Heavy metals and trace elements in atmospheric fall-out: Their relationship with topsoil and wheat element composition

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ABSTRACT

The objectives of this study were to determine the average concentrations and deposition rates of 28 elements in atmospheric bulk deposition and to elucidate associations among topsoil, bulk deposition and wheat element composition. The fluxes of arsenic (As), copper (Cu), lead (Pb) and zinc (Zn) deposition in Córdoba were higher than in other agro-ecosystems, which reflects both natural (geochemistry and topsoil removal) and anthropogenic sources. High lanthanide, uranium (U) and thorium (Th) concentrations revealed the impact of an open cast uranium mine. The highest enrichment factors (EF) were those of Cu, Pb, Zn and nickel (Ni), with calcium (Ca) being the most prominent in the surroundings of a cement plant. Industries and the transport of airborne urban pollutants were the main anthropogenic sources for Ca, Cu, Ni, Pb, Zn, cadmium (Cd), iron (Fe), manganese (Mn) and antimony (Sb). The concentrations of metals in wheat grain were predicted using the topsoil and atmospheric fall-out composition with $R^2 = 0.90$, with the latter being the best explanatory variable. The present study highlights the potential health hazards of wheat consumption (Environmental Protection Agency) by the assessment of heavy metals in bulk atmospheric deposition.

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1. Introduction

Atmospheric deposition is recognized as an important source of metals in soils from agro- and natural ecosystems [1–3], arising not only from naturally originated particles, but also by anthropogenic ones mainly derived from industrial activities [4–6] and vehicle emissions [7]. From a biogeochemical point of view, the characterization of atmospheric fall-out (bulk deposition) is useful for identifying the variability, fluxes and sources of atmospheric pollutants [1,8,9].

Atmospheric deposition increases the metal concentrations in soil, and consequently, in the food web [10]. Related to this, the accumulation of potentially toxic elements in vegetables and crops from soil and aerial deposition has been assessed by many researchers [11–13]. For instance, leafy vegetables have been reported to accumulate sizable amounts of toxic metals such as lead, chromium, cadmium and zinc [2,13,14]. In addition, wheat is known to accumulate metals from soils as a consequence of

domestic sewage sludge, phosphate fertilizer application [15,16], tannery effluent irrigation [17], and metal pollution combined with elevated CO_2 levels [18]. Moreover, it has been shown that the aerial deposition and absorption of atmospheric pollutants is an important factor influencing the element composition of wheat grain [12,19,20].

To investigate these relationships further, it is necessary to study the element composition in bulk deposition in order to understand and assess the sources, spatial differences and the impact on the agro-ecosystems. The objectives of this work were therefore: (a) to determine the average concentrations and fluxes of metals in atmospheric bulk deposition; (b) to identify natural and anthropogenic sources by using enrichment factors and multivariate analysis; and (c) to elucidate possible associations among topsoil, bulk deposition (concentrations and fluxes) and wheat (grain and straw) element composition.

2. Materials and methods

2.1. Area of study

The sampling zone was comprised of ten areas of Córdoba province, located in central Argentina (between 31°06′ and 32°03′S, and 63°33′ and 65°26′W, Fig. S1, Supplementary material). The land morphology is highly variable, ranging from a mean altitude of

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about 600 m in the southeast to more than 2500 m above sea level (masl) in the west. From a demographic point of view, large (Córdoba city) and medium-sized cities, along with many towns and villages are found in this area. The weather in the region is temperate, continental and sub-tropical, with a semi-arid tendency. Table S1 (Supplementary material) shows the climatic conditions of the monitoring periods in Córdoba province, and Fig. S2 (Supplementary material) presents the wind roses corresponding to the periods under study, revealing that winds were consistently north–north easterly. The areas studied were agro-ecosystems presumably affected by the different possible air pollution sources: (a) Yocsina (YOC, $n = 6$): cement plant and industrial waste incinerator (hazardous and non-hazardous materials), where Bermudez et al. [21,22] found extremely high enrichment factors of Co, Cu, Mn, Ni, Pb and Zn in top soils, as well as other lithogenic-related elements along a 7 km transect. (b) Río Tercero (RTE, $n = 6$): chemical and petrochemical industries, where a high enrichment of exchangeable heavy metals was found in top soils, such as Mn, Pb and Zn [21]. (c) Córdoba city (CBA, Los Sauces neighborhood, $n = 3$): sub-urban area with metal–mechanical industries, whose top soils are highly enriched in Cu, Mn, and Pb [21], and where wheat grains (when cultivated in the area) showed the highest non-carcinogenic health hazard index [23] in Córdoba province due to high metal concentrations [12]. (d) Despeñaderos (DES, $n = 3$): presumably affected by photochemical oxidants (O_3) and traffic-related metals due to downwind transportation from Córdoba city (1.5 million inhabitants, Fig. S2). In DES, Bermudez et al. [21] found the highest Zn concentrations within Córdoba province top soils, which were almost as high as the limit stated for residential areas [24]. Moreover, Bermudez et al. [12] assessed the high non-carcinogenic health hazard [23] in DES through wheat grain consumption. (e) Oliva (OLI, $n = 3$): part of the Chaco-Pampean plain, where the presence of arsenic in groundwater is associated with mineralogy and sediment texture, and where Bermudez et al. [21] found that the mean and maximum Ba topsoil concentrations surpassed the agricultural and industrial limits, respectively [24]. (f) Pozo de Tigre (PTI, $n = 3$) and Estación General Paz (EGP, $n = 3$): rural communities separated by only 4 km, with dove hunting in the PTI agricultural fields being the main difference between these sites. In these areas, Bermudez et al. [21] found a high enrichment of exchangeable Cu, Mn and Pb in top soils. Other non-agricultural areas were also studied, such as: (a) Schlagintweit Uranium Mine (SUM, $n = 3$): a former open-cast uranium mine, located in the Sierras Grandes mountains (SGM); (b) El Durazno (EDU, $n = 3$): also situated in the SGM, within the Achala batholith; and (c) Chancaní (CHA, $n = 3$), a natural forest reserve. In these areas, Bermudez et al. [21] found a slight enrichment of lanthanides and a large amount of actinides, associated with natural rock composition and mining activities.

2.2. Sampling

Bulk deposition was collected using glass, black-dyed containers (cylinder shape, 3 L capacity), with a jar mouth diameter of 0.10 m covered in a polyethylene web to prevent large parts of materials entering [4]. Three containers were fitted on artificial roofs at about 2.5 m above the ground in each sampling period and area under study. Both rainwater and the fallout of particles were collected continuously for six periods over almost two years of study: (a) 25th August–25th November 2005, (b) 25th November 2005–25th February 2006, (c) 25th February–25th May 2006, (d) 25th May–25 August 2006, (e) 25th August–25th November 2006, and (f) 25th November 2006–25th May 2007.

2.3. Chemical analysis

2.3.1. Bulk deposition

2.3.1.1. Total metal concentrations. After each period of exposure, one container was randomly selected in each sampling area and aliquots of a total volume of 50 mL of concentrated HNO_3 were successively added. The inner walls were washed and the mixture was stirred to dissolve the accumulated deposition. Then, the mixture was dried in crucibles on a hot plate to digest any remaining organic matter until the ashes were homogeneously white. Later, the crucibles were cooled and placed in a desiccator at room temperature in order to determine the dry weight (DW) of the ashes with an analytical balance. Afterwards, the residue was extracted with an aluminum spatula, placed in properly labeled polyethylene tubes, and analyzed by neutron activation analysis (NAA, CNEA, Argentina) for the determination of arsenic (As), barium (Ba), Ca, cerium (Ce), cobalt (Co), chromium (Cr), caesium (Cs), europium (Eu), Fe, hafnium (Hf), lanthanum (La), lutetium (Lu), sodium (Na), rubidium (Rb), Sb, scandium (Sc), samarium (Sm), tantalum (Ta), terbium (Tb), Th, U, ytterbium (Yb) and Zn. The general procedure used in this study was previously described by Marrero et al. [25]. Element concentrations ($\mu g\,g^{-1}$ DW) were calculated using software developed at the NAA laboratory.

2.3.1.2. Metal labile and pseudo-total concentrations. The two remaining bulk deposition samplers collected in each area in the first four periods were digested with *aqua regia* (pseudo-total extraction) to obtain the pseudo-total element concentrations. Initial processing was identical to that used to digest samples for determination by NAA. The dry residues resulting from the HNO_3 digestion were ashed in a muffle furnace at 450 °C for 4 h [26]. Once cooled, 10 mL HCl and 5 mL HNO_3 were added, stirred and allowed to stand for 24 h. This acid extraction is widely used in soils and sediments, and is similar to that used by Garnaud et al. [27] and Wannaz and Pignata [26]. Finally, the digested samples were filtered through 2 µm filter paper (Munktell, Germany), transferred into a 50 mL flask and brought to final volume with ultrapure water. The results were expressed as $\mu g\,g^{-1}$ DW and $mg\,m^{-2}\,day^{-1}$.

In contrast, the bulk deposition collected in the two remaining samplers over the last two periods was partially digested with HNO_3 at pH 1 (labile extraction) [28]. In each container, 25 mL of ultrapure water and concentrated HNO_3 were added to reach the final pH. The mixture was allowed to stand for 10 min and the pH was measured again and corrected when necessary with the addition of nitric acid. This procedure was repeated as many times as necessary in order to obtain a constant pH value equal to 1. After a one-week storage, samples were filtered through 2 µm filter paper (Munktell, Germany) and brought to a final volume of 100 mL with ultrapure water. The element concentrations were determined in duplicate using an atomic absorption spectrometer with a graphite furnace (GFAAS) (PerkinElmer AAnalyst 600) for Cd, Ni and Pb, and a flame atomic absorption spectrometer (FAAS) (PerkinElmer AA3110) for Ca, Cu, Fe, Mn and Zn. The results for HNO_3 (pH 1) partial extraction were expressed as $mg\,m^{-2}\,day^{-1}$.

2.3.2. Topsoil and wheat sampling and analytical procedures

For a detailed description of the soil sampling procedure, see Bermudez et al. [21]. Briefly, a total of ninety-four topsoil composite samples were collected in the study zone (from 5 to 15 sampling sites per sampling area) at a depth of 0–10 cm, from February to March 2006. In order to analyze the pseudo-total fraction, an extraction with *aqua regia* (HCl:HNO₃ 3:1) was performed [29]. Therefore, 5 g DW of each soil sample were placed in a muffle furnace at 450 °C for 4 h to remove the organic matter. After calcination, the samples were allowed to cool and 10 mL of HCl:HNO₃ 3:1 were added [30], with constant shaking for 1 h at

Table 1
Descriptive statistics for the rates of metal deposition in atmospheric fall-out in Córdoba province, central Argentina.

Element ($\mu g\,m^{-2}\,day^{-1}$)	Fraction	Descriptive statistics					
		n	Mean	Median	SE	Min	Max
Arsenic (As)	Total	57	4.4	2.8	0.5	0.8	18.8
Barium (Ba)	Total	58	195	138	25	15	959
Calcium (Ca)	Total	54	11,833	7399	1818	1524	86,666
	Labile	47	21.982	2.302	5.953	0.025	151.837
Cadmium (Cd)	Labile	49	0.369	0.207	0.059	0.031	1.515
Cerium (Ce)	Total	58	23.6	15.8	2.9	2.0	114.5
Cobalt (Co)	Total	58	4.55	3.48	0.52	0.60	19.60
Chromium (Cr)	Total	58	22.2	16.0	2.7	1.0	95.0
Caesium (Cs)	Total	58	2.5	1.8	0.3	0.2	12.5
Copper (Cu)	Labile	49	29.956	22.256	6.241	7.353	317.587
Europium (Eu)	Total	57	0.46	0.32	0.06	0.04	2.16
Iron (Fe)	Total	58	11,399	8430	1411	729	55,624
	Labile	49	5.486	4.424	0.574	0.686	15.399
Hafnium (Hf)	Total	58	2.5	1.6	0.3	0.1	12.3
Lanthanum (La)	Total	58	11.87	8.11	1.44	1.04	55.74
Lutetium (Lu)	Total	56	0.176	0.115	0.025	0.017	1.000
Manganese (Mn)	Labile	49	140.58	99.38	14.55	24.09	518.56
Sodium (Na)	Total	58	9139	6172	1166	942	38,696
Nickel (Ni)	Labile	48	4.158	3.015	0.395	0.320	10.856
Lead (Pb)	Labile	49	17.794	12.830	1.819	2.470	63.112
Rubidium (Rb)	Total	58	44	33	5	4	211
Antimony (Sb)	Total	58	0.83	0.54	0.12	0.08	5.93
Scandium (Sc)	Total	58	4.08	2.81	0.53	0.24	19.89
Samarium (Sm)	Total	58	2.32	1.52	0.30	0.20	11.78
Tantalum (Ta)	Total	58	0.41	0.31	0.05	0.04	2.07
Terbium (Tb)	Total	24	0.47	0.26	0.10	0.08	2.05
Thorium (Th)	Total	58	4.19	2.84	0.51	0.39	20.10
Uranium (U)	Total	54	1.3	1.0	0.2	0.1	5.9
Ytterbium (Yb)	Total	58	1.05	0.73	0.14	0.07	5.32
Zinc (Zn)	Total	58	297	152	51	17	1992
	Labile	47	179.94	104.61	30.27	12.74	808.22

The total fraction of elements was determined by NAA, while the labile fraction was extracted with HNO_3 (pH 1) and measured by FAAS and GFAAS.

room temperature. After 24 h, the samples were filtered through a 2 μm filter paper (Munktell, Germany), transferred to a 25 mL volumetric flask and brought to final volume with the addition of ultrapure water. Finally, the solutions were analyzed using an FAAS (PerkinElmer AA3110) to determine the concentrations of Cu, Ni, Mn and Pb (mg kg^{-1} DW). Total element concentrations were determined by NAA (CNEA, Argentina), and these results have already been published in Bermudez et al. [21] together with soil pH and percentage of organic matter (%OM).

Wheat data have been previously published in Bermudez et al. [12] so sampling and analytical procedures are only briefly described in this work. Wheat plants within a 5 m × 5 m square in the agricultural sampling areas (DES, RTE, OLI, PTI, EGP, YOC and CBA) were collected at harvest in November 2007 and divided into grain and straw. Grains were ashed at 450 °C for 6 h [16] digested with concentrated HNO$_3$, filtered, and the resulting samples were labeled in order to determine the metal concentrations using a GFAAS (PerkinElmer AAnalyst 600) for Cd, Cu, Ni and Pb, and an FAAS (PerkinElmer AA3110) for Fe and Mn. In addition, grain and straw wheat samples were analyzed by NAA for multi-element determination. 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) [31] and metal concentrations in wheat grain and straw were expressed as μg g^{-1} DW.

2.4. Quality control and quality assurance

See Supplementary material and Table S2 for the results of the certified material measurements and their interpretation.

2.5. Statistical analysis

Assumptions of normality and homocedasticity were tested using the Shapiro–Wilk (S–W) and Levene tests, respectively, and the variables that were not normally distributed were log$_{10}$ transformed. ANOVA was performed for each element (concentration and rate of deposition) according to the following model:

$$Y_{ij} = \mu + \alpha_i + \varepsilon_{ij}$$

where i = 1, 2,..., 12 (sampling area); Y_{ij} is the result of one replicate (NAA) or mean of two replicates (GFAAS and FAAS) obtained from the ith sampling site; μ is the population mean; α_i is the fixed effect of sampling area; ε_{ij} is the random error in the ith sampling area. Since not enough samples were available for each sampling period and technique, the seasonal variables could not be incorporated as a factor in our study. 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).

For total element concentrations determined by NAA, enrichment factors (EF) were calculated according to Huang et al. [4], using Sc as a soil marker (EF$_{Sc}$) and the local topsoil composition.

For those metals extracted with *aqua regia*, an enrichment factor was obtained with Fe$_{total}$ (EF$_{Fe}$) as a soil marker [32] using the same equation, with the exception of Ca$_{total}$ and Zn$_{total}$, whose concentration in bulk deposition and topsoil was only determined by NAA.

With the purpose of predicting the metal concentrations in wheat grain and straw, a step-wise multiple linear regression was performed using the topsoil (element concentrations, soil %OM and
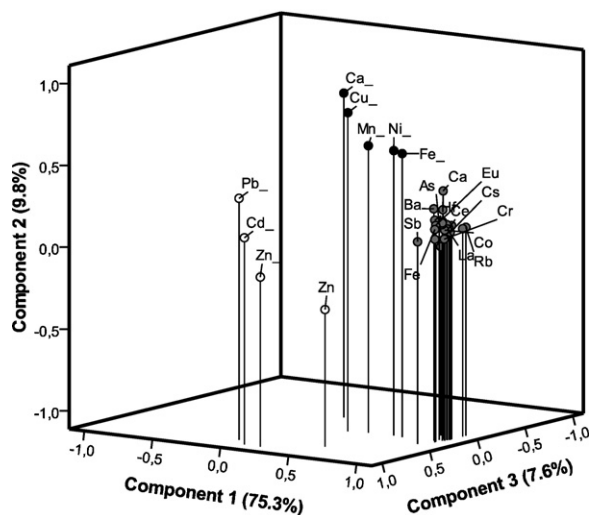
Fig. 1. Loadings of the rotated eigenvectors obtained in a principal component analysis (PCA, varimax rotation method) of the metal deposition rates in atmospheric fall-out in Córdoba province, Argentina.
Footnote: Percentages of total explained variance are given between brackets. (_) indicates the labile fraction (extracted with HNO_3, pH 1). Grey circles = elements mainly represented in component 1. Black circles = elements mainly represented in component 2. Open circles = elements mainly represented in component 3.

pH, previously published in Bermudez et al. [21]) and the bulk atmospheric deposition (element concentrations and rates of deposition) as independent variables. See Supplementary material for the model equation and characteristics.

3. Results and discussion

3.1. Rates of metal deposition in atmospheric fall-out

Table 1 shows the descriptive statistics for the deposition rates (μg m^{-2} day^{-1}) of metals in atmospheric bulk deposition in the province of Córdoba (Argentina). The annual bulk deposition fluxes for all sampling areas in this study were compared with data from different regions of the world (Table S3, Supplementary material). In general, the As, Cd, Cr, Cu, Ni, Pb and Zn rates of deposition in Córdoba, Argentina, were similar to studies performed in industrial, urban and rural areas of China, Croatia, Italy, Serbia and Turkey [4,6,9,33]. However, different results were found for the rates of Cu and Mn (labile fractions), reflecting the influence of agricultural activities and the contribution of airborne soil, respectively [27,34,35].

A principal component analysis (PCA) with Varimax rotation was performed in order to identify the sources of metals in bulk atmospheric deposition [4], with only components with Eigenvalues greater than one after rotation being retained. The three principal components (Fig. 1) contributed 92.7% of the total variance in the samples (Table S4, Supplementary material). The eigenvalue of the first component was the largest (23.347), accounting for 75.3% of the total variance, which suggests that topsoil is a dominant source of metals. This factor was mainly characterized by the elements measured in the total fraction, with Fe and Ni labile fractions, and Zn to a lesser extent, indicating a common crustal source. The second factor was associated with the labile fractions of Ca, Cu, Fe, Mn and Ni (Fig. 1), and this highlighted the presence of anthropogenic sources, mainly the cement plant and the metallurgical and metal–mechanical industries [4,22,34,36]. The third factor, accounting for 7.5% of the total variance, was mainly characterized by the total fraction of Zn and the labile fractions of Cd, Pb and Zn (Fig. 1), indicating an anthropogenic source,

Table 2
Analysis of variance (ANOVA) with the sampling area in Córdoba province (Argentina) as a factor for the mean ± SE deposition rates of labile elements (extracted with HNO_3, pH 1).

Sampling area	Element (μg m^{-2} day^{-1})							
	Ca	Cd	Cu	Fe	Mn	Ni	Pb	Zn
CBA	11.338 ± 4.558 c	0.318 ± 0.024 cde	102.98 ± 71.76	7.981 ± 2.356 abc	182.20 ± 113.60	6.377 ± 1.798 a	19.614 ± 4.504 abcd	125.20 ± 12.41 c
CHA	0.305 ± 0.084 c	0.071 ± 0.014 e	13.968 ± 3.595	5.799 ± 1.144 bcd	123.19 ± 29.93	4.139 ± 0.998 abc	5.750 ± 1.843 d	71.85 ± 20.60 c
DES	1.853 ± 0.875 c	0.778 ± 0.263 b	20.671 ± 6.593	4.218 ± 1.730 cde	133.41 ± 68.92	3.107 ± 1.243 bc	16.210 ± 6.335 abcd	438.74 ± 163.16 b
EGP	6.184 ± 0.804 c	0.161 ± 0.023 de	20.749 ± 5.167	4.596 ± 1.516 cde	190.33 ± 45.63	2.901 ± 0.867 bc	10.281 ± 2.507 cd	34.99 ± 6.56 c
EDU	1.780 ± 0.981 c	0.073 ± 0.004 e	12.992 ± 1.724	1.699 ± 0.473 de	71.92 ± 10.96	1.491 ± 0.318 c	8.090 ± 4.301 d	26.81 ± 8.18 c
OLI	2.623 ± 0.932 c	0.264 ± 0.059 cde	32.878 ± 9.598	5.495 ± 1.526 bcd	143.97 ± 66.96	2.987 ± 1.082 bc	18.282 ± 4.954 abcd	143.55 ± 31.79 c
PTI	0.373 ± 0.167 c	1.310 ± 0.069 a	21.552 ± 3.736	2.983 ± 0.213 de	92.72 ± 12.25	1.981 ± 0.164 c	26.042 ± 2.395 ab	645.42 ± 66.68 a
RTE I	0.651 ± 0.434 c	0.575 ± 0.201 bc	24.717 ± 6.812	3.198 ± 1.014 de	161.58 ± 40.60	5.964 ± 1.814 ab	25.761 ± 8.664 abc	163.11 ± 58.88 c
RTE II	1.062 ± 0.677 c	0.480 ± 0.228 bcd	22.237 ± 6.590	5.775 ± 2.172 bcd	176.48 ± 60.14	4.956 ± 1.315 ab	30.614 ± 11.534 a	139.56 ± 63.25 c
SUM	1.120 ± 0.157 c	0.055 ± 0.010 e	13.723 ± 1.897	0.874 ± 0.132 e	32.60 ± 3.80	1.392 ± 0.430 c	12.775 ± 4.788 bcd	50.03 ± 12.32 c
YOC I	107.590 ± 14.782 a	0.230 ± 0.033 de	35.057 ± 1.185	11.270 ± 1.233a	189.35 ± 9.93	7.008 ± 0.390a	11.788 ± 1.310 bcd	136.49 ± 52.83 c
YOC II	78.891 ± 15.759 b	0.152 ± 0.029 de	33.489 ± 6.023	9.321 ± 1.569 ab	179.56 ± 34.21	5.846 ± 1.078 ab	25.909 ± 5.662 abc	107.53 ± 26.07 c
p Value[a]	***	***	0.245	***	0.439	**	*	***

[a] Values on each vertical line followed by the same letter do not differ significantly ($p = 0.05$).
* Significant at 0.05 probability level.
** Significant at 0.01 probability level.
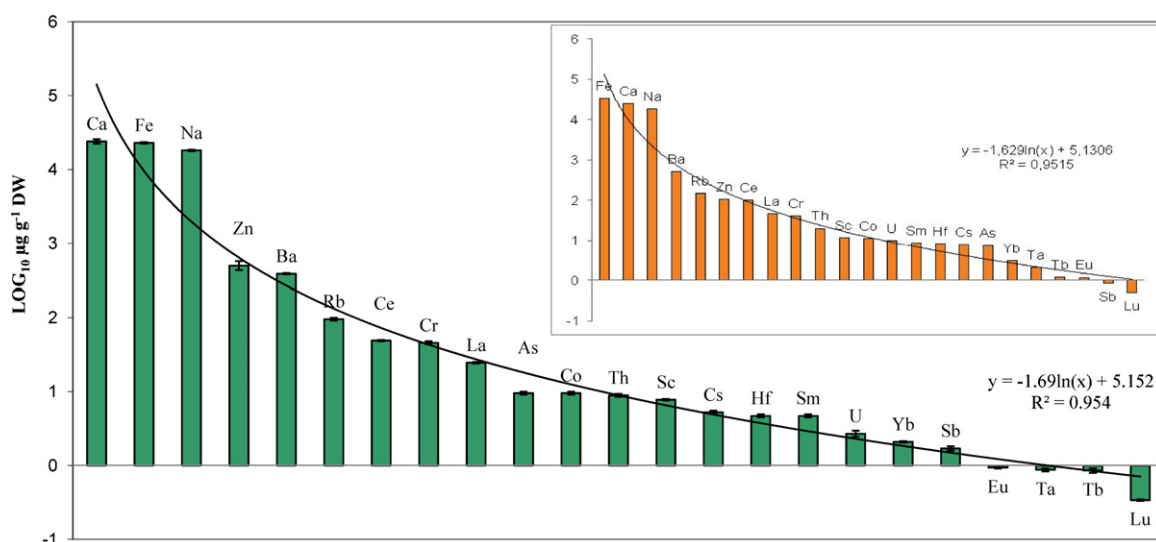*** Significant at 0.001 probability level.

Fig. 2. Mean ± SE metal concentrations (total fraction, $\log_{10} \mu g\, g^{-1}$ DW) in bulk atmospheric deposition (green) and top soils (orange) collected in Córdoba province (Argentina).

Footnote: Soil data were partially published in Bermudez et al. [21]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

possibly related to the use of agrochemicals and to traffic and industrial emissions [4–7,33,38]. It is worth mentioning that the atmospheric deposition of Zn in agricultural and urban areas has been reported to be increased by zinc-made roofs [7,28], which are commonly used in the barns and sheds of the Argentine rural areas.

Table 2 shows the ANOVA results for the fluxes of labile metals, indicating that the highest deposition rates of Ca, Fe and Ni were found in YOC and CBA. Moreover, Table 2 indicates the association of Pb with RTE, and that of Cd and Zn with PTI and DES. It is worth noting that labile Ca deposition fluxes were markedly higher in YOC, with differences being up to 2 orders of magnitude more than the rest of the sampling areas. The fluxes of labile metals in this work (with the exception of Ca) are in agreement with Bermudez et al. [12], who assessed the metal concentration in wheat grains grown in the same area of study. In addition, the highest hazard index for wheat intake (EPA Guidelines for Health Risk Assessment of Chemical Mixtures) [23] were found in CBA and DES, which was mainly ascribed to Mn and Zn pollution [12]. The ANOVA results for the deposition fluxes of elements in the total fraction (determined by NAA) are presented in Table S5 (Supplementary material). It is shown that the highest and lowest rates of deposition were found in CBA and SUM, with the exception of Zn, whose highest deposition rates were registered in PTI. Although these findings are not in agreement with the local soil composition [21,38,39], i.e. U rates of deposition in the city of Córdoba, for example, were higher than in the uranium mine (SUM), they might be accounted by for the high soil removal in CBA and, to a lesser extent, in OLI.

3.2. Total metal concentrations in atmospheric fall-out

Fig. 2 shows the mean metal concentrations ($\log_{10} \mu g\, g^{-1}$ DW) in bulk atmospheric deposition (green) and local top soils (orange), revealing that the order of elements – on a concentration basis – was similar in both matrices. In addition, the mean As and Zn concentrations in Córdoba province were similar to those reported by Huang et al. [4] for the Yangtze River Delta in China, which might indicate important As and Zn inputs. These findings may be ascribed to naturally As enriched soils in Córdoba because of loess composition in central Argentina [21,40], and also to anthropogenic Zn emissions [4,9,32,37].

Table 3 presents an analysis of variance (ANOVA) for the metal concentrations (total fraction, $\mu g\, g^{-1}$ DW) with the sampling area in Córdoba province (Argentina) as a factor. Regarding the lanthanides, most of these (Ce, La, Lu, Sm, Tb), in addition to the actinides (Th, U), As, Co and Cr showed the highest concentrations in the bulk samples collected in a former open-cast uranium mine (SUM). These findings are in agreement with the geochemical characteristics of the area [21,38,39] and provide further evidence of a crustal effect due to soil removal in the agricultural areas with high metal deposition fluxes (CBA and OLI). Fig. S3 (Supplementary material) confirms that the relatively high deposition rates in a natural reserve (CHA) had a crustal origin, since almost all elements in the atmospheric bulk deposition had a 1:1 relationship with the local topsoil composition.

3.3. Topsoil pseudo-total metal concentrations

Table 4 shows the descriptive statistics for the pseudo-total concentrations of Cu, Mn, Ni and Pb in top soils from Córdoba province, Argentina, which were lower than the limits stated by international legislation [24]. These concentrations in top soils were similar to the values found in other studies performed in Argentina [41] and Pakistan [42]. However, the concentrations of Cu, Mn and Ni in Córdoba were lower than those reported for agricultural top soils in China [43], Iran [44] and Spain [29,30].

3.4. Bulk deposition enrichment factors

The calculation of EFs in samples of atmospheric particulate matter, either in relation to local or background soil composition [4] or the earth's crust [9], has been used to evaluate emission sources of metals (natural or anthropogenic). We used the soil composition of each sampling area in order to take into account the regional geochemistry as well as to be able to speculate on the origin of the elements. Elements with EF values near unity may indicate a natural origin, while higher values reflect a potential anthropogenic source, especially for those elements with enrichment values greater than 10 [4].

The mean bulk deposition EFs are presented in Fig. 3, with the highest values being found for Cu (36.26), Ni (21.87), Pb (16.68) and Zn (14.43 and 11.66), which suggests an anthropogenic input,

Table 3
Analysis of variance (ANOVA) with the sampling area in Córdoba province (Argentina) as a factor for the mean ± SE concentrations of elements ($\mu g\,g^{-1}$ DW) in the total fraction (determined by NAA).

Element[a] ($\mu g\,g^{-1}$ DW)	Sampling area									
	CBA	CHA	DES	EGP	EDU	OLI	PTI	RTE I	RTE II	SUM
As***	8.7 ± 0.8 cde	6.8 ± 0.4 e	7.7 ± 0.8 de	7.7 ± 0.6 de	15.5 ± 1.5 b	10.4 ± 0.9 cd	11.7 ± 2.2 c	6.7 ± 0.6 e	8.5 ± 0.4 cde	20.0 ± 1.5 a
Ba	435 ± 26	338 ± 23	392 ± 40	427 ± 39	413 ± 41	386 ± 20	377 ± 28	412 ± 37	412 ± 26	389 ± 44
Ca	27,630 ± 10,334	15,340 ± 1967	20,432 ± 3486	38,445 ± 5734	37,993 ± 12,410	22,152 ± 1736	20,072 ± 3225	24,158 ± 2375	21,637 ± 5089	45,549 ± 11,221
Ce*	48.3 ± 4.4 cd	58.2 ± 7.0 abc	42.8 ± 4.8 d	43.7 ± 3.5 d	62.7 ± 8.7 ab	47.5 ± 1.6 cd	49.6 ± 2.1 bcd	41.1 ± 4.0 d	52.1 ± 2.6 abcd	64.0 ± 7.7 a
Co*	8.64 ± 0.55 b	11.35 ± 1.62 b	8.48 ± 0.99 b	9.02 ± 1.60 b	10.83 ± 2.34 b	8.08 ± 0.39 b	9.45 ± 0.52 b	8.16 ± 0.82 b	17.16 ± 4.97 a	13.15 ± 1.01 ab
Cr***	39.2 ± 2.0 cd	59.7 ± 5.1 b	44.2 ± 4.3 bcd	35.1 ± 0.5 d	40.2 ± 7.6 cd	36.4 ± 0.7 d	41.2 ± 4.2 cd	48.5 ± 3.4 bcd	57.1 ± 2.8 bc	83.7 ± 16.7 a
Cs***	4.9 ± 0.4 cd	6.3 ± 0.6 bc	5.0 ± 0.6 bcd	4.5 ± 0.3 d	6.6 ± 0.4 b	4.9 ± 0.2 cd	5.3 ± 0.1 bcd	4.3 ± 0.4 d	5.2 ± 0.3 bcd	8.4 ± 1.3 a
Eu	0.95 ± 0.06	1.04 ± 0.11	0.83 ± 0.04	0.92 ± 0.09	0.95 ± 0.18	0.86 ± 0.03	1.02 ± 0.02	0.80 ± 0.10	1.06 ± 0.05	1.06 ± 0.18
Fe	23,525 ± 1991	27,758 ± 3008	20,860 ± 2217	20,952 ± 579	19,749 ± 2005	22,775 ± 699	27,599 ± 983	21,594 ± 2876	25,380 ± 1414	23,085 ± 2565
Hf*	5.22 ± 0.34 abc	5.69 ± 0.41 a	4.35 ± 0.40 bcd	5.53 ± 0.58 ab	3.83 ± 0.28 d	4.99 ± 0.13 abcd	5.20 ± 0.16 abc	3.94 ± 0.37 d	5.29 ± 0.53 abc	4.08 ± 0.78 cd
La*	24.49 ± 1.96 bcd	29.03 ± 3.79 abc	21.39 ± 1.95 d	21.99 ± 1.65 cd	29.85 ± 3.81 ab	23.43 ± 0.72 bcd	25.66 ± 0.83 bcd	20.82 ± 2.34 d	26.84 ± 1.56 abcd	33.50 ± 4.67 a
Lu*	0.383 ± 0.045ab	0.413 ± 0.026 a	0.299 ± 0.018 bc	0.334 ± 0.019 abc	0.327 ± 0.036bc	0.336 ± 0.019 abc	0.366 ± 0.009 abc	0.282 ± 0.037c	0.343 ± 0.012 abc	0.411 ± 0.055 a
Na**	20,498 ± 2450 bc	15,610 ± 1272 c	15,506 ± 1754 c	17,446 ± 799 bc	26,189 ± 4438 a	22,524 ± 1582 ab	16,662 ± 621 c	16,675 ± 832 c	17,093 ± 877 bc	20,514 ± 1661 bc
Rb***	91 ± 5 bc	110 ± 11 b	79 ± 9 bc	81 ± 4 bc	185 ± 25 a	79 ± 2 bc	80 ± 4 bc	75 ± 9 c	89 ± 8 bc	174 ± 22 a
Sb	1.45 ± 0.15	1.50 ± 0.17	1.31 ± 0.19	1.48 ± 0.09	1.82 ± 0.20	1.21 ± 0.13	5.29 ± 3.13	1.71 ± 0.27	1.80 ± 0.12	3.22 ± 0.45
Sc***	8.52 ± 0.66 bc	10.70 ± 0.65 a	7.47 ± 0.72 bcd	7.84 ± 0.27 bcd	6.98 ± 0.52 cd	8.15 ± 0.21 bcd	7.76 ± 0.17 bcd	6.91 ± 0.70 d	8.92 ± 0.37 b	7.02 ± 0.82 cd
Sm*	5.82 ± 0.74 ab	5.39 ± 0.61 abc	4.29 ± 0.45 bc	3.99 ± 0.37 c	6.03 ± 0.90 a	4.12 ± 0.18 bc	4.78 ± 0.33 abc	3.96 ± 0.59 c	4.85 ± 0.38 abc	6.38 ± 1.07 a
Ta***	0.86 ± 0.09 bcd	1.09 ± 0.12 bc	0.75 ± 0.06 cd	0.86 ± 0.04 bcd	1.22 ± 0.09 b	0.65 ± 0.02 d	0.76 ± 0.07 cd	0.64 ± 0.07 d	0.84 ± 0.06 cd	1.71 ± 0.34 a
Tb	0.94 ± 0.18	0.97 ± 0.10	0.73 ± 0.11	0.82 ± 0.20	0.96 ± 0.03	–	0.94 ± 0.18	1.17 ± 0.00	0.64 ± 0.05	1.19 ± 0.02
Th***	8.76 ± 0.71 cd	9.71 ± 1.09 bc	7.64 ± 0.64 cd	8.20 ± 0.48 cd	11.54 ± 0.86 ab	8.15 ± 0.19 cd	8.66 ± 0.18 cd	6.98 ± 0.74 d	8.72 ± 0.48 cd	13.55 ± 2.08 a
U***	2.3 ± 0.2 b	2.5 ± 0.1 b	1.6 ± 0.2 b	2.2 ± 0.2 b	2.9 ± 0.4 b	2.6 ± 0.2 b	2.6 ± 0.2 b	2.2 ± 0.4 b	2.1 ± 0.1 b	13.2 ± 2.4 a
Yb	2.38 ± 0.15	2.39 ± 0.25	1.88 ± 0.15	2.03 ± 0.09	2.34 ± 0.35	1.99 ± 0.09	2.21 ± 0.08	1.64 ± 0.19	2.23 ± 0.12	2.27 ± 0.42
Zn***	168 ± 26 d	429 ± 141 cd	857 ± 263 bc	324 ± 148 cd	550 ± 168 cd	3.91 ± 138 cd	2293 ± 366 a	798 ± 242 cd	661 ± 205 cd	1498 ± 348 b
n	6	5	5	6	4	6	5	5	6	6

[a] Values on each horizontal line followed by the same letter do not differ significantly (LSD test, $p = 0.05$).
* Significant at 0.05 probability level.
** Significant at 0.01 probability level.
*** Significant at 0.001 probability level.

Table 4
Descriptive statistics for the pseudo-total metal concentrations (extracted with *aqua regia*) in top soils collected in Córdoba province, central Argentina.

Element (mg kg^{-1} DW)	Descriptive statistics					
	n	Mean	Median	SE	Min	Max
Cu	94	7.94	6.93	0.53	2.47	29.7
Mn	94	395	365	15	102	908
Ni	94	8.38	7.09	0.32	4.26	17.58
Pb	94	10.00	9.40	0.35	5.62	27.63

especially in atmospheric labile forms, as pointed out by Desboeufs et al. [45] and Sandroni and Migon [46]. These findings indicate a good match between the second and third factor of the PCA (anthropogenic sources) and EF calculations.

As far as the spatial differences in EFs are concerned, Fig. 4 depicts the mean EF$_{Fe}$ for the sampling areas in Córdoba province while Table S6 (Supplementary material) shows the LSD results of the ANOVA. Nickel was found to be highly enriched in RTE and YOC (Fig. 4a). Regarding Ca, although this was only slightly enriched in the average bulk deposition (EF$_{Fe}$: 3.14; EF$_{Sc}$: 2.29), it was highly enriched in the surroundings of a cement plant (Fig. 4b), thus revealing its influence [22,34,36,47]. In addition, the highest Zn enrichment factors were found in PTI and DES, indicating that vehicular traffic and zinc-made roofs were important sources of Zn [4,7,35,37].

Fig. 5 shows EF$_{Sc}$ in the atmospheric bulk deposition as a function of the topsoil enrichment, which was normalized by the upper continental crust composition [21]. In this plot, while topsoil EF$_{Sc}$ may indicate regional geochemical characteristics, atmospheric bulk EF$_{Sc}$ might show the presence of atmospheric (anthropogenic) sources. It can be observed that, while Zn was only slightly enriched in the topsoil, it was highly enriched in atmospheric fall-out.

3.5. Multiple regression models of metals in wheat grain and straw

Although the sampling of top soils, wheat grain and straw, and the atmospheric bulk deposition did not match temporally in this study, the concentrations of metals in these matrices were considered representative of the sampled areas in a first attempt to assess the element fluxes in the soil–air–plant system.

3.5.1. Wheat straw

The multiple regression analysis (Table 5) indicated that 82% of the total variance in straw composition (only elements determined by NAA) could be explained by the concentrations of metals in the topsoil (TPS) and atmospheric bulk deposition (cABD). However, neither %OM nor pH were statistically significant as independent variables. TPS was the variable with the highest marginal R^2, indicating that soil element composition is the major factor in determining concentrations of metals in straw. This last finding is in agreement with several authors who assessed the significant effect of heavy metal concentrations in soil on wheat straw, and who pointed out the importance of atmospheric fall-out in wheat contamination pathways [12,19,20,48]. In addition, Bermudez et al. [12] found high bio-concentration factors in wheat straw collected in the same areas as the current study, which were subject to natural (As) and anthropogenic pollution (Cr and Sb). Our findings might indicate that the contamination of wheat straw with heavy metals and trace elements could have environmental implications on health, due to the transfer of these elements to grains [12,19,20,48] and in biotechnologies using straw [49–51].

3.5.2. Wheat grain

Table 5 shows that the wheat grain element composition could be predicted by the metal concentrations in TPS and cABD (86% of the total variance, grain$_1$ model). These findings indicate a strong influence of soil and bulk deposition on the wheat grain heavy
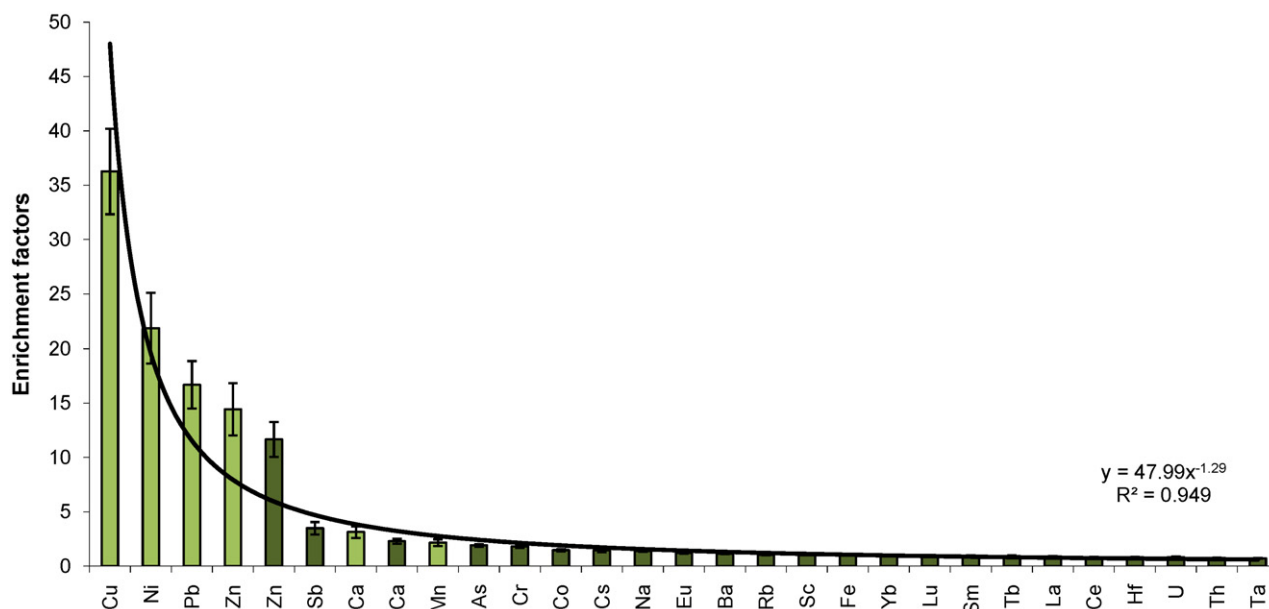

$$y = 47.99x^{-1.29}$$
$$R^2 = 0.949$$

Fig. 3. Enrichment factors (mean ± SE) in descending order of the deposition rate (g m^{-2} day^{-1}) of metals in their total (EF$_{Sc}$, green) or pseudo-total fractions (EF$_{Fe}$, light green) in Córdoba province, Argentina.
Footnote: The best fitted trend line (potential equation) and the value of the coefficient of determination (R^2) are shown in the plot. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

Table 5
Regression models for the metal concentrations in wheat grain and straw using the element concentrations in top soils and the rates and concentrations of elements in bulk atmospheric deposition in Córdoba province, central Argentina.

Dependent variable	Constant	Parameters	Model statistics			
			p	r	R^2	$R^2_{adjusted}$
$Straw_1$	$-1.581\ (\pm0.120)$[***]	$+0.975\ (\pm0.052)\times TPS$[***] $+0.146\ (\pm0.043)\times cABD$[***]	[***]	0.909	0.825	0.821
$Grain_1$	$-2.735\ (\pm0.143)$[***]	$+0.994\ (\pm0.052)\times TPS$[***] $+0.385\ (\pm0.046)\times cABD$[***]	[***]	0.930	0.864	0.860
$Grain_2$	$-1.793\ (\pm0.222)$[***]	$+0.763\ (\pm0.085)\times TPS$[***] $+0.280\ (\pm0.080)\times c/rABD$[***]	[***]	0.686	0.470	0.459
$Grain_3$	$-2.670\ (\pm0.134)$[***]	$+1.011\ (\pm0.049)\times TPS$[***] $+0.416\ (\pm0.045)\times c/rABD(-Ni)$[***]	[***]	0.913	0.834	0.830
$Grain_4$	$-1.982\ (\pm0.197)$[***]	$+0.493\ (\pm0.112)\times TPS$[***] $+0.341\ (\pm0.041)\times cABD$[***] $+0.530\ (\pm0.108)\times straw$[***]	[***]	0.963	0.952	0.901

TPS = $\log_{10}$ of the total concentrations ($\mu g\,g^{-1}$ DW) of elements in top soils. ABD = $\log_{10}$ of the total concentrations (cABD, $\mu g\,g^{-1}$ DW) or rates of deposition (rABD) of elements in atmospheric bulk deposition.

[***] Significant at 0.001 probability level. r = Spearman regression coefficient. R^2 = general coefficient of determination.

metal composition. In addition, our results might be useful for land management, since it would be possible to predict the element composition of wheat grains knowing the sources of metal pollution to which a specific area is subject to and the soil and atmospheric element concentrations. The residuals of each independent variable are plotted in Fig. S4a for TPS and in Fig. S4b for cABD (supplementary material), where it can be observed that soil composition was the best predictive independent variable. In addition, it was found that wheat grain had higher concentrations of Cr, Rb, Sb, Zn, Fe and Na than could be explained by TPS. Likewise, the Ba and Zn concentrations in wheat grain were lower than those explained by cDAT, indicating that Zn might have been mainly incorporated from the soil.

In order to lessen the effect of lithogenic metals, we decided to include the rates of deposition (rABD) of elements in their labile fraction (Table 5, grain$_2$ model). The value of R^2 was much lower than that of the previous model (0.459), which could be explained

by the fact that wheat grain Ni concentrations were higher than expected by TPS and rABD (data not shown). By extracting Ni from the regression model, R^2 increased to 0.830 (grain$_3$ model), which might indicate some specificity of wheat plants to accumulate this metal or the ease with which they could uptake Ni from the soil [10,52].

Finally, when incorporating the straw composition in the last regression model, the explained variance rose to 90.1% (Table 5, grain$_4$ model) and the best explanatory variable was cABD (marginal R^2: 0.549, data not shown). This could indicate that when the concentrations of metals in wheat grains increased greatly with a rise in wheat straw and TPS (based on their higher tangent values), the element composition of wheat grains was best explained by cABD, which is consistent with work of several authors who assessed the importance of air pollution on the metal content of vegetables grown in Argentina, France, India, and Sweden [2,3,12,13,19,20]. Moreover, the present study may allow the assessment of potential non-carcinogenic health hazards [23] through wheat consumption [12] by the evaluation of metals in bulk atmospheric deposition and top soils.

Taking our results together, they suggest that is better to avoid analyzing atmospheric deposition rates, concentrations or
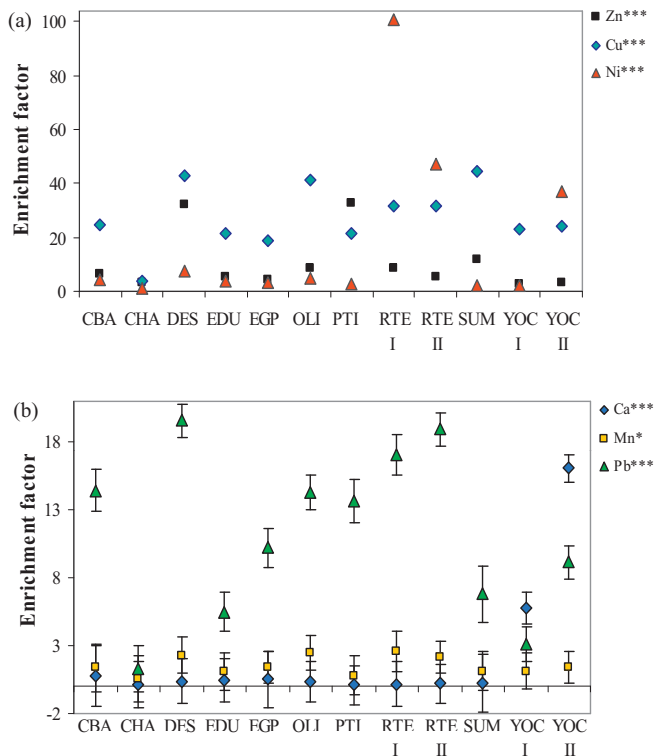

Fig. 4. Mean ± SE metal enrichment factors (pseudo-total fraction, EF$_{Fe}$) in atmospheric bulk deposition collected in sampling areas of Córdoba province (Argentina). (a) Cu, Ni and Zn. (b) Ca, Mn and Pb. ANOVA p-values are indicated with asterisks, while post hoc comparisons are shown in Table S6 (Supplementary material). *Footnote*: *Significant at 0.05 probability level. ***Significant at 0.001 probability level. SEs were omitted in (a) since they were smaller than the corresponding icon.
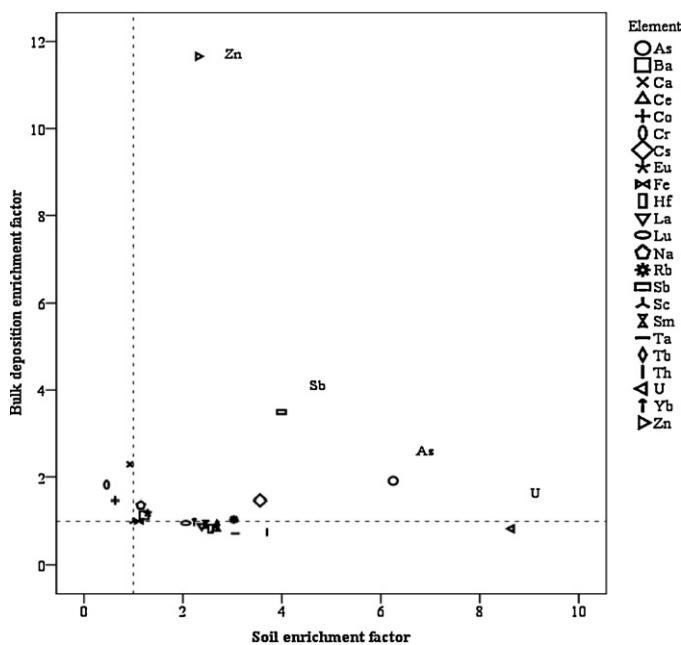

Fig. 5. Average enrichment factors (EF) of the total fraction of metals in atmospheric bulk deposition (EF$_{Sc}$) for all sampling areas in the province of Córdoba (y axis) as a function of the metal topsoil enrichment (normalized by the *upper continental crust composition*, EF$_{Sc(UCC)}$) (x axis). *Footnote*: The dotted lines indicate EF = 1.

enrichment factors separately, as they reflect different environmental constrains, i.e. the global input of metals, their possible sources (natural vs. anthropogenic) and the local or background geochemical characteristics. Likewise, we discourage the calculation of enrichment factors in atmospheric deposition with upper continental crust values, as they may show only the regional soil composition instead of leading to the identification of the origin of metals, particularly for those which may have both an atmospheric and a soil source.

Acknowledgments

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2012.02.023.

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