



# Heavy metal and trace element concentrations in wheat grains: Assessment of potential non-carcinogenic health hazard through their consumption

Gonzalo M.A. Bermudez<sup>a,b,\*</sup>, Raquel Jasan<sup>c</sup>, Rita Plá<sup>c</sup>, María Luisa Pignata<sup>a,b</sup>

<sup>a</sup> Instituto Multidisciplinario de Biología Vegetal (IMBIV), Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Argentina

<sup>b</sup> Cátedra de Química General, Facultad de Ciencias Exactas, Físicas y Naturales, Universidad Nacional de Córdoba, Avda. Vélez Sársfield 1611, Ciudad Universitaria (X5016 GCA), Córdoba, Argentina

<sup>c</sup> Técnicas Analíticas Nucleares, Comisión Nacional de Energía Atómica (CAE), Av. Del Libertador 8250 (1429), Buenos Aires, Argentina

## ARTICLE INFO

### Article history:

Received 21 January 2011

Received in revised form 5 July 2011

Accepted 15 July 2011

Available online 23 July 2011

### Keywords:

Soil pollution

Air pollution

Bio-concentration

Cement plant

Argentina

## ABSTRACT

Heavy metal and trace element concentrations were examined in wheat grains and straw to elucidate associations between air pollution sources and soil variables. The mean wheat grain concentrations of Cr, Cu, Fe, Mn and Zn surpassed the tolerance limits stated in the international legislation for wheat grain and foodstuffs. When topsoil Ba, Co, Cr and Zn concentrations were higher than the legislation thresholds for agricultural and residential soils, wheat grain concentrations were also increased. In addition, Cr, Cu, Mn, Ni, Pb, and Zn revealed an immobilization effect of a cement plant and the atmospheric deposition input, with Cd in wheat grains being associated with a cement plant and industrial waste incinerator. The health risks arising from wheat grain consumption indicated that the inhabitants of Argentina are experiencing significant non-carcinogenic risks (Hazard Index = 3.311), especially when consuming wheat grains affected by metallurgical or chemical factories, as well as by air transportation from big cities.

© 2011 Elsevier B.V. All rights reserved.

## 1. Introduction

When considering different kinds of soil pollutants, heavy metals represent a special hazard because of their persistence and toxicity [1]. For the human body, certain heavy metals are essential for the biological systems as structural and catalytic components of proteins and enzymes like zinc (Zn) and copper (Cu), and others are contaminants such as cadmium (Cd), arsenic (As), lead (Pb), chromium (Cr), nickel (Ni) and so on [2–5].

Soil behaves as a sink for heavy metals arriving by the aerial deposition of particles emitted by urban and industrial activities [6–10] as well as from agricultural practices [11–13]. High pollution levels in soils can lead to phytotoxicity and result in the transfer of heavy metals to the human diet from crop uptake or soil ingestion by grazing livestock [14,15]. However, the accumulation of potentially toxic elements in vegetables and crops has been assessed to occur not only from soil but also from aerial deposition and industrial sludge [8,16–20]. For instance, Pandey and Pandey [21] reported high accumulation of Pb, Cd and Cr in leafy vegetables

due to atmospheric deposition. In addition, Jamali et al. [16] and Chandra et al. [19] found a significant accumulation of heavy metals in wheat plants grown in soils amended with domestic sewage sludge or irrigated with industrial effluents.

Heavy metal contamination of vegetables through soil, water, and air-borne sources may pose a serious threat to human health in longrun. Sharma et al. [22] have demonstrated that, except for occupational exposure, dietary intake through contaminated food has become the main route for the human intake of heavy metals. In this context, Food and Agriculture Organization (FAO) and World Health Organization (WHO), European Commission (EC) and other regulatory bodies of other countries strictly regulate the allowable concentrations or maximum permitted concentrations of toxic heavy metals in foodstuffs [23,24]. The health risk associated with the intake of toxic metals can be evaluated by carcinogenic and non-carcinogenic methods. The Hazard Quotient (HQ) is a non-cancer risk evaluation that is calculated by using the ratio between the estimated dose of a contaminant and the dose level below which there will not be any appreciable risk, i.e., the Reference Dose. In addition, to determine the non-cancer hazard for all exposure routes and pathways, the Hazard Index (HI) can be used, which consists of the sum of the HQ determined for the individual pollutants. These methods were established by the United States Environmental Protection Agency (USEPA) [24], and have been widely used and shown to be valid for several foodstuffs [25–28].

The most important crop worldwide in basic food commodities is wheat (*Triticum aestivum* L.), followed by coarse grains and

\* Corresponding author at: Cátedra de Química General, Facultad de Ciencias Exactas, Físicas y Naturales, Universidad Nacional de Córdoba, Avda. Vélez Sársfield 1611, Ciudad Universitaria (X5016 GCA) Córdoba, Argentina. Tel.: +54 351 4344983; fax: +54 351 4332097.

E-mail address: [gbermudez@com.uncor.edu](mailto:gbermudez@com.uncor.edu) (G.M.A. Bermudez).

rice, with a global production of 626 million tonnes in 2007 [29]. The average worldwide per-capita consumption in 2005 was 68 kg, with 61 kg and 95 kg being consumed in developing and developed countries, respectively. A dramatic agricultural expansion has occurred in Argentina, which has triggered a severe native forest loss [30]. During the last three decades of the 20th century, the land cover changes in northern Córdoba have been dominated by the replacement of forests by crops, with a deforestation rate of about 2.75% year<sup>-1</sup> in the lowlands [31]. In addition to this significant landscape change, it is nowadays frequent to observe crops and cattle being grown and reared in the surroundings of big cities and industrial premises. As a consequence, the concentration of heavy metals in crops grown in polluted soils may represent a serious concern for the possible deleterious effects on human health through wheat ingestion.

The objectives of this study were: (a) to evaluate the elemental concentrations in wheat grain and straw collected in the vicinity of industries in Argentina, and (b) to assess the non-carcinogenic risk of wheat grain consumption in Argentina.

## 2. Materials and methods

### 2.1. Area of study

The sampling zone included seven areas of Córdoba province, located in central Argentina (between 31°06' and 32°11'S, and 63°33' and 64°22'W) (see supplementary material, Fig. S1). A total of 34 sampling points were chosen in seven areas sampled before the wheat harvest. As a detailed description of these sampling areas can be found in Bermudez et al. [7], these are only briefly discussed in this work. The sites were: (a) Despeñaderos (DES, 450 masl): presumably affected by photochemical oxidants (O<sub>3</sub>) due to downwind transportation from Córdoba city; (b) Río Tercero (RTE, 390 masl): characterized by the presence of important chemical, petrochemical and military factories; (c) Oliva (OLI, 260 masl): part of the Chaco-Pampean plain, where the presence of arsenic in groundwater is associated with mineralogy and sediment texture; (d) Pozo de Tigre (PTI) and Estación General Paz (EGP, 520 masl): rural communities separated by only 4 km, with dove hunting in the PTI agricultural fields being the main difference between these sites; (e) Yocsina (YOC, 600 masl): a well-developed cement industry, using 75% gas and 25% alternative fuels in forms such as industrial solid waste (hazardous and non-hazardous); and (f) Los Sauces neighborhood (Córdoba city, CBA, 410 masl): a city of 1.5 million inhabitants, with the main sources of pollution being mobile ones and from a variety of industrial plants.

### 2.2. Heavy metals and trace elements in wheat

#### 2.2.1. Sampling and sample preparation

Wheat plants at grain maturity (just before harvest) were randomly chosen within a 5 m × 5 m square, were cut with scissors at a height above 10 cm from the soil surface, and then put into labeled bags and transported to the lab. To take into account individual variability, not more than 5 ears of each plant were used to prepare each composite sample (50 g minimum). In the laboratory, the ears were threshed manually, with glumes and dust being removed with compressed air to separate the grains. Also, similar to agricultural and food-industry practices, no washing of the grains was performed.

#### 2.2.2. Atomic absorption spectrophotometry

A 5 g DW subsample was crushed in a mortar and ashed in a muffle furnace at 450 °C for 6 h [19]. If the ashes were not completely white, 2 mL of concentrated HNO<sub>3</sub> were added and the mixture was heated to boiling point on an electric plate heater until

**Table 1**

Quality control results (μg g<sup>-1</sup> DW) obtained in the analysis of IAEA SRM Lichen 336 by Neutron Activation Analysis (NAA).

Element	IAEA SRM Lichen 336	
	Certified	Experimental
As	0.63 ± 0.16	0.638 ± 0.078
Ba	6.4 ± 2.2	7.8 ± 4.9
Br	12.9 ± 3.4	12.6 ± 0.7
Ce	1.28 ± 0.34	1.303 ± 0.075
Co	0.29 ± 0.10	0.280 ± 0.018
Cr	1.06 ± 0.34 <sup>a</sup>	1.14 ± 0.15
Cs	0.110 ± 0.026	0.105 ± 0.019
Eu	0.023 ± 0.008 <sup>a</sup>	0.0238 ± 0.0031
Fe	430 ± 100	386 ± 15
Gd <sup>b</sup>	8.5 ± 0.6	7.4 ± 1.0
Hf <sup>b</sup>	6.5 ± 0.8	6.1 ± 0.4
La	0.66 ± 0.20	0.586 ± 0.016
Lu	0.0066 ± 0.0048 <sup>a</sup>	0.0070 ± 0.0021
Na	320 ± 80	318 ± 34
Rb	1.76 ± 0.44 <sup>a</sup>	1.81 ± 0.55
Sb	0.073 ± 0.020	0.0733 ± 0.0065
Sc	0.17 ± 0.04 <sup>a</sup>	0.1665 ± 0.0026
Se	0.22 ± 0.04	0.200 ± 0.058
Sm	0.106 ± 0.028	0.1103 ± 0.0017
Ta <sup>b</sup>	4.3 ± 0.6	4.02 ± 0.19
Tb	0.014 ± 0.004 <sup>a</sup>	0.0118 ± 0.0063
Th	0.14 ± 0.04	0.142 ± 0.012
Yb	0.037 ± 0.024 <sup>a</sup>	0.039 ± 0.012
Zn	30.4 ± 6.8	28.7 ± 2.1

<sup>a</sup> Informed values.

<sup>b</sup> Determined in GBW07105 (Rock).

the formation of nitrous fumes had stopped [32]. Then, the ashes were returned to the muffle at 450 °C for a further 2 h. Finally, the white ashes were digested with 3.60 mL of concentrated HNO<sub>3</sub>, filtered through 2 μm filter paper, transferred into a 25-mL flask and brought to volume with ultra-pure water to a final concentration of 10% HNO<sub>3</sub>. Analytical blanks were prepared in the same way, but without the addition of any sample.

Wheat grain samples were measured in duplicate in a Graphite Furnace Atomic Absorption Spectrophotometer (GFAAS) (Perkin-Elmer AAnalyst 600) for Cd, Cu, Ni and Pb quantification, whereas Fe and Mn concentrations were determined using a Flame Atomic Absorption Spectrophotometer (FAAS) (Perkin-Elmer AA3110). The chemical modifiers Mg(NO<sub>3</sub>)<sub>2</sub> 0.06%, palladium 0.1% and NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> 1% were prepared from stock solutions (Merck & Co., USA) and the results were expressed in mg kg<sup>-1</sup> DW.

### 2.2.3. Neutron Activation Analysis

Grain and straw wheat samples were analyzed by Instrumental Neutron Activation Analysis (NAA) for As, Ba, Br, Ca, Ce, Co, Cr, Cs, Eu, Fe, Gd, Hf, K, La, Lu, Na, Rb, Sb, Sc, Se, Sm, Ta, Tb, Th, Yb and Zn. Briefly, samples were irradiated for 5 h in the RA-3 reactor (thermal flux 3 × 10<sup>13</sup> cm<sup>-2</sup> s<sup>-1</sup>, 8 Mw) of the Ezeiza Atomic Center (CNEA) [33,34]. The element concentration was determined in one replicate of the wheat grain samples (n = 34), whereas the straw measurements were performed on one composite replicate (n = 17). Software developed at the NAA laboratory was used, with NIST SRM 1633b Coal Fly Ash being utilized as the calibration standard. The results of the wheat grain and straw element concentrations were expressed in mg kg<sup>-1</sup> DW.

### 2.2.4. Quality control and quality assurance

For NAA determinations, IAEA Lichen 336 and GBW07105 (Rock) were used for quality control purposes (Table 1), with the reference materials Hay IAEA-V-10 and Oriental tobacco leaves (CTA-OTL-1) being used for GFAAS and FAAS determinations (Table 2). Each analytical batch contained at least a method blank in GFAAS and FAAS measurements. Standard solutions were analyzed every 8 sample

**Table 2**  
Results of quality control analysis of IAEA-V-10 Hay and CTA-OTL-1 Tobacco leaves measured by GFAAS and FAAS ( $\mu\text{g g}^{-1}$  DW).

Element	IAEA-V-10 Hay		CTA-OTL-1 Tobacco	
	Certified	Experimental	Certified	Experimental
Cd <sub>GFAAS</sub>	0.03 ± 0.03	0.02 ± 0.00	1.12 ± 0.24	1.26 ± 0.17
Cu <sub>GFAAS</sub>	9.4 ± 0.9	10.5 ± 2.8	14.1 ± 1.0	12.8 ± 0.8
Fe <sub>FAAS</sub>	186 ± 13	151 ± 33	989 <sup>a</sup>	796 ± 82
Mn <sub>FAAS</sub>	47 ± 7	39.9 ± 3.5	412 ± 28	377 ± 48
Ni <sub>GFAAS</sub>	4.2 ± 1.1	3.68 ± 0.49	6.32 ± 1.30	5.05 ± 0.91
Pb <sub>GFAAS</sub>	1.6 ± 1.1	1.75 ± 0.40	4.91 ± 1.60	3.85 ± 1.12

<sup>a</sup> Informed values.

solutions as a check on the instrument performance. The precision of each sample was determined in duplicate, and only RSD values below 10% were accepted, with other samples outside this range being reanalyzed. The NAA, GFAAS and FAAS measurements were within the uncertainty margins of the reference materials, thus demonstrating the accuracy of our findings.

### 2.3. Heavy metals and trace elements in top soils

As a detailed description of the technical procedures has been already published in Bermudez et al. [7], these are only briefly discussed in this work. A total of 94 topsoil composite samples were collected in the study zone at a depth of 0–10 cm. The total multi-element concentrations were determined by NAA (CNEA, Argentina) and expressed as  $\mu\text{g g}^{-1}$  DW. In addition, with the aim of analyzing labile metals in top soils, a 0.5 M-hydrochloric acid extraction was performed. The concentrations of Co, Cu, Fe, Mn, Ni, Pb and Zn were determined using a FAAS (Perkin-Elmer AA3110) and expressed as  $\mu\text{g g}^{-1}$  DW.

### 2.4. Statistical methods

The Shapiro–Wilk test for normality was applied, with non-normal distributed elements being log-transformed before parametric statistics were performed. An analysis of covariance (ANCOVA) was used to determine the treatment effects on the element concentration (arbitrary category), with soil pH, soil organic matter (SOM) and the soil concentration of the element in question (with these data previously published in [7]) used as covariates (quantitative factors). The inclusion of a covariate into an ANOVA decreases the error term (by accounting for the variability explained by the regression of the response variable on the covariate) and thereby increases the power of the test [6,35]. The ANCOVA was performed for each element according to the following proposed model:

$$Y_{ij} = \mu + \alpha_i + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + e_{ij} \quad (1)$$

where  $i = 1, 2, \dots, 7$ ;  $Y_i$  is the mean of two replicates obtained from the  $i$ th sampling site;  $\mu$  is the population mean;  $\alpha_i$  is the fixed effect of the sampling area subjected to different pollution sources;  $\beta_1 X_1$  is the effect of soil pH;  $\beta_2 X_2$  is the effect of SOM;  $\beta_3 X_3$  is the effect of the topsoil concentration of the element in question (from the total concentration determined by NAA, or the concentration extracted with 0.5 M hydrochloric acid and measured in a FAAS [7]) on the sampling site;  $e_{ij}$  is the random error in the  $i$ th sampling area. Interactions of the form  $(\alpha\beta X)_{ix}$  were assumed to be not significant. The levels of statistical significance were represented by \* for  $p < 0.05$ , \*\* for  $p < 0.01$  and \*\*\* for  $p < 0.001$ . Whenever ANCOVA indicated significant differences, the Least Significant Difference (LSD) test was applied as a post hoc comparison of means.

## 3. Results and discussion

### 3.1. Elemental concentrations in wheat grains

The concentrations of the elements Ba, Br, Co, Cr, Eu, Fe, Mn, Pb, Sb and Se in wheat grain collected in Córdoba (Argentina) are shown in Table 3. These values were higher than those reported by Kabata-Pendias and Mukherjee [15], who compiled multi-element concentrations principally from Swedish wheat grain surveys. In our study, the Cd and Pb grain concentrations were lower than those from [8,19,32,36,37], but comparable to those of Kirchmann et al. [38], who examined the wheat grain composition in a national monitoring program in Sweden. Furthermore, the Cu, Ni and Zn concentrations were similar to the values encountered by Kirchmann et al. [38], Lavado et al. [36], Nan et al. [32] and Singh et al. [39], with similar Cu and Zn concentrations also being observed in an industrial town in China [25]. The concentrations of Fe and Mn surpassed the values reported by Kirchmann et al. [38] and the control values of Chandra et al. [19], with Mn being found at an even higher concentration than that reported for wheat plants irrigated with distillery and tannery effluents [19]. Compared with Kirchmann et al. [38], the Co and Se concentrations in wheat were higher, whereas the Cr concentration was similar. Nonetheless, grain Cr concentrations were lower than the values reported by Huang et al. [25] in China and those by Singh et al. [39] in India. The concentrations of actinides and lanthanides in wheat grains, as well as those of other trace elements, were mainly under the detection limits, which is in agreement with the values presented by several authors [15,40–42].

According to the international legislation on wheat grains and foodstuffs (Table 3) [15,23,24], the mean concentrations of As, Cd, Ni and Pb were below the tolerance limits. Nevertheless, the mean concentrations of Cr, Cu, Fe, Mn and Zn surpassed the limits stated by FAO/WHO [23].

### 3.2. Ancova

With the aim of incorporating quantitative factors (soil pH, SOM and soil element concentrations) into the effect of the arbitrary category (sampling area), an Ancova was performed. Table 4 shows that the sampling area category was significant for Ba, Br, Cd, Co, Cr, Cu, Fe, Mn, Na, Ni, Rb, Sb and Zn. Moreover, Ba, Cd, Co, Cr, Fe, Mn, Ni and Zn could be explained by co-variables such as soil pH and organic matter, with a high concentration of these elements occurring in top soils (Ba, Co, Cr, Ni and Zn). When grain heavy metal concentrations did not significantly co-vary with the topsoil element composition, ANCOVA showed evidence of the atmospheric input and/or heavy metal bio-availability in the topsoil.

The concentration of Ba in wheat grains was significantly higher in DES, OLI and YOC (11.0, 10.6 and 9.3 mg kg<sup>-1</sup> DW, respectively) (Table 5). In another study, it is worth noting that Bermudez et al. [7] found that the topsoil mean Ba concentration in OLI and DES was above the agricultural limit of 750 mg kg<sup>-1</sup> and that the maximum concentration surpassed the industrial limit of 2000 mg kg<sup>-1</sup> [43].

Regarding Br, its concentration in grains was higher in RTE and DES (19.8 and 13.9 mg kg<sup>-1</sup> DW, respectively) (Table 5), which could be due to the presence of chemical and petrochemical industries for the former, and to long-range transport for the latter. Kabata-Pendias and Mukherjee [15] point out that Br is related to K since it is a component of K fertilizers. In the present study, the Complex factory (Buffon SA) is located in RTE and produces 120,000 L of foliar fertilizers per day, including potassium sulfate and other K compounds.

The highest Co grain concentrations were found in RTE, OLI and CBA (0.245, 0.137 and 0.095 mg kg<sup>-1</sup> DW, respectively) (Table 5). Related to this, Bermudez et al. [7] reported that the maximum

**Table 3**Mean  $\pm$  standard errors of elemental concentrations (mg kg<sup>-1</sup> DW) measured in wheat grain, soil pH and soil organic matter from different areas of Córdoba.

Variable	Area of study							Mean	Range	Comparison values <sup>a</sup>	Tolerance limits
	EGP	PTI	OLI	DES	RTE	CBA	YOC				
As	<0.08	<0.06	<0.12	<0.05	<0.31	<0.15	<0.16	ND	ND	0.2	0.7 <sup>g</sup>
Ba	4.0 $\pm$ 0.2	12.5 $\pm$ 2.0	11.6 $\pm$ 2.5	4.8 $\pm$ 0.2	4.8 $\pm$ 0.2	5.6 $\pm$ 1.0	7.3 $\pm$ 1.2	7.3	3.4–19.2	3.2	
Br	4.73 $\pm$ 0.32	10.8 $\pm$ 0.8	1.38 $\pm$ 0.34	13.9 $\pm$ 0.1	19.8 $\pm$ 0.2	2.6 $\pm$ 0.4	10.9 $\pm$ 1.4	9.29	1.0–21.1	5.5	
Cd <sub>GFAAS</sub>	0.014 $\pm$ 0.003	0.018 $\pm$ 0.003	0.014 $\pm$ 0.002	0.011 $\pm$ 0.001	0.017 $\pm$ 0.002	0.012 $\pm$ 0.002	0.022 $\pm$ 0.002	0.017	0.006–0.043	0.070	0.1 <sup>g</sup> ; 0.24 <sup>f</sup>
Ce	<0.10	<0.12	<0.35	<0.08	<0.15	<0.17	<0.14	ND	ND	0.003	
Co	0.059 $\pm$ 0.019	0.039 $\pm$ 0.019	0.065 $\pm$ 0.001	0.032 $\pm$ 0.004	0.037 $\pm$ 0.005	0.044 $\pm$ 0.004	0.046 $\pm$ 0.010	0.047	0.013–0.153	0.005	
Cr	0.52 $\pm$ 0.06	0.41 $\pm$ 0.117	0.34 $\pm$ 0.01	0.66 $\pm$ 0.01	0.61 $\pm$ 0.14	0.68 $\pm$ 0.11	0.52 $\pm$ 0.03	0.54	0.22–1.00	0.01	0.02 <sup>e</sup> ; 1.0 <sup>g</sup>
Cs	0.012 $\pm$ 0.000	0.024	<0.022	<0.008	<0.010	<0.014	0.025 $\pm$ 0.006	0.022	ND – 0.037	0.021 <sup>d</sup>	
Cu <sub>GFAAS</sub>	3.30 $\pm$ 0.15	2.04 $\pm$ 0.14	2.43 $\pm$ 0.41	5.05 $\pm$ 0.43	5.11 $\pm$ 0.47	3.36 $\pm$ 0.41	4.41 $\pm$ 0.16	3.79	1.25–6.93	4.7	3.0 <sup>e</sup> ; 10 <sup>g</sup>
Eu	0.007 $\pm$ 0.002	0.005 $\pm$ 0.001	0.021 $\pm$ 0.006	0.004 $\pm$ 0.001	na	0.015 $\pm$ 0.003	0.009 $\pm$ 0.001	0.010	0.002–0.033	<0.0001	
Fe	54.8 $\pm$ 4.3	44.3 $\pm$ 4.6	54.7 $\pm$ 12.1	48.1 $\pm$ 1.5	43.1 $\pm$ 4.6	49.5 $\pm$ 2.6	45.0 $\pm$ 2.7	47.7	32.6–74.6	34	20 <sup>e</sup>
Fe <sub>FAAS</sub>	46.9 $\pm$ 2.6	45.1 $\pm$ 2.5	33.5 $\pm$ 3.7	50.1 $\pm$ 4.7	42.0 $\pm$ 5.7	45.4 $\pm$ 2.4	45.6 $\pm$ 1.7	43.5	21.4–62.5	34	20 <sup>e</sup>
Gd	<0.22	<0.22	<0.49	<0.14	<0.22	<0.28	<0.23	ND	ND	0.0002	
Hf	<0.011	<0.009	<0.017	<0.006	<0.009	<0.010	<0.008	ND	ND	0.0004	
La	0.021 $\pm$ 0.007	0.014 $\pm$ 0.001	0.016 $\pm$ 0.001	0.013 $\pm$ 0.000	0.009 $\pm$ 0.000	0.010 $\pm$ 0.000	0.006 $\pm$ 0.001	0.011	0.001–0.040	0.017	
Lu	<0.0040	<0.0017	<0.0043	<0.0012	<0.0020	<0.0021	<0.0022	ND	ND	<0.0001	
Mn <sub>FAAS</sub>	35.1 $\pm$ 1.7	50.4 $\pm$ 2.8	46.5 $\pm$ 1.5	58.1 $\pm$ 5.8	52.4 $\pm$ 5.9	66.5 $\pm$ 4.54	48.1 $\pm$ 1.7	49.8	28.4–83.7	25	2.0 <sup>e</sup>
Na	19.3 $\pm$ 2.2	16.6 $\pm$ 1.7	32.2 $\pm$ 2.9	20.0 $\pm$ 0.5	26.6 $\pm$ 7.5	20.4 $\pm$ 2.3	17.2 $\pm$ 1.9	20.0	9.8–37.1	42.3 <sup>b</sup>	
Ni <sub>GFAAS</sub>	0.335 $\pm$ 0.017	0.309 $\pm$ 0.043	0.125 $\pm$ 0.004	0.169 $\pm$ 0.007	0.218 $\pm$ 0.017	0.261 $\pm$ 0.018	0.219 $\pm$ 0.021	0.237	0.083–0.580	0.34	1.63 <sup>e</sup> ; 1.0 <sup>g</sup>
Pb <sub>GFAAS</sub>	0.080 $\pm$ 0.009	0.077 $\pm$ 0.011	0.074 $\pm$ 0.009	0.080 $\pm$ 0.009	0.086 $\pm$ 0.06	0.085 $\pm$ 0.011	0.096 $\pm$ 0.014	0.088	0.022–0.269	0.007	0.24 <sup>f</sup> ; 0.4 <sup>g</sup>
Rb	1.47 $\pm$ 0.10	1.05 $\pm$ 0.10	1.62 $\pm$ 0.11	1.88 $\pm$ 0.21	2.80 $\pm$ 0.79	1.80 $\pm$ 0.26	1.68 $\pm$ 0.12	1.67	0.90–3.59	2.6	
Sb	0.005 $\pm$ 0.001	0.007 $\pm$ 0.000	<0.003	0.006 $\pm$ 0.000	0.015 $\pm$ 0.001	0.008 $\pm$ 0.001	0.015 $\pm$ 0.001	0.008	ND – 0.016	0.0005	
Sc	0.009 $\pm$ 0.003	0.004 $\pm$ 0.002	0.006 $\pm$ 0.001	0.005 $\pm$ 0.000	0.004 $\pm$ 0.000	0.005 $\pm$ 0.001	0.003 $\pm$ 0.000	0.005	0.001–0.018	<0.01	
Se	0.204 $\pm$ 0.004	<0.090	<0.190	0.319 $\pm$ 0.012	0.313 $\pm$ 0.010	0.525 $\pm$ 0.276	0.267 $\pm$ 0.041	0.299	ND – 0.801	0.001	
Sm	<0.0049	<0.0033	<0.0044	<0.0015	<0.0047	<0.0055	<0.0046	ND	ND	0.0002	
Ta	<0.0058	<0.0028	<0.0166	<0.0020	<0.0044	<0.0059	<0.0050	ND	ND	0.0002	
Tb	<0.0049	<0.0048	<0.0135	<0.0042	<0.0060	<0.0062	<0.0129	ND	ND	<0.0001	
Th	<0.012	<0.012	<0.025	<0.007	<0.013	<0.015	<0.013	ND	ND	<0.005 <sup>c</sup>	
Yb	<0.006	<0.008	<0.008	<0.005	<0.011	<0.009	<0.010	ND	ND	<0.0001	
Zn	26.7 $\pm$ 2.5	29.0 $\pm$ 1.2	39.4 $\pm$ 0.3	52.4 $\pm$ 4.0	39.1 $\pm$ 0.3	25.7 $\pm$ 3.3	24.0 $\pm$ 2.2	29.2	7.8–56.4	24	27.4 <sup>e</sup> ; 50 <sup>g</sup>
pH	7.0 $\pm$ 0.1	6.8 $\pm$ 0.1	6.5 $\pm$ 0.1	6.4 $\pm$ 0.1	6.6 $\pm$ 0.1	7.1 $\pm$ 0.0	7.5 $\pm$ 0.0	7.1	6.4–7.7	–	
SOM	0.082 $\pm$ 0.001	0.084 $\pm$ 0.014	0.063 $\pm$ 0.002	0.051 $\pm$ 0.018	0.031 $\pm$ 0.003	0.062 $\pm$ 0.001	0.081 $\pm$ 0.004	0.071	0.030–0.080	–	

Elements without sub-index indicate that the concentration was determined by Neutron Activation Analysis (NAA). The sub-indexes GFAAS and FAAS indicate the elements that were measured using a Graphite Furnace Atomic Absorption Spectrophotometer and a Flame Atomic Absorption Spectrophotometer, respectively. SOM = soil organic matter. (SOM and pH values were extracted from Bermudez et al. [7].) ND = not detected. na = not analyzed.

<sup>a</sup> Data compiled by Kabata-Pendias and Mukherjee [15], unless otherwise stated.

<sup>b</sup> Balaji et al. [41].

<sup>c</sup> Kučera et al. [42].

<sup>d</sup> Wheat flour, Al-Dayel and Al-Kahtani [40].

<sup>e</sup> FAO/WHO [23].

<sup>f</sup> European Commission [24].

<sup>g</sup> Ministry of Health of PRC (China), cited by Huang et al. [25].

**Table 4**

Analysis of covariance (ANCOVA) of elements determined in wheat grain, with soil organic matter, pH and the element concentration in top soils as co-variables.

Element	Classification criterion				
	Model	Sampling area	pH	SOM	ECS <sup>a,b</sup>
Ba	**	**	*	ns	** a
Br	***	***	ns	ns	nd <sup>a,b</sup>
Cd <sub>GFAAS</sub>	***	***	***	ns	nd <sup>a,b</sup>
Co	*	*	**	**	* b
Cr	***	***	ns	ns	*** a
Cu <sub>GFAAS</sub>	***	***	ns	ns	ns <sup>b</sup>
Eu	**	ns	ns	ns	ns <sup>a</sup>
Fe	ns	ns	ns	ns	ns <sup>a,b</sup>
Fe <sub>FAAS</sub>	**	**	ns	**	ns <sup>a,b</sup>
La	ns	ns	ns	ns	ns <sup>a</sup>
Mn <sub>FAAS</sub>	***	***	ns	**	ns <sup>b</sup>
Na	*	*	ns	ns	ns <sup>a</sup>
Ni <sub>GFAAS</sub>	***	***	ns	ns	* b
Pb <sub>GFAAS</sub>	ns	ns	ns	ns	ns <sup>b</sup>
Rb	**	**	ns	ns	ns <sup>a</sup>
Sb	**	**	ns	ns	ns <sup>a</sup>
Sc	ns	ns	ns	ns	ns <sup>a</sup>
Se	ns	ns	ns	ns	nd <sup>a,b</sup>
Zn	***	*	**	ns	* a * b

Elements without sub-index indicate that the concentration was determined by NAA. ECS = element concentration (mg kg<sup>-1</sup>) in top soils already published in Bermudez et al. [7]. nd = not determined in soils. ns = not significant.

\* Significant at 0.05 probability level.

\*\* Significant at 0.01 probability level.

\*\*\* Significant at 0.001 probability level.

<sup>a</sup> Total metal concentration determined by NAA.

<sup>b</sup> Heavy metals that were extracted by 0.5M HCl and measured by FAAS.

Co concentration in top soils collected in OLI surpassed the agricultural and residential limits stated in international legislation. Consequently, our results may be explained by the significant transfer of Co from top soils in OLI, and possibly, to a combined effect with air pollution sources in RTE and CBA.

In the current work, the concentration of Cd in wheat grain was dependent on the soil pH (Table 4), which is in agreement with Bose and Bhattacharyya [18], Kirkham [44] and Nan et al. [32]. Furthermore, the highest Cd concentrations were found in YOC (0.030 mg kg<sup>-1</sup> DW), where a cement plant and an industrial incinerator are situated (Table 5). In fact, in nearly all publications on this subject, soil pH is listed as being one of the major factors controlling Cd mobilization and uptake by plants [44]. Moreover, Kabata-Pendias and Pendias [45] have noted that Cd is most mobile in acidic soils within the range of pH 4.5–5.5, whereas in alkaline soil Cd has little mobility. Considering that the soil pH was 7.5 in YOC (Table 3), this might indicate that Cd concentrations in grain

are revealing an atmospheric input of Cd to the wheat plants on the one hand [8,21,46] and/or a high Cd availability in YOC soils on the other.

Regarding Cu, its concentration in grains was higher in RTE, DES and YOC (5.11, 5.05 and 4.41 mg kg<sup>-1</sup> DW, respectively) (Table 5), which could be related to the presence of chemical industries and a cement plant. In YOC, the influence of the cement plant and industrial waste incinerator has been previously described by Bermudez et al. [6,7], by evaluating top soil metal concentrations and heavy metal enrichment.

The Mn concentration in wheat grains was significantly different among the sampling areas and was associated with soil organic matter (Table 4), with the highest concentrations being found in PTI, YOC and CBA (62.7, 58.2 and 52.7 mg kg<sup>-1</sup> DW, respectively) (Table 5), which is in agreement with Bermudez et al. [6,7]. These authors have also previously reported that Mn was possibly related to wind transportation from industrial areas in the city of Córdoba [6,47].

The highest Ni grain concentrations were found in RTE, PTI and EGP (0.338, 0.331 and 0.297 mg kg<sup>-1</sup> DW, respectively) (Table 5), which may be ascribed to a lithogenic input and to the chemical and petrochemical activities. It is worth noting that although YOC top soils were highly enriched with Ni [7], wheat plants in this area did not subsequently accumulate Ni in their grains. In general, the mobility of Ni is inversely related to the soil pH [15], with a drastic decrease of the Ni extractability occurring at soil pH values over 6.5 [48].

Zn in wheat grains was explained by soil pH and the concentration of this element in soils, in agreement with Lavado et al. [36] and Nan et al. [32], respectively (Table 4). Sb and Zn are – among other sources – traffic-related elements [15], which have been previously found at high levels in epiphytic plants of the *Tillandsia* genus from the same areas [34]. Bermudez et al. [7] reported high and comparable total topsoil Zn concentrations in YOC, DES, OLI and RTE, the same areas which had the highest Zn concentrations in wheat grains in the present study, except for YOC (DES = 142.5; OLI = 73.2; RTE = 48.6 mg kg<sup>-1</sup> DW) (Table 5). It should be noted that the similar findings described for Ni may be due to the same factors as those explaining Zn and Pb, i.e. high levels of these elements occurred in the YOC top soils but, apparently, in a fraction which was either immobile or unextractable by wheat roots [15].

### 3.3. Transfer and bio-concentration factors

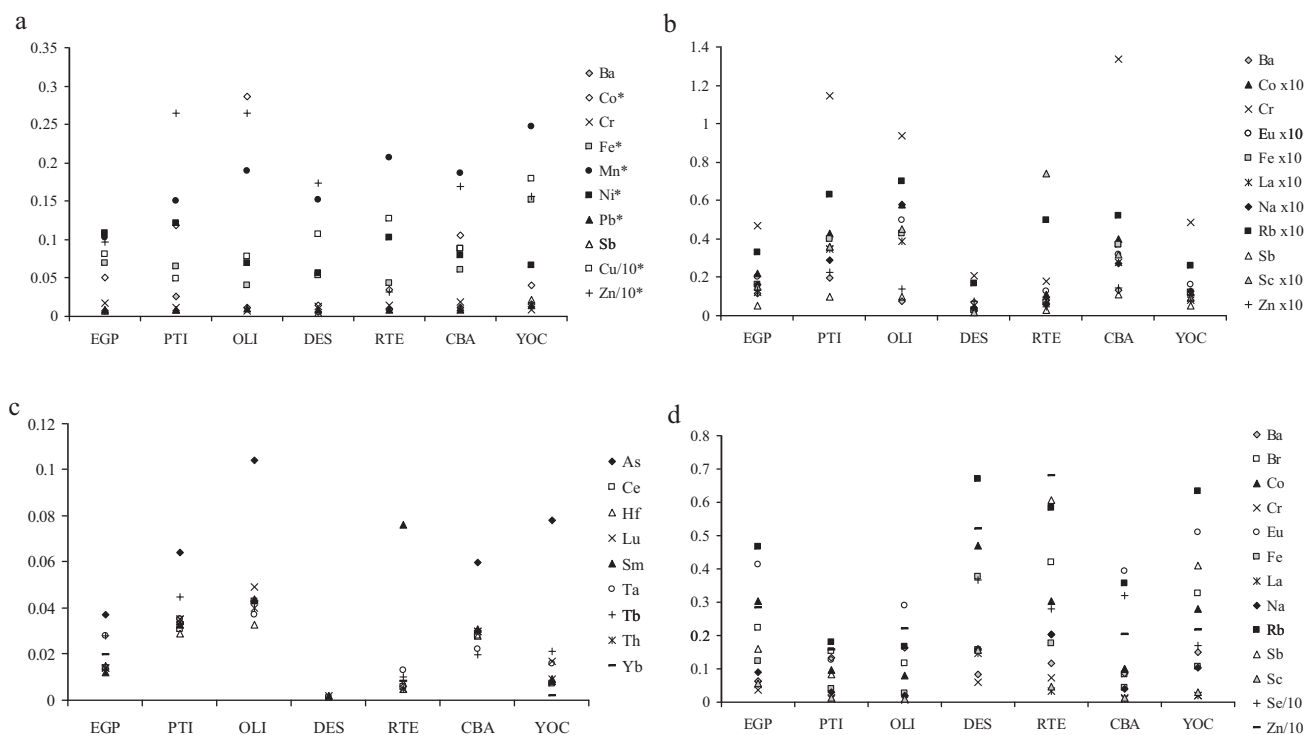
The bio-concentration factor (BCF) and translocation factor (TF) are important parameters in heavy metal uptake studies. BCF is the ratio of the element concentration in plant tissues (grains,

**Table 5**

Results of the post hoc multi-comparison test LSD (Least Significant Distance) of the analysis of covariance (ANCOVA) shown in Table 4.

Variable	Sampling area						
	EGP	PTI	OLI	DES	RTE	CBA	YOC
Ba	4.3 bcd	6.9 abc	10.6 a	11.0 a	−0.9 d	3.2 cd	9.3 ab
Br	4.7 cd	10.8 bc	1.4 d	13.9 ab	19.8 a	2.6 d	10.9 bc
Cd <sub>GFAAS</sub>	0.012 b	0.011 b	0.002 c	−0.003 c	0.006 bc	0.010 b	0.030 a
Co	0.078 cd	−0.016 e	0.137 b	−0.269 f	0.245 a	0.095 c	0.042 d
Cr	0.79 a	0.54 b	0.49 b	0.69 a	0.37 c	0.75 a	0.36 c
Cu <sub>GFAAS</sub>	3.30 bc	2.04 d	2.43 cd	5.05 a	5.11 a	3.36 b	4.41 a
Eu	0.007 bc	0.005 bc	0.021 a	0.004 c	na	0.015 ab	0.009 bc
Fe <sub>FAAS</sub>	61.2 a	59.3 a	17.5 c	19.0 c	−19.4 d	29.4 b	54.8 a
Mn <sub>FAAS</sub>	47.4 b	62.7 a	32.8 c	31.3 c	−0.4 d	52.7 ab	58.2 a
Na	19.3 b	16.6 b	32.2 a	20.0 b	26.6 ab	20.4 b	17.2 b
Ni <sub>GFAAS</sub>	0.297 ab	0.338 a	0.255 bc	0.133 c	0.331 ab	0.258 abc	0.187 cd
Rb	1.47 bc	1.05 c	1.62 bc	1.88 b	2.80 a	1.80 b	1.68 bc
Sb	0.005 c	0.007 c	0.050 a	0.006 c	0.015 b	na	0.015 b
Zn	9.0 d	46.9 c	73.2 b	142.5 a	48.6 b	43.3 c	−1.0 d

Different letters (descending order) indicate significant differences at  $p < 0.05$ . na = not analyzed.



**Fig. 1.** Mean Transfer (TF) and bio-concentration factors (BCF) of some elements measured in wheat plants grown in different areas of Córdoba, Argentina. (a)  $BCF_{G-TS}$ ; (b and c)  $BCF_{S-TS}$ ; (d) TF. S = straw; G = grain; TS = topsoil. \*Topsoil heavy metals that were extracted with 0.5 M HCl and measured by FAAS.

shoots, straw, etc.) and in their rooted soils, whereas TF is the ratio of the concentration of one element in two parts of the plant. Fig. 1 shows  $TF_{G-S}$  (grain/straw),  $BCF_{S-TS}$  (straw/topsoil) and  $BCF_{G-TS}$  (grain/topsoil) on a DW basis for the sampling areas studied.

Regarding  $BCF_{G-TS}$  (Fig. 1a), the mean Pb bio-concentration in grains was similar to the values reported by Duoay et al. [8], Huang et al. [25] and Nan et al. [32]. Moreover, the mean Ni bio-concentration was in agreement with Jamali et al. [16], Lavado [49] and Wang et al. [50]. However, our present study found the Cu bio-concentrations to be higher, or in some cases much greater, than the values reported by other researchers [16,25,32,49,50], with a similar pattern of results also occurring for Zn [16,25,32]. As the Pb, Ni, Cu and Zn bio-concentration values were calculated for soil heavy metals extracted by 0.5 M HCl [7], we may conclude that the 0.5 M-hydrochloric technique did not reflect the effective transfer of bio-available Pb and Ni to wheat plants. Fig. 1a also shows that the bio-concentration of Cu in wheat grains was effective ( $>1$ ) in YOC, RTE and DES. In addition, wheat grains from YOC had higher bio-concentration values for Fe, Mn, Pb and Sb, and in agreement with previously discussed Zn findings, the YOC wheat grains accumulated Zn to a lesser extent than those in other sampling areas.

The  $BCF_{S-TS}$  and  $TF_{G-S}$  and values for Zn and Cr (Fig. 1b and d), are similar to those of Lavado [49], who studied the accumulation of these elements by wheat grains in non-contaminated areas of the Argentinean Pampa. The DES and RTE areas showed the highest Zn  $TF_{G-S}$  values, and for Se the translocation from the wheat straw to grains was significant ( $>1$ ) (Fig. 1d). It is worth noting that although Cr was effectively bio-concentrated in straw collected in CBA and PTI, it was not translocated to the grains, since very low  $TF_{G-S}$  values were observed (especially in CBA and PTI).

Concerning lanthanides and actinides, only  $BCF_{S-TS}$  could be calculated in most cases, since their concentrations in wheat grains were below the detection limits (Fig. 1c). These findings are in agreement with Liang et al. [51,52], who reported lower concen-

trations of lanthanides in wheat grains compared to those in soils or in different fractions of the roots, stems and leaves.

### 3.4. Health risk from consuming wheat grain

#### 3.4.1. Hazard Quotient calculation

In 2008, it was reported that Argentinean per capita consumption of wheat was of  $91.4 \text{ kg hab}^{-1} \text{ year}^{-1}$  [53], just below the average for developed countries ( $95 \text{ kg hab}^{-1} \text{ year}^{-1}$ ). Therefore, it can be calculated that the daily intake of wheat for an average citizen of Argentina is  $250 \text{ g day}^{-1}$ .

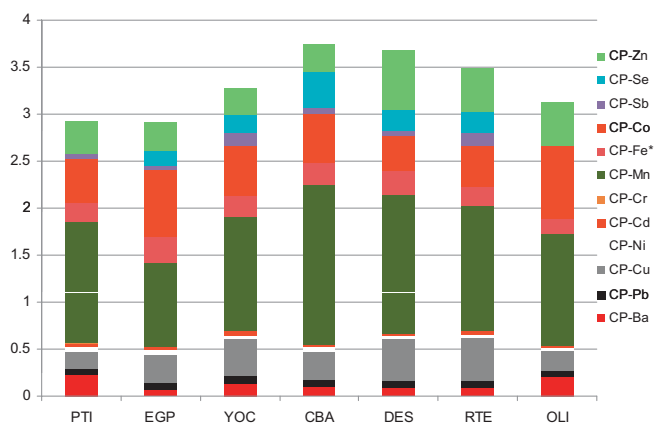
A potential non-cancer risk for individual heavy metals is expressed as the Hazard Quotient (HQ) [24], and can be calculated as follows:

$$HQ = \frac{CDI}{RfDo} \quad (2)$$

$$CDI \text{ (mg/kg day)} = \frac{CF \times IR \times EF \times ED}{BW \times AT} \quad (3)$$

in which the Chronic Daily Intake (CDI) is the exposure expressed as the mass of a substance per unit body weight per unit time, averaged over a long period of time (a lifetime), and RfDo is the oral reference dose ( $\text{mg kg}^{-1} \text{ day}^{-1}$ ). CF is the median concentration of a heavy metal in wheat grain ( $\text{mg kg}^{-1}$ ); IR is the ingestion rate of wheat grain ( $\text{kg person}^{-1} \text{ day}^{-1}$ ); EF is the exposure frequency ( $365 \text{ days year}^{-1}$ ); ED is the exposure duration (70 years for adults); BW is the average body weight (70 kg for Argentinean adults), and AT is the average exposure time for non-carcinogenic effects ( $ED \times 365 \text{ days year}^{-1}$ ). If the CDI exceeds the threshold (*i.e.*, if HQ exceeds unity), potential non-cancer effects may be a concern.

RfDo is an estimation of the daily exposure to which the human population is likely to be without any appreciable risk of deleterious effects during a lifetime. The RfDo values used were  $2.0 \times 10^{-1}$ ,  $1.0 \times 10^{-3}$ ,  $3.0 \times 10^{-4}$ ,  $4.0 \times 10^{-2}$ ,  $7.0 \times 10^{-1}$ ,  $1.4 \times 10^{-2}$ ,  $2.0 \times 10^{-2}$ ,  $4.0 \times 10^{-4}$ ,  $5.0 \times 10^{-3}$ , and  $3.0 \times 10^{-1} \text{ mg kg}^{-1} \text{ day}^{-1}$  for Ba, Cd, Co, Cu, Fe, Mn, Ni, Sb, Se and Zn, respectively [54]. However, as the US



**Fig. 2.** Hazard Quotient (HQ) for selected elements and the total Hazard Index (HI) for aggregate non-cancer risks through wheat grain consumption for different sampling areas of Córdoba, Argentina. \*Calculated with Fe concentrations determined by NAA.

EPA has not yet established RfDo values for Pb or total Cr [54], the ones used in this paper were  $4.0 \times 10^{-3}$  and  $1.5 \text{ mg kg}^{-1} \text{ day}^{-1}$  for Pb and Cr, respectively, as described by Huang et al. [25].

#### 3.4.2. Risk of individual elements and aggregate effects of consuming wheat grains

The results of the HQs for individual elements are shown in Fig. 1. The majority of the elements had HQ values lower than unity, with the exception of Mn. The mean HQ values for Argentinean consumers showed the following decreasing order of non-cancer risk: Mn (1.302) > Co (0.547) > Zn (0.402) > Cu (0.328) > Se (0.232) > Fe (0.220) > Ba (0.129) > Sb (0.082) > Pb (0.075) > Ni (0.042) > Cd (0.030) > Cr (0.001).

In order to assess the overall potential for non-carcinogenic effects posed by more than one HM, a Hazard Index (HI) approach has been developed based on the EPA's Guidelines for Health Risk Assessment of Chemical Mixtures [55]. This Hazard Index is given by the sum of the Hazard Quotients, as described in Eq. (4) [24].

$$HI = \sum HQ = \frac{CDI_1}{RfDo_1} + \frac{CDI_2}{RfDo_2} + \dots + CDI_i = RfDo_i \quad (4)$$

When the Hazard Index exceeds unity, there may be a concern for potential health effects. Our findings (mean: 3.311) were similar to those of Zheng et al. [27], but had higher HI values than those reported by Huang et al. [25] and Wang et al. [26] for the consumption of wheat grains, or for the whole diet intake in Chinese populations. The HI values in our study indicate that the highest non-cancer risks were those of wheat grains grown in CBA (3.753) followed by DES (3.676) and RTE (3.491) (Fig. 2). The YOC HI values were relatively lower (3.275), strengthening the likelihood of an immobilization outcome of sub-alkaline top soils and/or effects of the cement plants and industrial waste incinerator emissions. Taking into account that Argentinean wheat production almost completely supplies the domestic consumption, it is therefore of great concern that the inhabitants are experiencing a significant potential health risk solely due to the consumption of wheat. Furthermore, these non-cancer risks are higher when consuming wheat grains grown near cities, in areas affected by metallurgical and metal-mechanical industries, air-transported pollutants from big cities, and chemical and petrochemical factories.

## 4. Conclusions

The metal concentrations in wheat grains grown in different areas of Córdoba, Argentina, showed their dependence on soil

parameters such as pH, organic matter, and topsoil element concentrations. The mean As, Cd, Ni and Pb concentrations were below the tolerance limits stated in the international legislation for wheat grains and foodstuffs. However, the mean concentrations of Cr, Cu, Fe, Mn and Zn surpassed these limits. For Ba, Co, Cr and Zn, when the topsoil concentrations were higher than the legislation thresholds for agricultural and residential soils, or the guidelines levels for environmental health, the wheat grain concentrations were also greater. Nevertheless, Cu, Mn, Ni and Pb, as well as Cr and Zn in some cases, behaved differently in YOC, CBA, DES and RTE, possibly revealing an influence of the cement plant liming and the input of heavy metals via atmospheric deposition. Related to this, Cd and Br, two highly volatile elements [15], were clearly associated with the cement plant and chemical industries, respectively. However, future studies on the bulk deposition and  $PM_{10}$  composition are necessary to elucidate these hypotheses. The variability of the wheat grain elemental concentration was mainly accounted for by lithogenic elements and the effect of urban-industrial activities (cement plant, chemical factories and air-transported pollutants from Córdoba city). Summing up, the health risks posed by exposure to metals through the consumption of polluted wheat grains were assessed, indicating that the inhabitants of Argentina are experiencing significant potential non-carcinogenic risks. Furthermore, these risks were increased when consuming wheat grains grown in areas subject to the effects of metallurgical, metal-mechanical and chemical factories, as well as to air pollution transportation from big cities.

## Acknowledgements

This work was partially supported by the Agencia Nacional de Promoción Científica y Tecnológica (FONCyT), CONICET and the Secretaría de Ciencia y Técnica de la Universidad Nacional de Córdoba (SECYT-UNC). Special thanks to Dr. P. Hobson (native speaker) for language revision.

## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2011.07.058.

## References

- [1] D.C. Adriano, Trace Elements in Terrestrial Environments. Biogeochemistry, Bioavailability and Risks of Metals, Springer-Verlag, New York, 2001.
- [2] S.V.S. Rana, Metals and apoptosis: recent developments, J. Trace Elem. Med. Biol. 22 (2008) 262–284.
- [3] L. Järup, Hazards of heavy metal contamination, Br. Med. Bull. 68 (2003) 167–182.
- [4] W. Maret, H.H. Sandstead, Zinc requirements and the risks and benefits of zinc supplementation, J. Trace Elem. Med. Biol. 20 (2006) 3–18.
- [5] M.J. McLaughlin, D.R. Parker, J.M. Clarke, Metals and micronutrients – food safety issues, Field Crops Res. 60 (1999) 143–163.
- [6] G.M.A. Bermudez, M. Moreno, R. Invernizzi, R. Plá, M.L. Pignata, Heavy metal pollution in topsoils near a cement plant: the role of organic matter and distance to the source to predict total and HCl-extracted heavy metal concentrations, Chemosphere 78 (2010) 375–381.
- [7] G.M.A. Bermudez, M. Moreno, R. Invernizzi, R. Plá, M.L. Pignata, Evaluating top soil trace element pollution in the vicinity of a cement plant and a former open-cast uranium mine in central Argentina, J. Soils Sediments 10 (2010) 1308–1323.
- [8] F. Duoay, H. Roussel, C. Pruvot, C. Waterlot, Impact of a smelter closedown on metal contents of wheat cultivated in the neighbourhood, Environ. Sci. Pollut. Res. 15 (2008) 162–169.
- [9] G. Fabietti, M. Biasioli, R. Barberis, F. Ajmone-Marsan, Soil contamination by organic and inorganic pollutants at the regional scale: the case of Piedmont, Italy, J. Soils Sediments 10 (2010) 290–300.
- [10] M. Schuhmacher, M. Nadal, J.L. Domingo, Environmental monitoring of PCDD/Fs and metals in the vicinity of a cement plant after using sewage sludge as a secondary fuel, Chemosphere 74 (2009) 1502–1508.
- [11] T. Chen, X. Liu, M. Zhu, K. Zhao, J. Wu, J. Xu, P. Huang, Identification of trace element sources and associated risk assessment in vegetable soils of the urban-rural transitional area of Hangzhou, China, Environ. Pollut. 151 (2008) 67–78.

- [12] S. Dragović, N. Mihailović, B. Gajić, Heavy metals in soils: distribution, relationship with soil characteristics and radionuclides and multivariate assessment of contamination sources, *Chemosphere* 72 (2008) 491–495.
- [13] C. Micó, L. Recatalá, M. Peris, J. Sánchez, Assessing heavy metal sources in agricultural soils of an European Mediterranean area by multivariate analysis, *Chemosphere* 65 (2006) 863–872.
- [14] P.W. Abrahams, Soils: their implications to human health, *Sci. Total Environ.* 291 (2002) 1–32.
- [15] A. Kabata-Pendias, A.B. Mukherjee, Trace Elements From Soil to Human, Springer-Verlag, Berlin, 2007.
- [16] M.K. Jamali, T.G. Kazi, M.B. Arain, H.I. Afridi, N.J. Jalbani, G.A. Kandhro, A.Q. Shah, J.A. Baig, Heavy metal accumulation in different varieties of wheat (*Triticum aestivum* L.) grown in soil amended with domestic sewage sludge, *J. Hazard. Mater.* 164 (2009) 1368–1391.
- [17] T.-M. Lee, H.Y. Lai, Z.-S. Chen, Effect of chemical amendments on the concentration of cadmium and lead in long-term contaminated soils, *Chemosphere* 57 (2004) 1459–1471.
- [18] S. Bose, A.K. Bhattacharyya, Heavy metal accumulation in wheat plant grown in soil amended with industrial sludge, *Chemosphere* 70 (2008) 1264–1272.
- [19] R. Chandra, R.N. Bharagava, S. Yadav, D. Mohan, Accumulation and distribution of toxic metals in wheat (*Triticum aestivum* L.) and Indian mustard (*Brassica campestris* L.) irrigated with distillery and tannery effluents, *J. Hazard. Mater.* 162 (2009) 1514–1521.
- [20] J. Pandey, R. Pandey, K. Shubhashish, Air-borne heavy metal contamination to dietary vegetables: a case study from India, *Bull. Environ. Contam. Toxicol.* 83 (2009) 931–936.
- [21] J. Pandey, U. Pandey, Accumulation of heavy metals in dietary vegetables and cultivated soil horizon on organic farming system in relation to atmospheric deposition in a seasonally dry tropical region of India, *Environ. Monit. Assess.* 148 (2009) 61–74.
- [22] R.K. Sharma, M. Agrawal, F. Marshall, Heavy metal contamination of soil and vegetables in suburban areas of Varanasi, India, *Ecotoxicol. Environ. Saf.* 66 (2007) 258–266.
- [23] FAO/WHO, Contaminants, Codex Alimentarius, vol. XVII, Edition 1, FAO/WHO, Codex Alimentarius Commission, Rome, 1984.
- [24] European Commission, Commission Regulation (EC) No. 466/2001 Setting Maximum Levels for Certain Contaminants in Foodstuffs, 2002.; US EPA, Risk Assessment Guidance for Superfund, Human Health Evaluation Manual (Part A), Interim Final, vol. I. Washington (DC), United States Environmental Protection Agency, EPA/540/1-89/002, 1989.
- [25] M. Huang, S. Zhou, B. Sun, Q. Zhao, Heavy metal in wheat grain: assessment of potential health risk for inhabitants in Kunshan, China, *Sci. Total Environ.* 405 (2008) 54–61.
- [26] X. Wang, T. Sato, B. Xing, S. Tao, Health risks of heavy metals to the general public in Tianjin, China via consumption of vegetables and fish, *Sci. Total Environ.* 350 (2005) 28–37.
- [27] N. Zheng, Q. Wang, X. Zhang, D. Zheng, Z. Zhang, S. Zhang, Population health risk due to dietary intake of heavy metals in the industrial area of Huludao city, China, *Sci. Total Environ.* 387 (2007) 96–104.
- [28] J.H. Rodriguez, A. Klump, A. Fangmeier, M.L. Pignata, Effects of elevated CO<sub>2</sub> concentrations and fly ash amended soils on trace element accumulation and translocation among roots, stems and seeds of *Glycine max* (L.) Merr., *J. Hazard. Mater.* 187 (2011) 58–66.
- [29] FAO, FAO Forecasts Record Cereal Crop for 2007, 2007, <http://www.fao.org/newsroom/en/news/2007/1000533/index.html> (accessed 5 June 2010).
- [30] M.A. Aizen, L.A. Garibaldi, M. Dondo, Expansión de la soja y diversidad de la agricultura argentina, *Ecol. Aust.* 19 (2009) 45–54.
- [31] M.R. Zak, M. Cabido, D. Cáceres, S. Díaz, What drives accelerated land cover change in central Argentina? Synergistic consequences of climatic, socio-economic, and technological factors, *Environ. Manage.* 42 (2008) 181–189.
- [32] Z. Nan, C. Zhao, J. Li, F. Chen, W. Sun, Relations between soil properties and selected heavy metal concentrations in spring wheat (*Triticum aestivum* L.) grown in contaminated soils, *Water Air Soil Pollut.* 133 (2002) 205–213.
- [33] M.L. Pignata, R.R. Plá, R.C. Jasan, M.S. Martínez, J.H. Rodríguez, E.D. Wannaz, G.L. Gudiño, H.A. Carreras, C.M. González, Distribution of atmospheric trace elements and assessment of air quality in Argentina employing the lichen *Ramalina celastri* as a passive biomonitor: detection of air pollution emission sources, *Int. J. Environ. Health* 1 (2007) 29–46.
- [34] E.D. Wannaz, C.A. Harguinteguy, R. Jasan, R.R. Plá, M.L. Pignata, Identification of atmospheric trace-element sources by passive biomonitoring employing PCA and variogram analysis, *Int. J. Environ. Anal. Chem.* 88 (2008) 229–243.
- [35] T.J. Barret, M.A. Tingley, K.R. Munkittrick, R.B. Lowell, Dealing with heterogeneous regression slopes in analysis of covariance: new methodology applied to environmental effects monitoring fish survey data, *Environ. Monit. Assess.* 166 (2010) 279–291.
- [36] R.S. Lavado, M. Rodríguez, R. Alvarez, M.A. Taboada, M.S. Zubillaga, Transfer of potentially toxic elements from biosolid-treated soils to maize and wheat crops, *Agric. Ecosyst. Environ.* 118 (2007) 312–318.
- [37] C. Pruvot, F. Douay, F. Hervé, C. Waterlot, Heavy metals in soil, crops and grass as a source of human exposure in the former mining areas, *J. Soils Sediments* 6 (2006) 215–220.
- [38] H. Kirchmann, L. Mattsson, J. Eriksson, Trace element concentration in wheat grains: results from the Swedish long-term soil fertility experiments and national monitoring program, *Environ. Geochem. Health* 31 (2009) 561–571.
- [39] A. Singh, R. Kumar Sharma, M. Agrawal, F.M. Marshall, Health risk assessment of heavy metals via dietary intake of foodstuffs from the wastewater irrigated site of a dry tropical area of India, *Food Chem. Toxicol.* 48 (2010) 611–619.
- [40] O.A.F. Al-Dayel, S.A. Al-Kahtani, Elemental content in wheat products of Al-Quasum region, Saudi Arabia using the INAA technique, *J. Radioanal. Nucl. Chem.* 252 (2002) 605–609.
- [41] T. Balaji, R.N. Acharya, A.G.C. Nair, A.V.R. Reddy, K.S. Rao, G.R.K. Naidu, S.B. Monohar, Multielement analysis in cereals and pulses by  $k_0$  instrumental neutron activation analysis, *Sci. Total Environ.* 253 (2000) 75–79.
- [42] J. Kučera, J. Mizera, Z. Řanda, M. Vávrová, Pollution of agricultural crops with lanthanides, thorium and uranium studied by instrumental and radiochemical neutron activation analysis, *J. Radioanal. Nucl. Chem.* 271 (2007) 581–587.
- [43] CCME, Canadian soil quality guidelines for the protection of environmental and human health: summary tables (2007), in: Canadian Environmental Quality Guidelines, CCME, Winnipeg, 1999.
- [44] M.B. Kirkham, Cadmium in plants on polluted soils: effects of soil factors, hyper-accumulation, and amendments, *Geoderma* 137 (2006) 19–32.
- [45] A. Kabata-Pendias, H. Pendias, Trace Elements in Soils and Plants, CRS Press, Boca Raton, 2001.
- [46] R. Weber, B. Hryńczuk, Effect of leaf and soil contaminations on heavy metals content in spring wheat crops, *Nukleonika* 45 (2000) 137–140.
- [47] G.M.A. Bermudez, J.H. Rodriguez, M.L. Pignata, Comparison of the air pollution biomonitoring ability of three *Tillandsia* species and the lichen *Ramalina celastri* in Argentina, *Environ. Res.* 109 (2009) 6–14.
- [48] G. Siebielec, R.L. Chaney, Manganese fertilizer requirement to prevent manganese deficiency when liming to remediate Ni-phytotoxic soils, *Commun. Soil Sci. Plant Anal.* 37 (2006) 1–17.
- [49] R.S. Lavado, Concentration of potentially toxic elements in field crops grown near and far from cities of the Pampas (Argentina), *J. Environ. Manage.* 80 (2006) 116–119.
- [50] S. Wang, Z. Nan, X. Liu, Y. Li, S. Qin, H. Ding, Accumulation and bioavailability of copper and nickel in wheat plants grown in contaminated soils from the oasis, northwest China, *Geoderma* 152 (2009) 290–295.
- [51] T. Liang, B. Yan, S. Zhang, L. Wang, N. Wang, H. Liu, Contents and the biogeochemical characteristics of rare earth elements in wheat seeds, *Biogeochemistry* 54 (2001) 41–49.
- [52] T. Liang, S. Ding, W. Song, Z. Chong, C. Zhang, H. Li, A review of fractionations of rare earth elements in plants, *J. Rare Earths* 26 (2008) 7–15.
- [53] E. Lezcano, Informe Coyuntural Mensual, Sector farinaceos (Agosto 2009), Ministerio de la Producción. Dirección de Industria Alimentaria y Agroindustrias, 2009.
- [54] US EPA (United States Environmental Protection Agency), Region 9, Preliminary Remediation Goals, 2010. <http://www.epa.gov/region9/superfund/prg/index.html> (accessed 17 May 2010).
- [55] USEPA, Guidelines for the health risk assessment of chemical mixtures, *Fed. Reg.* 51 (1986) 34014–34025.