II (March–September, 2010) 80% of the variance was explained by 4 factors. Factor 1 was again mainly represented by most of the elements analyzed by NAA (Na, Sm, Lu, U, Yb, Ba, Sb, La, Zn, Se, Ce, Th, Cr, Hf, Cs, Tb and Sc) and Fe_{FAAS}, with coefficients > 0.70 toward the W, in particular next to the waste

Table 2
Factor loadings of heavy metals and trace elements in *T. capillaris* leaves.

Elements	Sampling period I				Sampling period II				Sampling period III			
	PC 1	PC 2	PC 3	PC 4	PC 1	PC 2	PC 3	PC 4	PC 1	PC 2	PC 3	PC 4
Cu[a]	−0.362	**0.819**	0.233		−0.121		0.641	0.481	0.290	0.698	0.381	−0.201
Zn[a]	0.232	0.361		**0.696**	0.234	−0.158	0.227	**0.717**	0.405	**0.757**		−0.167
Ni[a]	−0.343	**0.789**	0.243		0.101		0.629	**0.567**		**0.918**	0.324	0.117
Cd[a]	−0.139	**0.951**	−0.141		−0.410		**0.740**		−0.273		0.639	−0.202
Pb[a]		**0.944**	0.105	0.165			**0.874**		0.394		**0.830**	
Co[a]		**0.904**			−0.239		**0.695**	−0.203		0.144	**0.847**	
Fe[a]	0.134	0.610	0.618	−0.200	0.814	0.186		0.258	0.118	**0.923**	0.179	0.103
Mn[a]	0.475	0.250	**0.659**	−0.125	0.442	0.183		0.339		**0.911**		
Ca		**0.933**			0.140		**0.688**	0.300		0.480	**0.806**	0.164
Br	0.495		−0.265	−0.286			**0.747**	0.230	−0.130			**0.829**
Na	**0.861**	−0.202	0.210	0.218	**0.741**			0.397	**0.903**			
Sm	**0.901**				**0.958**				**0.919**	0.172	0.176	−0.185
Lu	**0.922**	−0.112	0.215	0.175	**0.940**				**0.910**	0.177		−0.187
U	**0.799**	−0.132	0.297	0.132	**0.931**			−0.148	**0.776**	0.185		0.147
Yb	**0.886**		0.249	0.193	**0.971**				**0.919**	0.156		−0.202
Ba	**0.812**	0.320	0.126	0.250	**0.881**				**0.878**			
As	**0.822**	−0.264	0.340	0.122	0.516		−0.153	−0.461	**0.727**		−0.225	0.405
Sb	0.433	−0.158		**0.788**	**0.831**			−0.137	0.665	0.260		−0.140
La	**0.948**	−0.105	−0.131		**0.958**		−0.124	0.129	**0.912**	0.108	0.208	−0.171
Zn	**0.722**		−0.193	0.397	**0.864**			0.205	0.551	0.234		−0.429
Se	**0.757**	0.112			**0.912**		−0.153	0.124	**0.791**		−0.11	
Ce	**0.962**				**0.954**		−0.141	0.150	**0.894**	0.106	0.135	
Th	**0.959**	−0.117			**0.965**		−0.135		**0.966**			
Cr			**0.778**	0.451	**0.729**			0.445	**0.787**	0.424	0.155	0.226
Hf	**0.969**	−0.110			**0.971**		−0.133		**0.954**	0.104		
Cs	**0.709**	0.559	0.189	0.223	**0.791**		0.412	−0.221	0.279	0.625	**0.648**	0.170
Tb	**0.902**	−0.188			**0.907**	−0.106			**0.782**	0.107	0.182	0.351
Sc	**0.945**		0.226	0.153	**0.983**				**0.972**	0.164		
Rb	**0.837**		0.249	0.311		**0.892**			0.437	0.497	0.577	0.318
Fe	**0.981**					**0.982**			**0.957**	0.196	0.132	
Co	**0.956**		0.181	0.146		**0.979**			**0.948**	0.206		
Ta	**0.908**	−0.105	0.214	0.215		**0.963**			**0.931**			
Eu	**0.984**				−0.105	**0.946**	−0.119		**0.916**	0.143	0.258	
Eigen value	17.527	6.051	2.330	2.109	15.330	4.707	4.071	2.234	16.557	5.095	3.864	1.717
Variance %	53.113	18.336	7.060	6.392	46.454	14.264	12.338	6.771	50.173	15.440	11.709	5.202
Cumulative %	53.113	71.449	78.509	84.901	46.454	60.718	73.056	79.827	50.173	65.613	77.322	82.254

[a] Elements extracted with HNO_3 (pseudototal metals) and measured by FAAS. Values of dominant elements in each factor are reported in bold. Coefficient values with an absolute value < 0.1 were suppressed. Extraction method: PCA, Rotation method: Varimax with Kaiser Normalization.

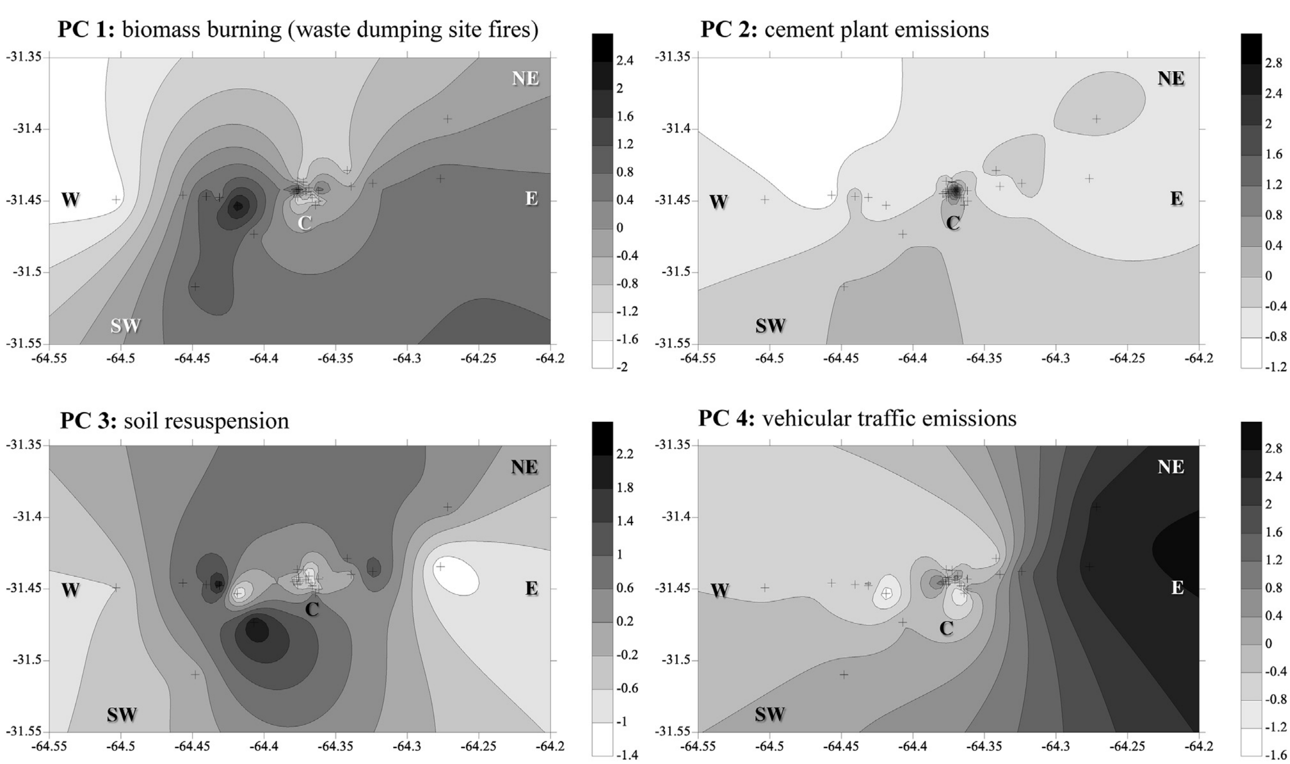

Fig. 2. Spatial mapping of the Principal Component value patterns for each sampling site for factor assignment to each source of pollution identified (sampling period I).

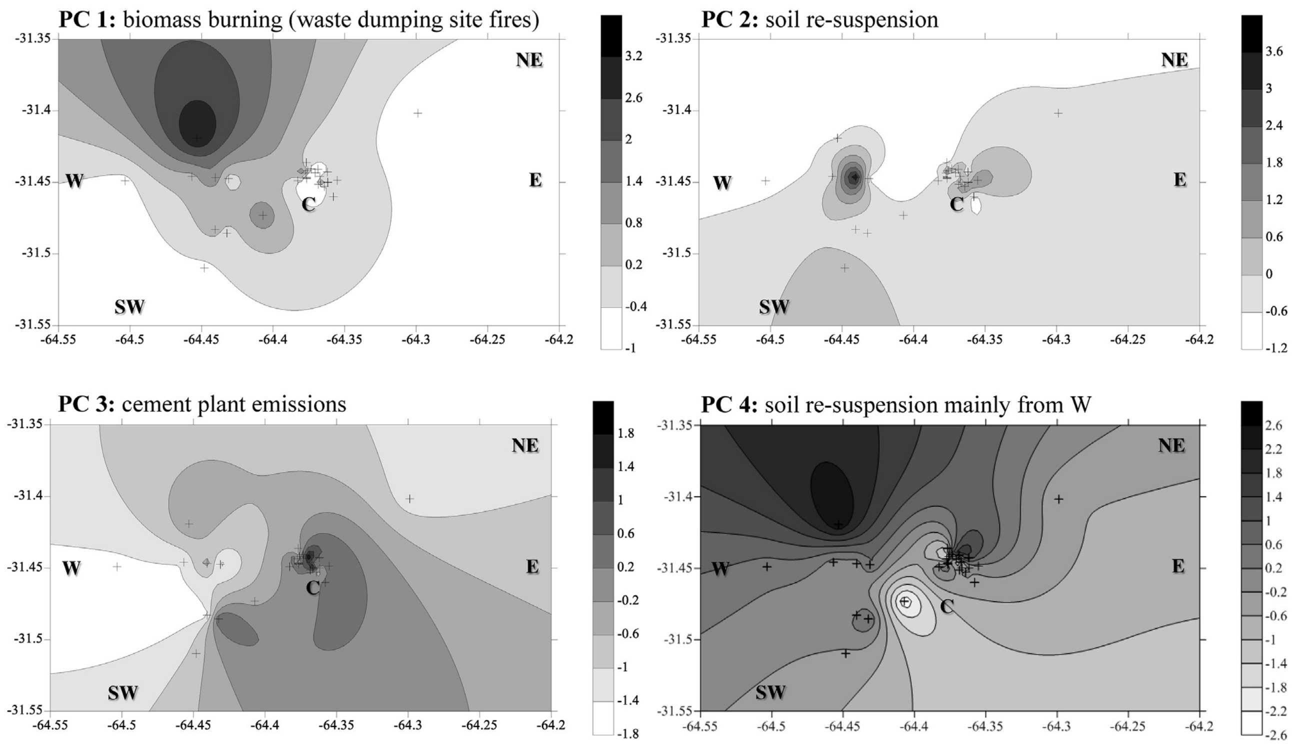

Fig. 3. Spatial mapping of the Principal Component value patterns for each sampling site for factor assignment to each source of pollution identified (sampling period II).

dumping site (Fig. 3). Factor 2 was represented by Rb, Fe_{NAA}, Co_{NAA}, Ta and Eu, which could have been related to soil re-suspension (mainly from the W) taking into account that no significant differences were found in the ANOVA analysis. Factor 3 was represented by Cd, Pb, Co, Ca and Br with coefficients ≥ 0.70. On the distribution map of this Factor (Fig. 3), it can be seen that the highest values were found at the vicinities of the cement plant. Factor 4 was represented by Ni and Zn, which was associated to soil re-suspension (mainly from the W, Fig. 3) and to emissions from cement plant, also revealed by the lack of significance in the analysis of variance.

For the sampling period III (September–March, 2010–2011) 82% of the variance was explained by 4 factors. Factor 1 was mainly

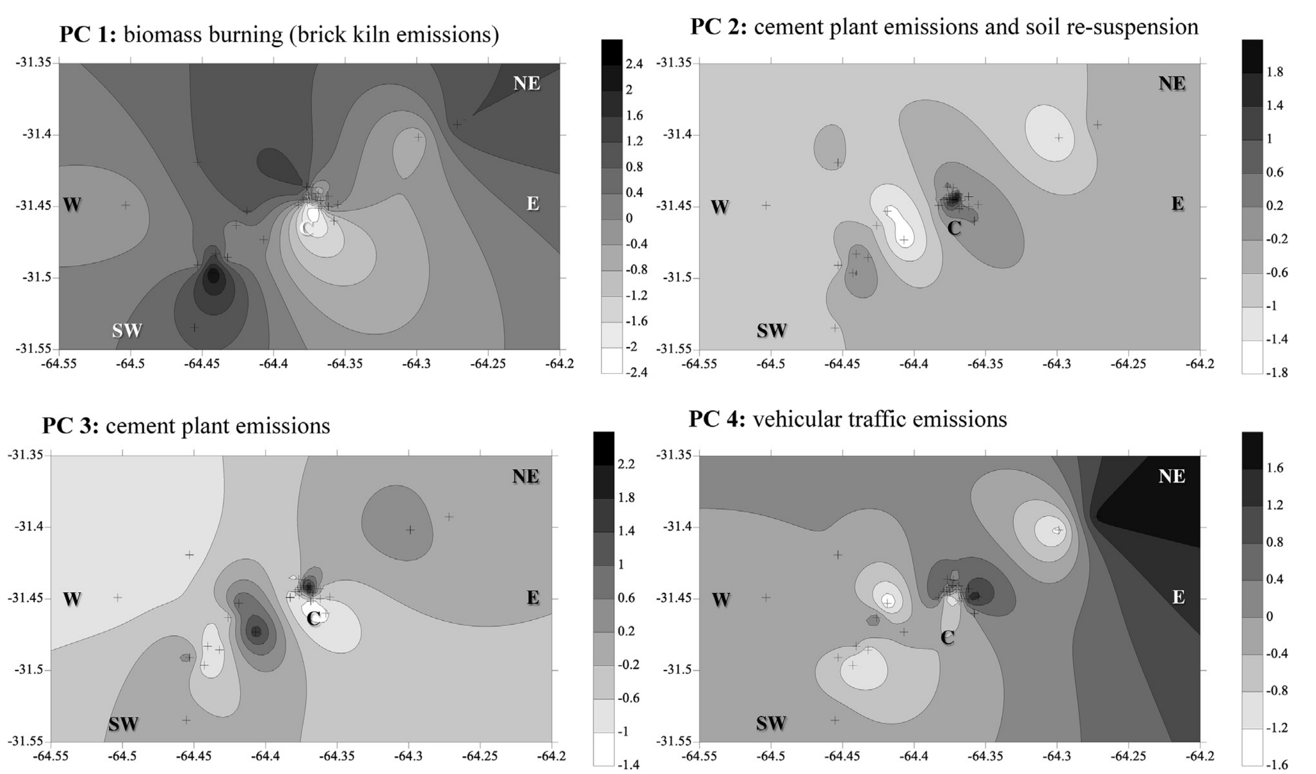

Fig. 4. Spatial mapping of the Principal Component value patterns for each sampling site for factor assignment to each source of pollution identified (sampling period III).

represented by most of the elements analyzed by NAA (Na, Sm, Lu, U, Yb, Ba, As, La, Se, Ce, Th, Cr, Hf, Tb, Fe, Co, Ta, Eu) with coefficients > 0.70 which were found toward the SW, where several brick kilns are located. Factor 2 was represented by Cu, Zn, Ni, Fe and Mn, being probably related to soil re-suspension. Factor 3 was represented by Cd, Co_{FAAS}, Pb, Ca and Cs, thus associating these elements with the cement plant emissions. Factor 4 was represented by Br, which could have been related to vehicular traffic emissions, as shown in the distribution map (Fig. 4, with maximum values toward the city of Córdoba).

Despite the fact that every sampling period showed that the heavy metal and trace element composition and concentration values varied within the study area (Table S7), it was possible to associate certain elements to different atmospheric sources of pollution. These variations may have been due to meteorological variables and also to the irregularity of the behavior of sources of emission. Furthermore, the maps from the PCA analysis for the three sampling periods showed that the irregular topography toward W and prevalent winds from N, NE and NNE played an important role in the dispersion of pollutants at the study area, detecting a distribution of the pollutants emitted mainly toward S and SW directions. The emissions from the cement plant (583 m.a.s.l.) had a local effect with dispersion toward SW and no effects were observed from this source toward the W, mainly due to the topography acting as a barrier for this direction; the emissions from the waste dumping site (797 m.a.s.l.) had a local effect and a dispersion toward S; brick kiln emissions had a local effect and toward S and SW; and traffic emissions had a local effect at E and NE directions (not affected by prevalent winds at the study area).

4. Conclusions

The following atmospheric emission sources of heavy metals and trace elements were characterized in the town of Malagueño:

- Cement plant: located at C with a local dispersion in the vicinities and toward the SW (given by prevalent winds) of the elements Cd, Pb, Co, Ni and Ca. No effects were observed from this source toward the W, mainly due to the topography acting as a barrier for this direction.
- Biomass burning:
  - Waste dumping site fires: located at the W of the study area with local and more extensive dispersion toward the S of the lithogenic elements Sm, Yb, Ba, La, Zn, Ce, Th and Hf.
  - Brick kiln emissions: located at the SW of the study area with local effects and dispersion toward the S of the elements Na, Ba, As, Se, Cr, Tb, Sc, Fe, Co, Ta.
- Vehicle traffic: particularly at the E and NE, with effects that were detected mainly in these areas (Zn_{FAAS} and Sb emissions).
- Soil re-suspension: high levels of Ni, Zn_{FAAS}, Br, U, Mn, Rb and Eu were detected in the vicinities of the sources (cement plant and waste dumping site), but which were also distributed in the area.

The use of *T. capillaris* as a biomonitor species allowed us to characterize different emission sources at a local scale, differentiating on the one hand stationary sources such as cement plant, biomass burning (fire in a waste dumping site and emissions from brick kilns) and re-suspension of soil, and on the other hand, mobile sources such as traffic. Normally, biomonitoring studies of air pollution are usually conducted on a regional scale, whereas the present study was focused on a local scale, in an area characterized by multiple sources, and with complex topography and wind dynamics. Here, biomonitoring studies employing *T. capillaris* allowed us to provide new data to contribute to the progress in applications and analysis of this useful and effective air quality monitoring tool.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ecolind.2014.01.008.

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