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

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PII: S0304-3894(12)00169-0
DOI: doi:10.1016/j.jhazmat.2012.02.023
Reference: HAZMAT 14010

To appear in: *Journal of Hazardous Materials*

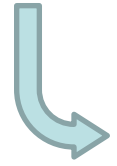
Received date: 22-9-2011
Revised date: 26-1-2012
Accepted date: 8-2-2012

Please cite this article as: G.M.A. Bermudez, R. Jasan, R. Plá, M.L. Pignata, Heavy metals and trace elements in atmospheric fall-out: Their relationship with topsoil and wheat element composition, *Journal of Hazardous Materials* (2010), doi:10.1016/j.jhazmat.2012.02.023

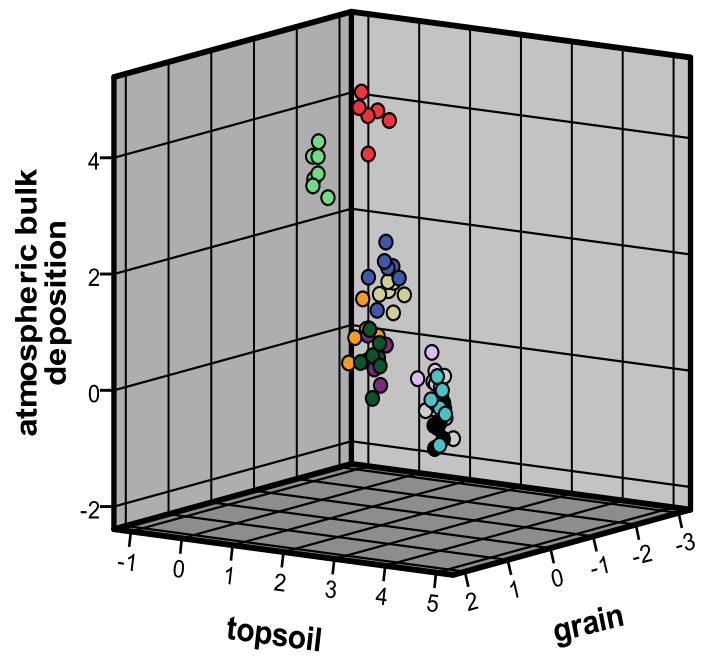
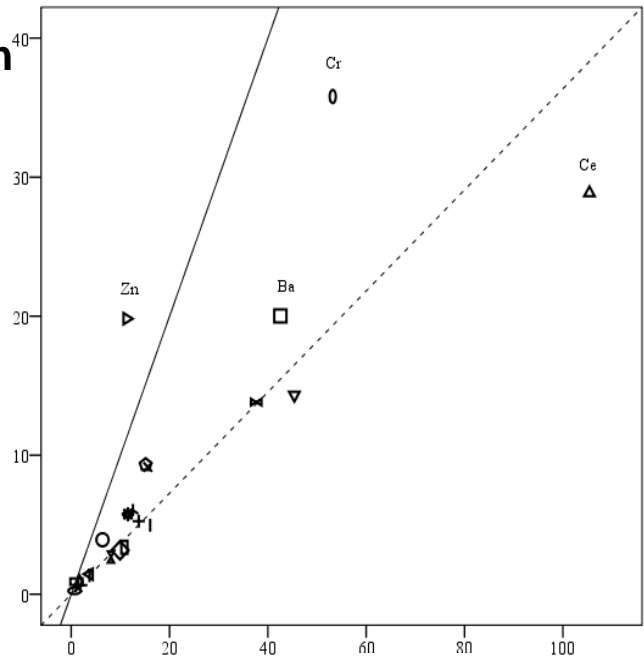
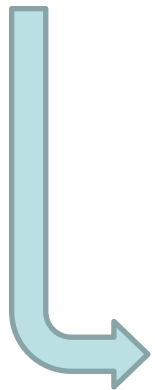
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Atmospheric bulk deposition



Soil



Research Highlights

- Metal and trace element deposition rates and concentrations in bulk samples.
- Anthropogenic vs. natural sources were identified using enrichment factors and PCA.
- Anthropogenic sources for Ca, Cd, Cu, Fe, Mn, Ni, Pb, Sb, U, Zn and lanthanides.
- Main sources were a cement plant, chemical-mechanical industries, cities and mining.
- Metals in wheat grain were predicted by soil and bulk deposition composition.

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1 **Heavy metals and trace elements in atmospheric fall-out: Their relationship with**
2
3 **topsoil and wheat element composition**
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1 20 **Abstract**

2
3 21 The objectives of this study were to determine the average concentrations and
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5 22 deposition rates of 28 elements in atmospheric bulk deposition and to elucidate
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7 23 associations among topsoil, bulk deposition and wheat element composition. The fluxes
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9 24 of arsenic (As), copper (Cu), lead (Pb) and zinc (Zn) deposition in Córdoba were higher
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11 25 than in other agro-ecosystems, which reflects both natural (geochemistry and topsoil
12
13 26 removal) and anthropogenic sources. High lanthanide, uranium (U) and thorium (Th)
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15 27 concentrations revealed the impact of an open cast uranium mine. The highest
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17 28 enrichment factors (EF) were those of Cu, Pb, Zn and nickel (Ni), with calcium (Ca)
18
19 29 being the most prominent in the surroundings of a cement plant. Industries and the
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21 30 transport of airborne urban pollutants were the main anthropogenic sources for Ca, Cu,
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23 31 Ni, Pb, Zn, cadmium (Cd), iron (Fe), manganese (Mn) and antimony (Sb). The
24
25 32 concentrations of metals in wheat grain were predicted using the topsoil and
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27 33 atmospheric fall-out composition with $R^2=0.90$, with the latter being the best
28
29 34 explanatory variable. The present study highlights the potential health hazards of wheat
30
31 35 consumption (Environmental Protection Agency) by the assessment of heavy metals in
32
33 36 bulk atmospheric deposition.

34
35 37 **Key-words:** Bulk deposition; Cement plant; Industrial incinerator; *Triticum aestivum*
36
37 38 L.; Argentina.

39 1. Introduction

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

46 Atmospheric deposition increases the metal concentrations in soil, and consequently, in
47 the food web [10]. Related to this, the accumulation of potentially toxic elements in
48 vegetables and crops from soil and aerial deposition has been assessed by many
49 researchers [11-13]. For instance, leafy vegetables have been reported to accumulate
50 sizable amounts of toxic metals such as lead, chromium, cadmium and zinc [2,13,14]. In
51 addition, wheat is known to accumulate metals from soils as a consequence of domestic
52 sewage sludge, phosphate fertilizer application [15,16], tannery effluent irrigation [17],
53 and metal pollution combined with elevated CO₂ levels [18]. Moreover, it has been
54 shown that the aerial deposition and absorption of atmospheric pollutants is an
55 important factor influencing the element composition of wheat grain [12,19,20].

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

1 62 among topsoil, bulk deposition (concentrations and fluxes) and wheat (grain and straw)
2
3 63 element composition.
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7 8 65 **2. Materials and Methods**

9 10 66 2.1 Area of study

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13 67 The sampling zone was comprised of ten areas of Córdoba province, located in central
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15 68 Argentina (between 31°06' and 32°03' S, and 63°33' and 65°26' W, Fig. S1,
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17 69 supplementary material). The land morphology is highly variable, ranging from a mean
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19 70 altitude of about 600 m in the southeast to more than 2,500 meters above sea level
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21 71 (masl) in the west. From a demographic point of view, large (Córdoba city) and
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23 72 medium-sized cities, along with many towns and villages are found in this area. The
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25 73 weather in the region is temperate, continental and sub-tropical, with a semi-arid
26
27 74 tendency. Table S1 (supplementary material) shows the climatic conditions of the
28
29 75 monitoring periods in Córdoba province, and Fig. S2 (supplementary material) presents
30
31 76 the wind roses corresponding to the periods under study, revealing that winds were
32
33 77 consistently north-north easterly. The areas studied were agro-ecosystems presumably
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35 78 affected by the different possible air pollution sources: (a) Yocsina (YOC, n=6): cement
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37 79 plant and industrial waste incinerator (hazardous and non-hazardous materials), where
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39 80 Bermudez et al. [21,22] found extremely high enrichment factors of Co, Cu, Mn, Ni, Pb
40
41 81 y Zn in top soils, as well as other lithogenic-related elements along a 7 km transect. (b)
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43 82 Río Tercero (RTE, n=6): chemical and petrochemical industries, where a high
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45 83 enrichment of exchangeable heavy metals was found in top soils, such as Mn, Pb and
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47 84 Zn [21]. (c) Córdoba city (CBA, Los Sauces neighborhood, n=3): sub-urban area with
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49 85 metal-mechanical industries, whose top soils are highly enriched in Cu, Mn, and Pb
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1 86 [21], and where wheat grains (when cultivated in the area) showed the highest non-
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3 87 carcinogenic health hazard index [23] in Córdoba province due to high metal
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5 88 concentrations [12]. (d) Despeñaderos (DES, n=3): presumably affected by
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7 89 photochemical oxidants (O₃) and traffic-related metals due to downwind transportation
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9 90 from Córdoba city (1.5 million inhabitants, Fig. S2). In DES, Bermudez et al. [21]
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11 91 found the highest Zn concentrations within Córdoba province top soils, which were
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13 92 almost as high as the limit stated for residential areas [24]. Moreover, Bermudez et al.
14
15 93 [12] assessed the high non-carcinogenic health hazard [23] in DES through wheat grain
16
17 94 consumption. (e) Oliva (OLI, n=3): part of the Chaco-Pampean plain, where the
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19 95 presence of arsenic in groundwater is associated with mineralogy and sediment texture,
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21 96 and where Bermudez et al. [21] found that the mean and maximum Ba topsoil
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23 97 concentrations surpassed the agricultural and industrial limits, respectively [24]. (f)
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25 98 Pozo de Tigre (PTI, n=3) and Estación General Paz (EGP, n=3): rural communities
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27 99 separated by only 4 km, with dove hunting in the PTI agricultural fields being the main
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29 100 difference between these sites. In these areas, Bermudez et al. [21] found a high
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31 101 enrichment of exchangeable Cu, Mn and Pb in top soils. Other non-agricultural areas
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33 102 were also studied, such as: (a) Schlagintweit Uranium Mine (SUM, n=3): a former
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35 103 open-cast uranium mine, located in the Sierras Grandes mountains (SGM); (b) El
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37 104 Durazno (EDU, n=3): also situated in the SGM, within the Achala batholith; and (c)
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39 105 Chancaní (CHA, n=3), a natural forest reserve. In these areas, Bermudez et al. [21]
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41 106 found a slight enrichment of lanthanides and a large amount of actinides, associated
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43 107 with natural rock composition and mining activities.
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54 108 2.2 Sampling

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1 109 Bulk deposition was collected using glass, black-dyed containers (cylinder shape, 3 L
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3 110 capacity), with a jar mouth diameter of 0.10 m covered in a polyethylene web to prevent
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6 111 large parts of materials entering [4]. Three containers were fitted on artificial roofs at
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8 112 about 2.5 m above the ground in each sampling period and area under study. Both
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10 113 rainwater and the fallout of particles were collected continuously for six periods over
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12 114 almost two years of study: a) 25th August–25th November 2005, b) 25th November 2005–
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14 115 25th February 2006, c) 25th February–25th May 2006, d) 25th May–25 August 2006, e)
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16 116 25th August–25th November 2006, and f) 25th November 2006–25th May 2007.
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22 118 2.3 Chemical analysis

23 119 2.3.1 Bulk deposition

24 120 2.3.1.1 Total metal concentrations

25 121 After each period of exposure, one container was randomly selected in each sampling
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27 122 area and aliquots of a total volume of 50 mL of concentrated HNO₃ were successively
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29 123 added. The inner walls were washed and the mixture was stirred to dissolve the
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31 124 accumulated deposition. Then, the mixture was dried in crucibles on a hot plate to
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33 125 digest any remaining organic matter until the ashes were homogeneously white. Later,
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35 126 the crucibles were cooled and placed in a desiccator at room temperature in order to
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37 127 determine the dry weight (DW) of the ashes with an analytical balance. Afterwards, the
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39 128 residue was extracted with an aluminum spatula, placed in properly labeled
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41 129 polyethylene tubes, and analyzed by neutron activation analysis (NAA, CNEA,
42
43 130 Argentina) for the determination of arsenic (As), barium (Ba), Ca, cerium (Ce), cobalt
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45 131 (Co), chromium (Cr), caesium (Cs), europium (Eu), Fe, hafnium (Hf), lanthanum (La),
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47 132 lutetium (Lu), sodium (Na), rubidium (Rb), Sb, scandium (Sc), samarium (Sm),
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1 133 tantalum (Ta), terbium (Tb), Th, U, ytterbium (Yb) and Zn. The general procedure used
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3 134 in this study was previously described by Marrero et al. [25]. Element concentrations
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5 135 ($\mu\text{g g}^{-1}$ DW) were calculated using software developed at the NAA laboratory.
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10 137 *2.3.1.2 Metal labile and pseudo-total concentrations*

13 138 The two remaining bulk deposition samplers collected in each area in the first four
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15 139 periods were digested with *aqua regia* (pseudo-total extraction) to obtain the pseudo-
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17 140 total element concentrations. Initial processing was identical to that used to digest
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19 141 samples for determination by NAA. The dry residues resulting from the HNO_3 digestion
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21 142 were ashed in a muffle furnace at $450\text{ }^\circ\text{C}$ for 4 hours [26]. Once cooled, 10 mL HCl and
22
23 143 5 mL HNO_3 were added, stirred and allowed to stand for 24 h. This acid extraction is
24
25 144 widely used in soils and sediments, and is similar to that used by Garnaud et al. [27] and
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27 145 Wannaz and Pignata [26]. Finally, the digested samples were filtered through $2\text{ }\mu\text{m}$
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29 146 filter paper (Munktell, Germany), transferred into a 50-mL flask and brought to final
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31 147 volume with ultrapure water. The results were expressed as $\mu\text{g g}^{-1}$ DW and $\text{mg m}^{-2}\text{ day}^{-1}$.
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40 149 In contrast, the bulk deposition collected in the two remaining samplers over the last
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42 150 two periods was partially digested with HNO_3 at pH 1 (labile extraction) [28]. In each
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44 151 container, 25 mL of ultrapure water and concentrated HNO_3 were added to reach the
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46 152 final pH. The mixture was allowed to stand for 10 min and the pH was measured again
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48 153 and corrected when necessary with the addition of nitric acid. This procedure was
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50 154 repeated as many times as necessary in order to obtain a constant pH value equal to 1.
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52 155 After a one-week storage, samples were filtered through $2\text{ }\mu\text{m}$ filter paper (Munktell,
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55 156 Germany) and brought to a final volume of 100 mL with ultrapure water. The element
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1 157 concentrations were determined in duplicate using an atomic absorption spectrometer
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3 158 with a graphite furnace (GFAAS) (Perkin-Elmer AAnalyst 600) for Cd, Ni and Pb, and
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5 159 a flame atomic absorption spectrometer (FAAS) (Perkin-Elmer AA3110) for Ca, Cu,
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8 160 Fe, Mn and Zn. The results for HNO₃ (pH 1) partial extraction were expressed as mg m⁻²
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10 161 day⁻¹.

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13 163 2.3.2. Topsoil and wheat sampling and analytical procedures

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16 164 For a detailed description of the soil sampling procedure, see Bermudez et al. [21].
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18 165 Briefly, a total of ninety-four topsoil composite samples were collected in the study
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21 166 zone (from 5 to 15 sampling sites per sampling area) at a depth of 0–10 cm, from
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23 167 February to March 2006. In order to analyze the pseudo-total fraction, an extraction
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26 168 with *aqua regia* (HCl: HNO₃ 3:1) was performed [29]. Therefore, 5 g DW of each soil
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29 169 sample were placed in a muffle furnace at 450 °C for 4 h to remove the organic matter.
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32 170 After calcination, the samples were allowed to cool and 10 mL of HCl: HNO₃ 3:1 were
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35 171 added [30], with constant shaking for 1 h at room temperature. After 24 h, the samples
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38 172 were filtered through a 2 µm filter paper (Munktell, Germany), transferred to a 25-mL
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40 173 volumetric flask and brought to final volume with the addition of ultrapure water.
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42 174 Finally, the solutions were analyzed using an FAAS (Perkin-Elmer AA3110) to
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44 175 determine the concentrations of Cu, Ni, Mn and Pb (mg kg⁻¹ DW). Total element
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47 176 concentrations were determined by NAA (CNEA, Argentina), and these results have
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49 177 already been published in Bermudez et al. [21] together with soil pH and percentage of
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51 178 organic matter (%OM).

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54 179 Wheat data have been previously published in Bermudez et al. [12] so sampling and
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57 180 analytical procedures are only briefly described in this work. Wheat plants within a 5 x
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181 5 m square in the agricultural sampling areas (DES, RTE, OLI, PTI, EGP, YOC and
182 CBA) were collected at harvest in November 2007 and divided into grain and straw.
183 Grains were ashed at 450 °C for 6 h [16] digested with concentrated HNO₃, filtered, and
184 the resulting samples were labeled in order to determine the metal concentrations using
185 a GFAAS (Perkin-Elmer AAnalyst 600) for Cd, Cu, Ni and Pb, and an FAAS (Perkin-
186 Elmer AA3110) for Fe and Mn. In addition, grain and straw wheat samples were
187 analyzed by NAA for multi-element determination. Samples were irradiated for 5 h in
188 the RA-3 reactor (thermal flux $3 \times 10^{13} \text{ cm}^{-2} \text{ s}^{-1}$, 8 Mw) of the Ezeiza Atomic Center
189 (CNEA) [31] and metal concentrations in wheat grain and straw were expressed as $\mu\text{g g}^{-1}$
190 DW.

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192 2.4 Quality control and quality assurance

193 See the supplementary material section and Table S2 for the results of the certified
194 material measurements and their interpretation.

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196 2.5 Statistical analysis

197 Assumptions of normality and homocedasticity were tested using the Shapiro–Wilk (S-
198 W) and Levene tests, respectively, and the variables that were not normally distributed
199 were LOG₁₀ transformed. ANOVA was performed for each element (concentration and
200 rate of deposition) according to the following model:

$$201 Y_{ij} = \mu + \alpha_i + \varepsilon_{ij}$$

202 where $i = 1, 2, \dots, 12$ (sampling area); Y_{ij} is the result of one replicate (NAA) or mean
203 of two replicates (GFAAS and FAAS) obtained from the i th sampling site; μ is the
204 population mean; α_i is the fixed effect of sampling area; ε_{ij} is the random error in the i th

1 205 sampling area. Since not enough samples were available for each sampling period and
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3 206 technique, the seasonal variables could not be incorporated as a factor in our study.
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5 207 When the ANOVA null hypothesis was rejected (significance level < 0.05), post hoc
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7 208 comparisons were performed to investigate differences between pairs of means (Least
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9 209 Significant Difference, LSD).

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12 210 For total element concentrations determined by NAA, enrichment factors (EF) were
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14 211 calculated according to Huang et al. [4], using Sc as a soil marker (EF_{Sc}) and the local
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16 212 topsoil composition.

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19 213 For those metals extracted with *aqua regia*, an enrichment factor was obtained with
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21 214 Fe_{total} (EF_{Fe}) as a soil marker [32] using the same equation, with the exception of Ca_{total}
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23 215 and Zn_{total} , whose concentration in bulk deposition and topsoil was only determined by
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25 216 NAA.

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28 217 With the purpose of predicting the metal concentrations in wheat grain and straw, a
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30 218 step-wise multiple linear regression was performed using the topsoil (element
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32 219 concentrations, soil %OM and pH, previously published in Bermudez et al. [21]) and
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34 220 the bulk atmospheric deposition (element concentrations and rates of deposition) as
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36 221 independent variables. See the supplementary material section for the model equation
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38 222 and characteristics.

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46 224 **3. Results and discussion**

47 225 3.1 Rates of metal deposition in atmospheric fall-out

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50 226 Table 1 shows the descriptive statistics for the deposition rates ($\mu\text{g m}^{-2} \text{ day}^{-1}$) of metals
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52 227 in atmospheric bulk deposition in the province of Córdoba (Argentina). The annual bulk
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54 228 deposition fluxes for all sampling areas in this study were compared with data from
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1 229 different regions of the world (Table S3, supplementary material). In general, the As,
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3 230 Cd, Cr, Cu, Ni, Pb and Zn rates of deposition in Córdoba, Argentina, were similar to
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5 231 studies performed in industrial, urban and rural areas of China, Croatia, Italy, Serbia and
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7
8 232 Turkey [4,6,9,33]. However, different results were found for the rates of Cu and Mn
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10 233 (labile fractions), reflecting the influence of agricultural activities and the contribution
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12 234 of airborne soil, respectively [27,34,35].

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14
15 235 A principal component analysis (PCA) with Varimax rotation was performed in order to
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17 236 identify the sources of metals in bulk atmospheric deposition [4], with only components
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19 237 with Eigenvalues greater than one after rotation being retained. The three principal
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21 238 components (Fig. 1) contributed 92.7% of the total variance in the samples (Table S4,
22
23 239 supplementary material). The eigenvalue of the first component was the largest
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25 240 (23.347), accounting for 75.3% of the total variance, which suggests that topsoil is a
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27 241 dominant source of metals. This factor was mainly characterized by the elements
28
29 242 measured in the total fraction, with Fe and Ni labile fractions, and Zn to a lesser extent,
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31 243 indicating a common crustal source. The second factor was associated with the labile
32
33 244 fractions of Ca, Cu, Fe, Mn and Ni (Fig. 1), and this highlighted the presence of
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35 245 anthropogenic sources, mainly the cement plant and the metallurgical and metal-
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37 246 mechanical industries [4,22,34,36]. The third factor, accounting for 7.5% of the total
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39 247 variance, was mainly characterized by the total fraction of Zn and the labile fractions of
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41 248 Cd, Pb and Zn (Fig. 1), indicating an anthropogenic source, possibly related to the use
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43 249 of agrochemicals and to traffic and industrial emissions [4-7,33,38]. It is worth
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45 250 mentioning that the atmospheric deposition of Zn in agricultural and urban areas has
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47 251 been reported to be increased by zinc-made roofs [7,28], which are commonly used in
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57 252 the barns and sheds of the Argentine rural areas.
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1 253 Table 2 shows the ANOVA results for the fluxes of labile metals, indicating that the
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3 254 highest deposition rates of Ca, Fe and Ni were found in YOC and CBA. Moreover,
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5 255 Table 2 indicates the association of Pb with RTE, and that of Cd and Zn with PTI and
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8 256 DES. It is worth noting that labile Ca deposition fluxes were markedly higher in YOC,
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10 257 with differences being up to 2 orders of magnitude more than the rest of the sampling
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12 258 areas. The fluxes of labile metals in this work (with the exception of Ca) are in
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14 259 agreement with Bermudez et al. [12], who assessed the metal concentration in wheat
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16 260 grains grown in the same area of study. In addition, the highest hazard index for wheat
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18 261 intake (EPA Guidelines for Health Risk Assessment of Chemical Mixtures) [23] were
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20 262 found in CBA and DES, which was mainly ascribed to Mn and Zn pollution [12]. The
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22 263 ANOVA results for the deposition fluxes of elements in the total fraction (determined
23
24 264 by NAA) are presented in Table S5 (supplementary material). It is shown that the
25
26 265 highest and lowest rates of deposition were found in CBA and SUM, with the exception
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28 266 of Zn, whose highest deposition rates were registered in PTI. Although these findings
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30 267 are not in agreement with the local soil composition [21,38,39], *i.e.* U rates of
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32 268 deposition in the city of Córdoba, for example, were higher than in the uranium mine
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34 269 (SUM), they might be accounted for by the high soil removal in CBA and, to a lesser
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36 270 extent, in OLI.
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47 272 3.2 Total metal concentrations in atmospheric fall-out

48 273 Fig. 2 shows the mean metal concentrations ($\text{LOG}_{10} \mu\text{g g}^{-1} \text{DW}$) in bulk atmospheric
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50 274 deposition (green) and local top soils (orange), revealing that the order of elements –on
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52 275 a concentration basis– was similar in both matrices. In addition, the mean As and Zn
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54 276 concentrations in Córdoba province were similar to those reported by Huang et al. [4]
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1 277 for the Yangtze River Delta in China, which might indicate important As and Zn inputs.
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3 278 These findings may be ascribed to naturally As enriched soils in Córdoba because of
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5 279 loess composition in central Argentina [21,40], and also to anthropogenic Zn emissions
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8 280 [4,9,32,37].
9

10 281 Table 3 presents an analysis of variance (ANOVA) for the metal concentrations (total
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12 282 fraction, $\mu\text{g g}^{-1}$ PS) with the sampling area in Córdoba province (Argentina) as a factor.
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14 283 Regarding the lanthanides, most of these (Ce, La, Lu, Sm, Tb), in addition to the
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16 284 actinides (Th, U), As, Co and Cr showed the highest concentrations in the bulk samples
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18 285 collected in a former open-cast uranium mine (SUM). These findings are in agreement
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20 286 with the geochemical characteristics of the area [21,38,39] and provide further evidence
21
22 287 of a crustal effect due to soil removal in the agricultural areas with high metal
23
24 288 deposition fluxes (CBA and OLI). Fig. S3 (supplementary material) confirms that the
25
26 289 relatively high deposition rates in a natural reserve (CHA) had a crustal origin, since
27
28 290 almost all elements in the atmospheric bulk deposition had a 1:1 relationship with the
29
30 291 local topsoil composition.
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38 293 3.3 Topsoil pseudo-total metal concentrations

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40 294 Table 4 shows the descriptive statistics for the pseudo-total concentrations of Cu, Mn,
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42 295 Ni and Pb in top soils from Córdoba province, Argentina, which were lower than the
43
44 296 limits stated by international legislation [24]. These concentrations in top soils were
45
46 297 similar to the values found in other studies performed in Argentina [41] and Pakistan
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48 298 [42]. However, the concentrations of Cu, Mn and Ni in Córdoba were lower than those
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50 299 reported for agricultural top soils in China [43], Iran [44] and Spain [29,30].
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1 301 3.4 Bulk deposition enrichment factors

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3 302 The calculation of enrichment factors (EFs) in samples of atmospheric particulate
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6 303 matter, either in relation to local or background soil composition [4] or the earth's crust
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8 304 [9], has been used to evaluate emission sources of metals (natural or anthropogenic).
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10 305 We used the soil composition of each sampling area in order to take into account the
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12 306 regional geochemistry as well as to be able to speculate on the origin of the elements.
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14 307 Elements with EF values near unity may indicate a natural origin, while higher values
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16 308 reflect a potential anthropogenic source, especially for those elements with enrichment
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18 309 values greater than 10 [4].
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23 310 The mean bulk deposition EFs are presented in Fig. 3, with the highest values being
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25 311 found for Cu (36.26), Ni (21.87), Pb (16.68) and Zn (14.43 and 11.66), which suggests
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27 312 an anthropogenic input, especially in atmospheric labile forms, as pointed out by
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29 313 Desboeufs et al. [45] and Sandroni and Migon [46]. These findings indicate a good
30
31 314 match between the second and third factor of the PCA (anthropogenic sources) and EF
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33 315 calculations.
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37 316 As far as the spatial differences in EFs are concerned, Fig. 4 depicts the mean EF_{Fe} for
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39 317 the sampling areas in Córdoba province while Table S6 (supplementary material) shows
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41 318 the LSD results of the analysis of variance (ANOVA). Nickel was found to be highly
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43 319 enriched in RTE and YOC (Fig. 4a). Regarding Ca, although this was only slightly
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45 320 enriched in the average bulk deposition (EF_{Fe} : 3.14; EF_{Sc} : 2.29), it was highly enriched
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47 321 in the surroundings of a cement plant (Fig. 4b), thus revealing its influence
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49 322 [22,34,36,47]. In addition, the highest Zn enrichment factors were found in PTI and
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51 323 DES, indicating that vehicular traffic and zinc-made roofs were important sources of Zn
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53 324 [4,7,35,37].
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1 325 Fig. 5 shows EF_{Sc} in the atmospheric bulk deposition as a function of the topsoil
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3 326 enrichment, which was normalized by the upper continental crust composition [21]. In
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6 327 this plot, while topsoil EF_{Sc} may indicate regional geochemical characteristics,
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8 328 atmospheric bulk EF_{Sc} might show the presence of atmospheric (anthropogenic)
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10 329 sources. It can be observed that, while Zn was only slightly enriched in the topsoil, it
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13 330 was highly enriched in atmospheric fall-out.

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16 332 3.5 Multiple regression models of metals in wheat grain and straw

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18 333 Although the sampling of top soils, wheat grain and straw, and the atmospheric bulk
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20 334 deposition did not match temporally in this study, the concentrations of metals in these
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23 335 matrices were considered representative of the sampled areas in a first attempt to assess
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25
26 336 the element fluxes in the soil-air-plant system.

27 337 3.5.1 Wheat straw

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29 338 The multiple regression analysis (Table 5) indicated that 82% of the total variance in
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32 339 straw composition (only elements determined by NAA) could be explained by the
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35 340 concentrations of metals in the topsoil (TPS) and atmospheric bulk deposition (cABD).
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38 341 However, neither %OM nor pH were statistically significant as independent variables.
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41 342 TPS was the variable with the highest marginal R^2 , indicating that soil element
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44 343 composition is the major factor in determining concentrations of metals in straw. This
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47 344 last finding is in agreement with several authors who assessed the significant effect of
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50 345 heavy metal concentrations in soil on wheat straw, and who pointed out the importance
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53 346 of atmospheric fall-out in wheat contamination pathways [12,19,20,48]. In addition,
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56 347 Bermudez et al. [12] found high bio-concentration factors in wheat straw collected in
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58
59 348 the same areas as the current study, which were subject to natural (As) and
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1 349 anthropogenic pollution (Cr and Sb). Our findings might indicate that the contamination
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3 350 of wheat straw with heavy metals and trace elements could have environmental
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6 351 implications on health, due to the transfer of these elements to grains [12,19,20,48] and
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8 352 in biotechnologies using straw [49-51].
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10 353

13 354 3.5.2 *Wheat grain*

15 355 Table 5 shows that the wheat grain element composition could be predicted by the metal
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17
18 356 concentrations in TPS and cABD (86% of the total variance, grain₁ model). These
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20 357 findings indicate a strong influence of soil and bulk deposition on the wheat grain heavy
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23 358 metal composition. In addition, our results might be useful for land management, since
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25 359 it would be possible to predict the element composition of wheat grains knowing the
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28 360 sources of metal pollution to which a specific area is subject to and the soil and
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30 361 atmospheric element concentrations. The residuals of each independent variable are
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32 362 plotted in Fig. S4a for TPS and in Fig. S4b for cABD (supplementary material), where
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35 363 it can be observed that soil composition was the best predictive independent variable. In
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37 364 addition, it was found that wheat grain had higher concentrations of Cr, Rb, Sb, Zn, Fe
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40 365 and Na than could be explained by TPS. Likewise, the Ba and Zn concentrations in
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42 366 wheat grain were lower than those explained by cDAT, indicating that Zn might have
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45 367 been mainly incorporated from the soil.

47 368 In order to lessen the effect of lithogenic metals, we decided to include the rates of
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49 369 deposition (rABD) of elements in their labile fraction (Table 5, grain₂ model). The value
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52 370 of R^2 was much lower than that of the previous model (0.459), which could be
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54 371 explained by the fact that wheat grain Ni concentrations were higher than expected by
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57 372 TPS and rABD (data not shown). By extracting Ni from the regression model, R^2
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1 373 increased to 0.830 (grain₃ model), which might indicate some specificity of wheat
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3 374 plants to accumulate this metal or the ease with which they could uptake Ni from the
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6 375 soil [10,52].
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8 376 Finally, when incorporating the straw composition in the last regression model, the
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10 377 explained variance rose to 90.1% (Table 5, grain₄ model) and the best explanatory
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12 378 variable was cABD (marginal R²: 0.549, data not shown). This could indicate that when
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14 379 the concentrations of metals in wheat grains increased greatly with a rise in wheat straw
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16 380 and TPS (based on their higher tangent values), the element composition of wheat
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18 381 grains was best explained by cABD, which is consistent with work of several authors
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20 382 who assessed the importance of air pollution on the metal content of vegetables grown
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22 383 in Argentina, France, India, and Sweden [2,3,12,13,19,20]. Moreover, the present study
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24 384 may allow the assessment of potential non-carcinogenic health hazards [23] through
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26 385 wheat consumption [12] by the evaluation of metals in bulk atmospheric deposition and
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28 386 top soils.
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34 387 Taking our results together, they suggest that is better to avoid analyzing atmospheric
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36 388 deposition rates, concentrations or enrichment factors separately, as they reflect
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38 389 different environmental constrains, *i.e.* the global input of metals, their possible sources
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40 390 (natural vs. anthropogenic) and the local or background geochemical characteristics.
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42 391 Likewise, we discourage the calculation of enrichment factors in atmospheric deposition
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44 392 with upper continental crust values, as they may show only the regional soil
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46 393 composition instead of leading to the identification of the origin of metals, particularly
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48 394 for those which may have both an atmospheric and a soil source.
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53 396 **Acknowledgements**

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1 397 This work was partially supported by ANPCyT (FONCyT), CONICET and (SECYT-
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3 398 UNCórdoba). Special thanks to Carla Allende and Gabriela A. Abril for technical
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6 399 support and to Dr. P. Hobson (native speaker) for language revision.
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560 **TABLE TITLES**

1 561 **Table 1.** Descriptive statistics for the rates of metal deposition in atmospheric fall-out in
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 3 562 Córdoba province, central Argentina.

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 8 564 **Table 2.** Analysis of variance (ANOVA) with the sampling area in Córdoba province
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 10 565 (Argentina) as a factor for the mean \pm SE deposition rates of labile elements (extracted with
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 13 566 HNO₃, pH 1).

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 18 568 **Table 3.** Analysis of variance (ANOVA) with the sampling area in Córdoba province
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 20 569 (Argentina) as a factor for the mean \pm SE concentration of elements ($\mu\text{g g}^{-1}$ PS) in the total
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 23 570 fraction (determined by NAA).

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 25 571
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 28 572 **Table 4.** Descriptive statistics for the pseudo-total metal concentrations (extracted with *aqua*
 29
 30 573 *regia*) in top soils collected in Córdoba province, central Argentina.

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 32 574
 33
 34
 35 575 **Table 5.** Regression models for the metal concentrations in wheat grain and straw using the
 36
 37 576 element concentrations in top soils and the rates and concentrations of elements in bulk
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 39
 40 577 atmospheric deposition in Córdoba province, central Argentina.

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44
45 579 **FIGURE CAPTIONS**

46
 47 580 **Fig. 1.** Loadings of the rotated eigenvectors obtained in a principal component analysis (PCA,
 48
 49 581 varimax rotation method) of the metal deposition rates in atmospheric fall-out in Córdoba
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 52 582 province, Argentina.

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 54 583 **Footnote:** Percentages of total explained variance are given between brackets. _ indicates the
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 56
 57 584 labile fraction (extracted with HNO₃, pH 1). Grey circles = elements mainly represented in

585 component 1. Black circles = elements mainly represented in component 2. Open circles =
 1 586 elements mainly represented in component 3.

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 6 588 **Fig. 2.** Mean \pm SE metal concentrations (total fraction, $\text{LOG}_{10} \mu\text{g g}^{-1}$ DW) in bulk atmospheric
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 8 589 deposition (green) and top soils (orange) collected in Córdoba province (Argentina).

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 11 590 **Footnote:** Soil data were partially published in Bermudez et al. [21].

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 13 591
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 15 592 **Fig. 3.** Enrichment factors (mean \pm SE) in descending order of the deposition rate ($\text{g m}^{-2} \text{day}^{-1}$)
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 18 593 of metals in their total (EF_{Sc} , green) or pseudo-total fractions (EF_{Fe} , light green) in Córdoba
 19
 20 594 province, Argentina.

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 23 595 **Footnote:** The best fitted trend line (potential equation) and the value of the coefficient of
 24
 25 596 determination (R^2) are shown in the plot.

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 27 597
 28
 29
 30 598 **Fig. 4.** Mean \pm SE metal enrichment factors (pseudo-total fraction, EF_{Fe}) in atmospheric bulk
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 32
 33 599 deposition collected in sampling areas of Córdoba province (Argentina). (a) Cu, Ni and Zn. (b)
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 35 600 Ca, Mn and Pb. ANOVA p-values are indicated with asterisks, while *post hoc* comparisons are
 36
 37 601 shown in Table S6 (supplementary material).

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 39
 40 602 **Footnote:** * Significant at 0.05 probability level. *** Significant at 0.001 probability level. SEs
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 42 603 were omitted in (a) since they were smaller than the corresponding icon.

43
 44 604
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 47 605 **Fig. 5.** Average enrichment factors (EF) of the total fraction of metals in atmospheric bulk
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 49
 50 606 deposition (EF_{Sc}) for all sampling areas in the province of Córdoba (y axis) as a function of the
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 52 607 metal topsoil enrichment (normalized by the *upper continental crust composition*, $\text{EF}_{\text{Sc}}(\text{UCC})$) (x
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 54 608 axis).

55
 56
 57 609 **Footnote:** The dotted lines indicate $\text{EF} = 1$.

Figure 1_revised

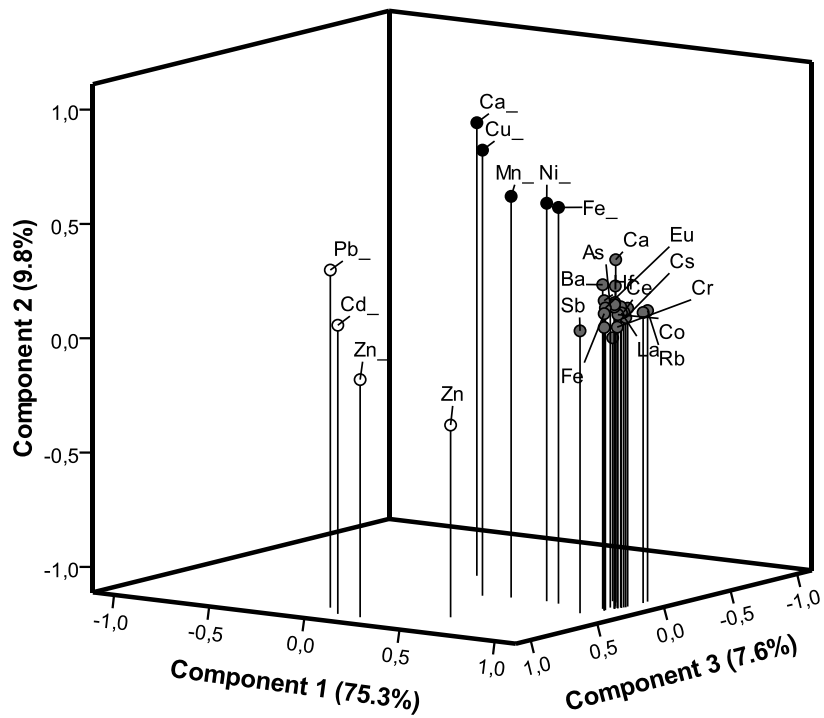


Figure 1

Figure 2_Bermudez

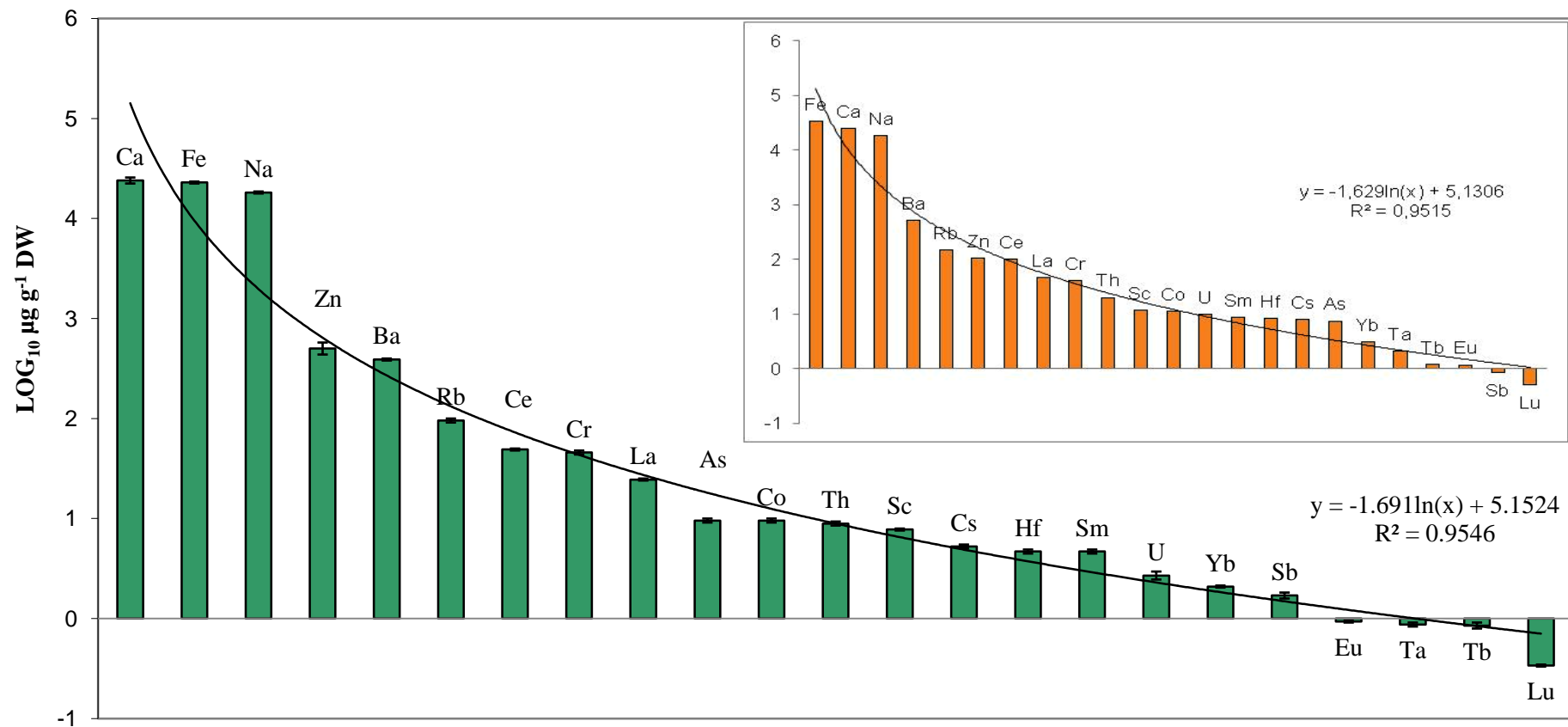


Figure 2

Figure 3_Bermudez

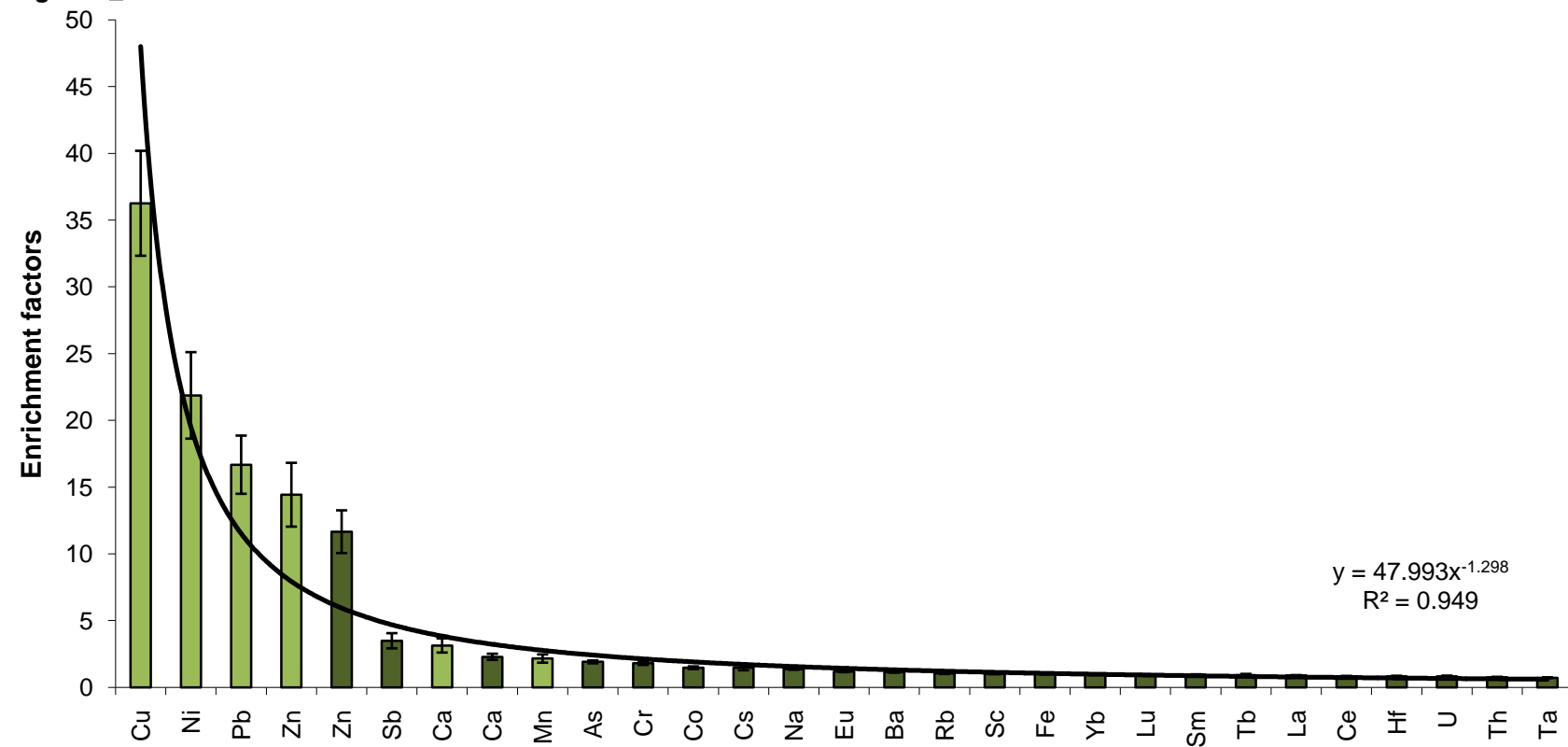
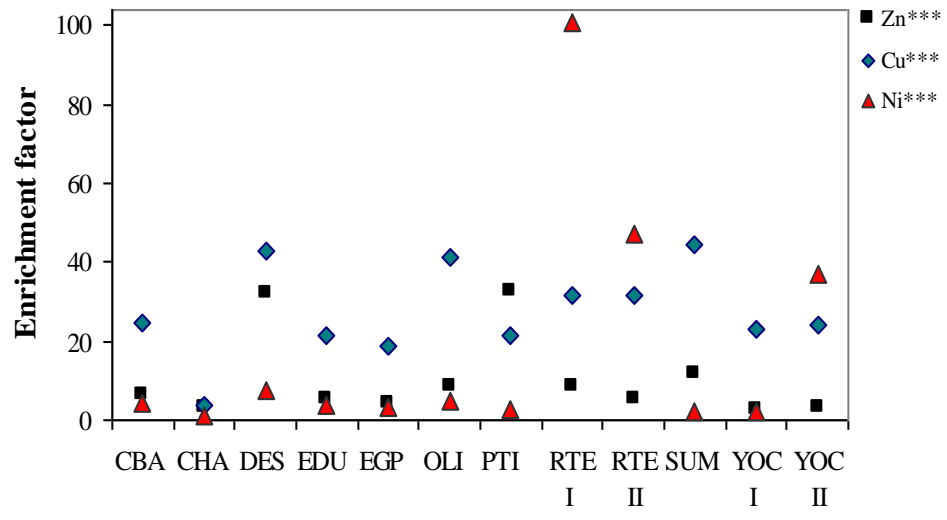


Figure 3

Figure 4_Bermudez

a)



b)

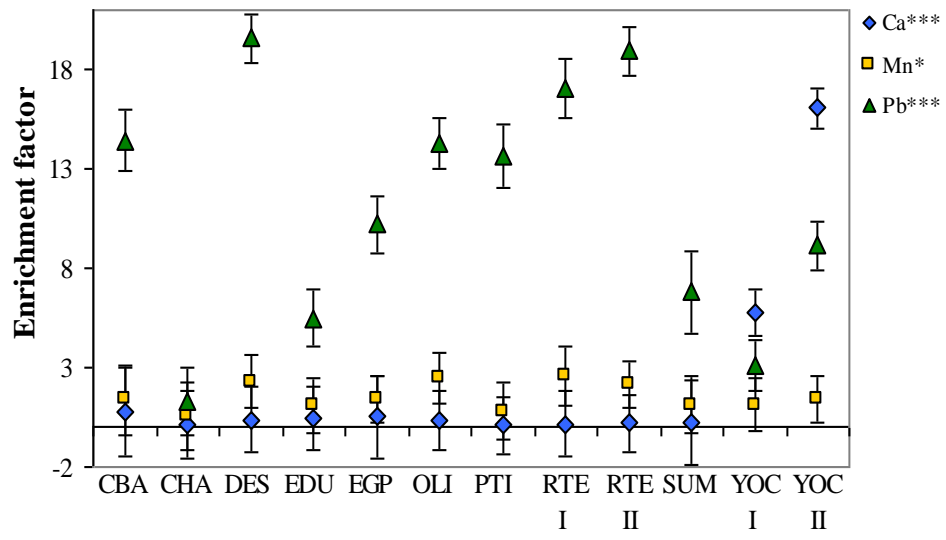


Figure 4

Figure 5. Bermudez

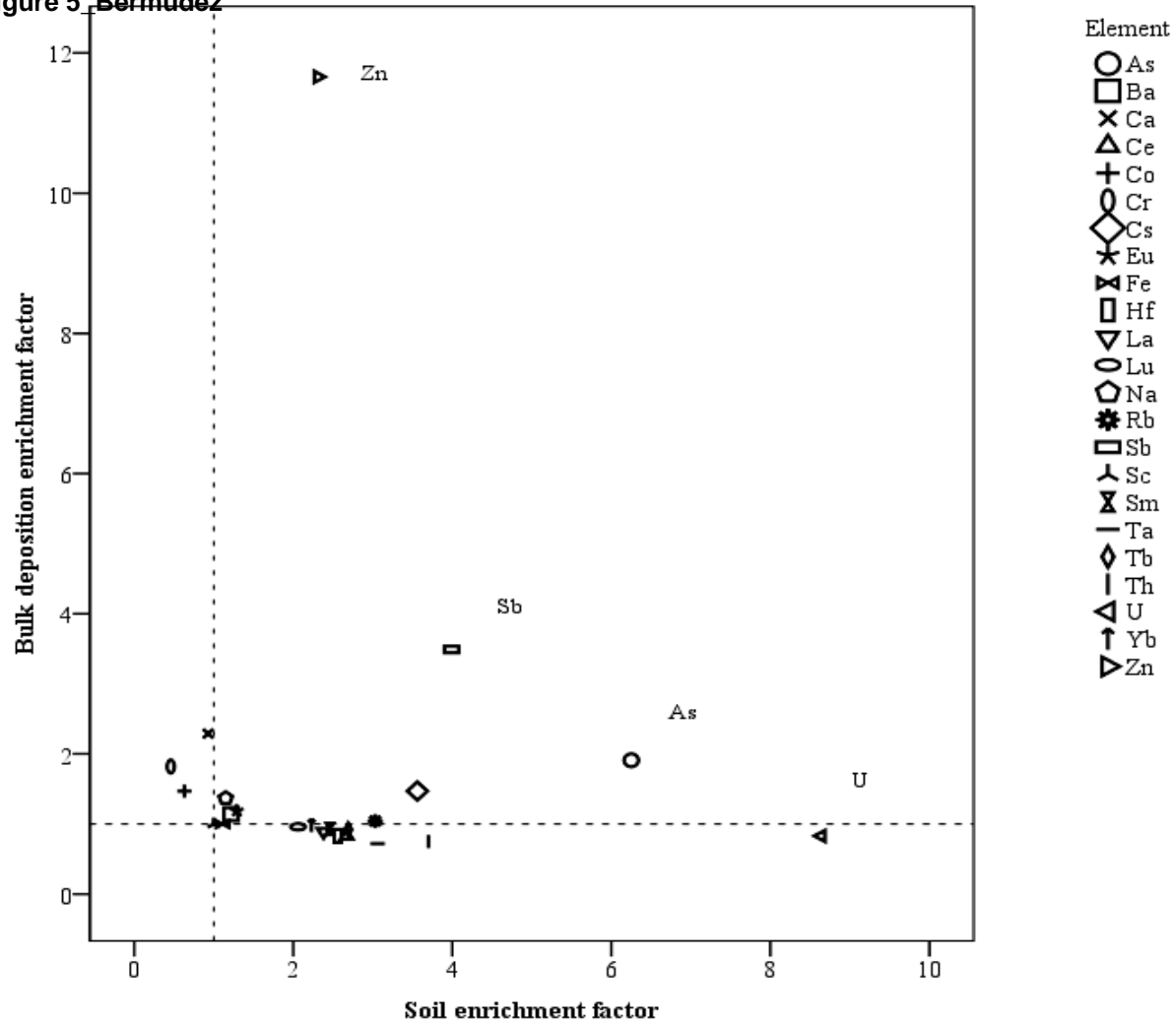


Figure 5

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

Element ($\mu\text{g m}^{-2} \text{ day}^{-1}$)	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	11833	7399	1818	1524	86666
	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	11399	8430	1411	729	55624
	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	38696
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 y GFAAS.

Table 2. Analysis of variance (ANOVA) with the sampling area in Córdoba province (Argentina) as a factor for the mean \pm SE deposition rates of labile elements (extracted with HNO₃, pH 1).

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

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

Element ^a ($\mu\text{g g}^{-1}$ PS)	Sampling area									
	CBA	CHA	DES	EGP	EDU	OLI	PTI	RTE I	RTE II	SUM
As***	8.7 \pm 0.8 cde	6.8 \pm 0.4 e	7.7 \pm 0.8 de	7.7 \pm 0.6 de	15.5 \pm 1.5 b	10.4 \pm 0.9 cd	11.7 \pm 2.2 c	6.7 \pm 0.6 e	8.5 \pm 0.4 cde	20.0 \pm 1.5 a
Ba	435 \pm 26	338 \pm 23	392 \pm 40	427 \pm 39	413 \pm 41	386 \pm 20	377 \pm 28	412 \pm 37	412 \pm 26	389 \pm 44
Ca	27630 \pm 10334	15340 \pm 1967	20432 \pm 3486	38445 \pm 5734	37993 \pm 12410	22152 \pm 1736	20072 \pm 3225	24158 \pm 2375	21637 \pm 5089	45549 \pm 11221
Ce*	48.3 \pm 4.4 cd	58.2 \pm 7.0 abc	42.8 \pm 4.8 d	43.7 \pm 3.5 d	62.7 \pm 8.7 ab	47.5 \pm 1.6 cd	49.6 \pm 2.1 bcd	41.1 \pm 4.0 d	52.1 \pm 2.6 abcd	64.0 \pm 7.7 a
Co*	8.64 \pm 0.55 b	11.35 \pm 1.62 b	8.48 \pm 0.99 b	9.02 \pm 1.60 b	10.83 \pm 2.34 b	8.08 \pm 0.39 b	9.45 \pm 0.52 b	8.16 \pm 0.82 b	17.16 \pm 4.97 a	13.15 \pm 1.01 ab
Cr***	39.2 \pm 2.0 cd	59.7 \pm 5.1 b	44.2 \pm 4.3 bcd	35.1 \pm 0.5 d	40.2 \pm 7.6 cd	36.4 \pm 0.7 d	41.2 \pm 4.2 cd	48.5 \pm 3.4 bcd	57.1 \pm 2.8 bc	83.7 \pm 16.7 a
Cs***	4.9 \pm 0.4 cd	6.3 \pm 0.6 bc	5.0 \pm 0.6 bcd	4.5 \pm 0.3 d	6.6 \pm 0.4 b	4.9 \pm 0.2 cd	5.3 \pm 0.1 bcd	4.3 \pm 0.4 d	5.2 \pm 0.3 bcd	8.4 \pm 1.3 a
Eu	0.95 \pm 0.06	1.04 \pm 0.11	0.83 \pm 0.04	0.92 \pm 0.09	0.95 \pm 0.18	0.86 \pm 0.03	1.02 \pm 0.02	0.80 \pm 0.10	1.06 \pm 0.05	1.06 \pm 0.18
Fe	23525 \pm 1991	27758 \pm 3008	20860 \pm 2217	20952 \pm 579	19749 \pm 2005	22775 \pm 699	27599 \pm 983	21594 \pm 2876	25380 \pm 1414	23085 \pm 2565
Hf*	5.22 \pm 0.34 abc	5.69 \pm 0.41 a	4.35 \pm 0.40 bcd	5.53 \pm 0.58 ab	3.83 \pm 0.28 d	4.99 \pm 0.13 abcd	5.20 \pm 0.16 abc	3.94 \pm 0.37 d	5.29 \pm 0.53 abc	4.08 \pm 0.78 cd
La*	24.49 \pm 1.96bc	29.03 \pm 3.79abc	21.39 \pm 1.95 d	21.99 \pm 1.65 cd	29.85 \pm 3.81 ab	23.43 \pm 0.72 bcd	25.66 \pm 0.83 bcd	20.82 \pm 2.34 d	26.84 \pm 1.56abcc	33.50 \pm 4.67 a
Lu*	0.383 \pm 0.045a	0.413 \pm 0.026 a	0.299 \pm 0.018bc	0.334 \pm 0.019abc	0.327 \pm 0.036bc	0.336 \pm 0.019abc	0.366 \pm 0.009abc	0.282 \pm 0.037c	0.343 \pm 0.012abc	0.411 \pm 0.055 a
Na**	20498 \pm 2450bc	15610 \pm 1272 c	15506 \pm 1754 c	17446 \pm 799 bc	26189 \pm 4438 a	22524 \pm 1582 ab	16662 \pm 621 c	16675 \pm 832 c	17093 \pm 877 bc	20514 \pm 1661bc
Rb***	91 \pm 5 bc	110 \pm 11 b	79 \pm 9 bc	81 \pm 4 bc	185 \pm 25 a	79 \pm 2 bc	80 \pm 4 bc	75 \pm 9 c	89 \pm 8 bc	174 \pm 22 a
Sb	1.45 \pm 0.15	1.50 \pm 0.17	1.31 \pm 0.19	1.48 \pm 0.09	1.82 \pm 0.20	1.21 \pm 0.13	5.29 \pm 3.13	1.71 \pm 0.27	1.80 \pm 0.12	3.22 \pm 0.45
Sc***	8.52 \pm 0.66 bc	10.70 \pm 0.65 a	7.47 \pm 0.72 bcd	7.84 \pm 0.27 bcd	6.98 \pm 0.52 cd	8.15 \pm 0.21 bcd	7.76 \pm 0.17 bcd	6.91 \pm 0.70 d	8.92 \pm 0.37 b	7.02 \pm 0.82 cd
Sm*	5.82 \pm 0.74 ab	5.39 \pm 0.61 abc	4.29 \pm 0.45 bc	3.99 \pm 0.37 c	6.03 \pm 0.90 a	4.12 \pm 0.18 bc	4.78 \pm 0.33 abc	3.96 \pm 0.59 c	4.85 \pm 0.38 abc	6.38 \pm 1.07 a
Ta***	0.86 \pm 0.09 bcd	1.09 \pm 0.12 bc	0.75 \pm 0.06 cd	0.86 \pm 0.04 bcd	1.22 \pm 0.09 b	0.65 \pm 0.02 d	0.76 \pm 0.07 cd	0.64 \pm 0.07 d	0.84 \pm 0.06 cd	1.71 \pm 0.34 a
Tb	0.94 \pm 0.18	0.97 \pm 0.10	0.73 \pm 0.11	0.82 \pm 0.20	0.96 \pm 0.03	-	0.94 \pm 0.18	1.17 \pm 0.00	0.64 \pm 0.05	1.19 \pm 0.02
Th***	8.76 \pm 0.71 cd	9.71 \pm 1.09 bc	7.64 \pm 0.64 cd	8.20 \pm 0.48 cd	11.54 \pm 0.86 ab	8.15 \pm 0.19 cd	8.66 \pm 0.18 cd	6.98 \pm 0.76 d	8.72 \pm 0.48 cd	13.55 \pm 2.08 a
U***	2.3 \pm 0.2 b	2.5 \pm 0.1 b	1.6 \pm 0.2 b	2.2 \pm 0.2 b	2.9 \pm 0.4 b	2.6 \pm 0.2 b	2.6 \pm 0.2 b	2.2 \pm 0.4 b	2.1 \pm 0.1 b	13.2 \pm 2.4 a
Yb	2.38 \pm 0.15	2.39 \pm 0.25	1.88 \pm 0.15	2.03 \pm 0.09	2.34 \pm 0.35	1.99 \pm 0.09	2.21 \pm 0.08	1.64 \pm 0.19	2.23 \pm 0.12	2.27 \pm 0.42
Zn***	168 \pm 26 d	429 \pm 141 cd	857 \pm 263 bc	324 \pm 148 cd	550 \pm 168 cd	3.91 \pm 138 cd	2293 \pm 366 a	798 \pm 242 cd	661 \pm 205 cd	1498 \pm 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	EE	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

*** Significant at 0.001 probability level.

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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 (±0.120)***	+ 0.975 (±0.052) x TPS*** + 0.146 (±0.043) x cABD***	***	0.909	0.825	0.821
grain ₁	-2.735 (±0.143)***	+ 0.994 (±0.052) x TPS*** + 0.385 (±0.046) x cABD***	***	0.930	0.864	0.860
grain ₂	-1.793 (±0.222)***	+ 0.763 (±0.085) x TPS*** + 0.280 (±0.080) x c/rABD***	***	0.686	0.470	0.459
grain ₃	-2.670 (±0.134)***	+ 1.011 (±0.049) x TPS*** + 0.416 (±0.045) x c/rABD(-Ni)***	***	0.913	0.834	0.830
grain ₄	-1.982 (±0.197)***	+ 0.493 (±0.112) x TPS*** + 0.341 (±0.041) x cABD*** + 0.530 (±0.108) x straw***	***	0.963	0.952	0.901

TPS = LOG₁₀ of the total concentrations (μg g⁻¹ DW) of elements in top soils. ABD = LOG₁₀ of the total concentrations (cABD, μg g⁻¹ DW) or rates of deposition (rABD) of elements in atmospheric bulk deposition. *** Significant at 0.001 probability level. r = Spearman regression coefficient. R² = general coefficient of determination.