Journal of Geochemical Exploration 145 (2014) 129–134

Contents lists available at ScienceDirect

Journal of Geochemical Exploration

journal homepage: www.elsevier.com/locate/jgeoexp

Assessment of Pb and Zn contents in agricultural soils and soybean crops near to a former battery recycling plant in Córdoba, Argentina

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ARTICLE INFO

Article history:
Received 22 February 2014
Accepted 31 May 2014
Available online 9 June 2014

Keywords:
Glycine max
Heavy metals
Battery recycling plant
Crop quality parameters

ABSTRACT

A field study was carried out in the vicinity of a former battery recycling plant, with heavy metal content (Pb and Zn), the toxicological risk of seed consumption of soybean crops [*Glycine Max* (L.) Merr.] grown on these soils and their relation with seed quality being evaluated. The concentrations of Pb and Zn in soybeans (roots, stems, pods and seeds) and in top soils were investigated and their potential risk to the health of consumers was estimated. Furthermore, quality-related seed parameters (standard germination test, tetrazolium test, biomass and weight of 1000 seeds) were obtained. The results show that the concentrations of Pb in soybeans at all sites (controls and close to the smelter) were above the maximum permitted levels. Seed quality decreased as the lead concentration increased in seeds from sites near to the former battery recycling plant. Moreover, the greatest accumulation of Zn in seeds was found at sites with high concentrations of Pb in soils. Taking into account these findings, future studies need to be performed in order to evaluate the parameters influencing the mobility and bioavailability of toxic metals in agricultural soils, with the purpose of not only assessing the current state of crops in terms of food security but also evaluating possible soil remediation techniques.

1. Introduction

Heavy metal contents of agricultural soils (either due to atmospheric deposition, urban–industrial activities or agricultural practices) can affect human beings directly, through the food web by ingestion of crops and/or animals, or indirectly, through damaging the environmental health (Hao et al., 2011; Kabata-Pendias, 2011; Kachenko and Singh, 2006; Nriagu, 1990). In general, agricultural areas are often affected by industrial emissions since they are often located in peripheral areas to urban agglomerations (Agrawal et al., 2003; Bermudez et al., 2009; Yan et al., 2007). Many developing countries have experienced a progressive degradation in air quality as a consequence of their rapid development over the last two decades (Agrawal et al., 2003). In particular, although the levels of air pollutants are increasing rapidly in urban and peri-urban areas of the developing world, this is not accompanied by effective environmental regulations. This poses a potential toxicological risk from the consumption of crops that are grown under these conditions (Cui et al., 2004; Peralta-Videa et al., 2009; Wang et al., 2006; Zheng et al., 2007), with studies conducted on heavy metal transfer from soil into crops also having shown that soybean may accumulate more potentially toxic elements than other crops (Hao et al., 2011; Lavado, 2006; Lavado et al., 2001; Li et al., 2008; Rodriguez et al., 2011a; Salazar et al., 2012). In Argentina, soybean (*Glycine max*) represents the most important crop in terms of yield, with the province of Córdoba being one of the most productive (INTA, 2013). In fact, the cultivated area is steadily increasing, and other crops and livestock production being replaced by soy farming (FAO STAT, 2012; Singh, 2010). The high demand for soybean has resulted in this crop being cultivated even near pollutant emission sources such as highways with high vehicular traffic and industries (Bermudez et al., 2009; Rodriguez et al., 2011b; Salazar et al., 2012). Moreover, the so-called secondary lead smelters (recycling of Pb from Pb-containing products) have been cited as important sources of heavy metals in agricultural soils (Cala and Kunimine, 2003; Fernandez-Turiel et al., 2001), in which the metals Cd, Pb and Zn may be found (Cala and Kunimine, 2003; Cui et al., 2005; Lu et al., 2010; Sterckeman et al., 2002). Previous studies have reported high values of Pb in agricultural topsoils around a former Pb- smelter plant in the town of Bouwer, a peri-urban area of Córdoba city (CONAE, 2006; Salazar and Pignata, 2014; Salazar et al., 2012). Furthermore, Salazar et al. (2012) found concentrations of Pb and Cd in soybeans above the maximum permitted levels at some of the sites evaluated in the present study. In this area, the cultivation of soybean is widespread, which could entail a risk to the health of the population living there, both due to direct contamination from high levels of lead in air and

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http://dx.doi.org/10.1016/j.gexplo.2014.05.025
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absorption through direct contact with the soil as well as due to contamination via the food chain when consuming food at the polluted sites.

Environmental conditions also play an important role for the uptake of heavy metal by plants, with the soil–plant transfer of metals, being a very complex process governed by several factors (both natural and anthropogenic) such as soil heavy metal content, the sorptive capacity of soil, redox conditions, organic matter and pH (Alloway, 1995). These factors are known to control the processes of mobility and availability of metals in soils (Kabata-Pendias, 2004).

We assume that earlier activities of the former Pb smelter plant in Bouwer may pose a potential risk to food safety in the region. Therefore, a toxicological evaluation of this area is necessary. The objectives of this study were (i) to determine the concentrations of Pb and Zn in soil and soybean in the study area, (ii) to evaluate the accumulation of Pb and Zn from soil in different soybean organs and its relation to crop quality and (iii) to determine the toxicological risk from the consumption of seeds under the conditions of the present study.

2. Material and methods

2.1. Site and sampling points

The study area was located in Bouwer, a peri-urban town with a population of approximately 2,000 inhabitants, which is situated 18 km south of Córdoba city in central Argentina (Fig. 1). The climate is mild, with an annual mean temperature of about 15 °C and an average annual rainfall of 500–900 mm. The soil is an Entic Haplustoll and this area characterized by a former battery recycling plant (31°33′34.02″S; 64°11′9.05″W) surrounded by agricultural crops (mostly soybean). This town is one of the most environmentally affected areas in the province, characterized by a waste disposal area, scrap car dumps and a former battery recycling plant (Salazar, 2013), which was closed in the year 2005 due to functional problems because emissions were found to be approximately 35 times higher than permitted values (Comuna de Bouwer, 2008). The study area is mainly cultivated with soybean, which is subjected to zero tillage and with the fertilizers applied in general being simple superphosphates in proportions ranging from 50 to 100 kg ha^{-1}.

The sampling sites were chosen by taking into account the main direction of the winds and the distance to the emission source obtained from a preliminary study (Salazar and Pignata, 2014). These were (a) Smelter area, characterized by 7 sampling points located within 0.05 and 0.30 km from the smelter, and (b) control area, characterized by 7 sampling points located within 2 and 6 km from the smelter, without any pollution source in the vicinity.

2.2. Sampling procedure and analysis preparations

Sampling was conducted during the soybean harvest season of the Southern Hemisphere at the maturity stage (R8), as defined by Fehr and Caviness (1977). Soybean plants and topsoil samples were collected at the sampling sites, with each site consisting of a 25 m^2 square with 9 sub-sampling points, systematically arranged with a 2.5 m gap between them. Three plants were collected at each point, making a total of 27 plants at every sampling site. Plants were collected using a stainless steel shovel to extract the whole root. In addition, bulk topsoil subsamples were gathered at the nine points using a stainless steel spade at a depth of 0–10 cm, with stones and foreign objects being taken away by hand. Soil and plants were kept in plastic bags until being processed in the laboratory.

Soybean samples were sorted into roots, stems, seeds and pods and then washed and sonicated with ultrapure water for the purpose of removing soil remains attached to the organs. Subsequently, the plant samples were oven-dried at 60 °C to constant dry weight (DW), homogeneously mixed, and each composite sample from each site and plant was stored in the dark until analytical procedures were carried out.

Topsoils were oven-dried at 40 °C for 24 h, after which the samples were sieved to <2 mm (using a polyethylene sieve) and stored in darkness until analytical procedures were carried out. Each composite sample was made by mixing and homogenizing 150 g of each of the topsoil sieved subsamples.

2.3. Chemical analysis

2.3.1. Topsoils

Topsoil pH and electrical conductivity (EC) were measured in 1:5 soil:water suspension in triplicate (Bäcktröm et al., 2004). In order to calculate the dry weight (DW), samples were oven-dried at 105 °C to constant weight (Al-Khashman and Shawabkeh, 2006). The percentage of organic matter (%OM) was determined according, to Peltola and Åström (2003), by combustion of the samples at 500 °C for 4 h.

The soil samples were obtained according to Salazar et al. (2012) for which a 0.5 M hydrochloric acid extraction in topsoils for exchangeable metal fractions was carried out. Topsoils were sieved at 63 μm with a stainless steel mesh, and each sample was extracted using 7 g of topsoil with 25 mL 0.5 M HCl, which was homogenized at room temperature for 30 min. After 24 h, the solution was filtered and analyzed using a Perkin-Elmer AA3110 atomic absorption spectrometer (Norwalk, CT, USA) to measure Pb_{Exch}, and Zn_{Exch}.

The pseudototal concentrations of metals (Pst) were measured according to Ketterer et al. (2001), for which 5 g of topsoil (reduced to ashes at 450 °C for 4 h) was digested with hydrochloric and nitric acid extraction (HCl:HNO_3, 3:1 V/V) and homogenized at room temperature for 30 min. After 24 h, the solution was filtered and analyzed using a Perkin-Elmer AA3110 spectrophotometer to measure Pb_{Pst} and Zn_{Pst}.

2.3.2. Soybeans

The Pb and Zn content were analyzed in seeds, pods, stems and roots (3 g DW) using 20% HCl and HNO_3. The samples were ashed at 450 °C for 4 h and then digested using 2.5 mL 20% HCl and 0.5 mL HNO_3, according to Rodriguez et al. (2011a). The heavy metal concentrations in plant samples were measured using a Perkin-Elmer AA3110 atomic absorption spectrometer.

The standard germination test and the tetrazolium test (% vigour) were performed, and the morphological parameters (biomass production for each organ expressed as dry weight, weight of 1000 seeds, number of seeds per plant, number of pods per plant and number of seeds per pod) were determined as described by Salazar et al. (2012).

2.4. Quality control

As a quality control, blanks and samples of the standard reference material “CTA-OTL-1” (oriental tobacco leaves, Institute of Nuclear Chemistry and Technology) for plants and reference certificated material (CRM GBW07405 Soil-NRCCRM, China) for soils were prepared in the same way as described above and were run after ten determinations to calibrate the instrument and monitor the potential sample contamination during analysis. These results were found to be between 90% and 92% of the certified value for CTA-OTL-1 and between 87% and 91% for CRM GBW07405 Soil-NRCCRM, with the data indicating a small error of typically less than 15%. The coefficient of variation of the replicate analyses was calculated for different determinations, with variations being found to be less than 10%.

2.5. Data analyses

2.5.1. Statistical analysis

The assumptions for normality and homogeneity of variance were previously verified numerically (Shapiro–Wilks test for normality,

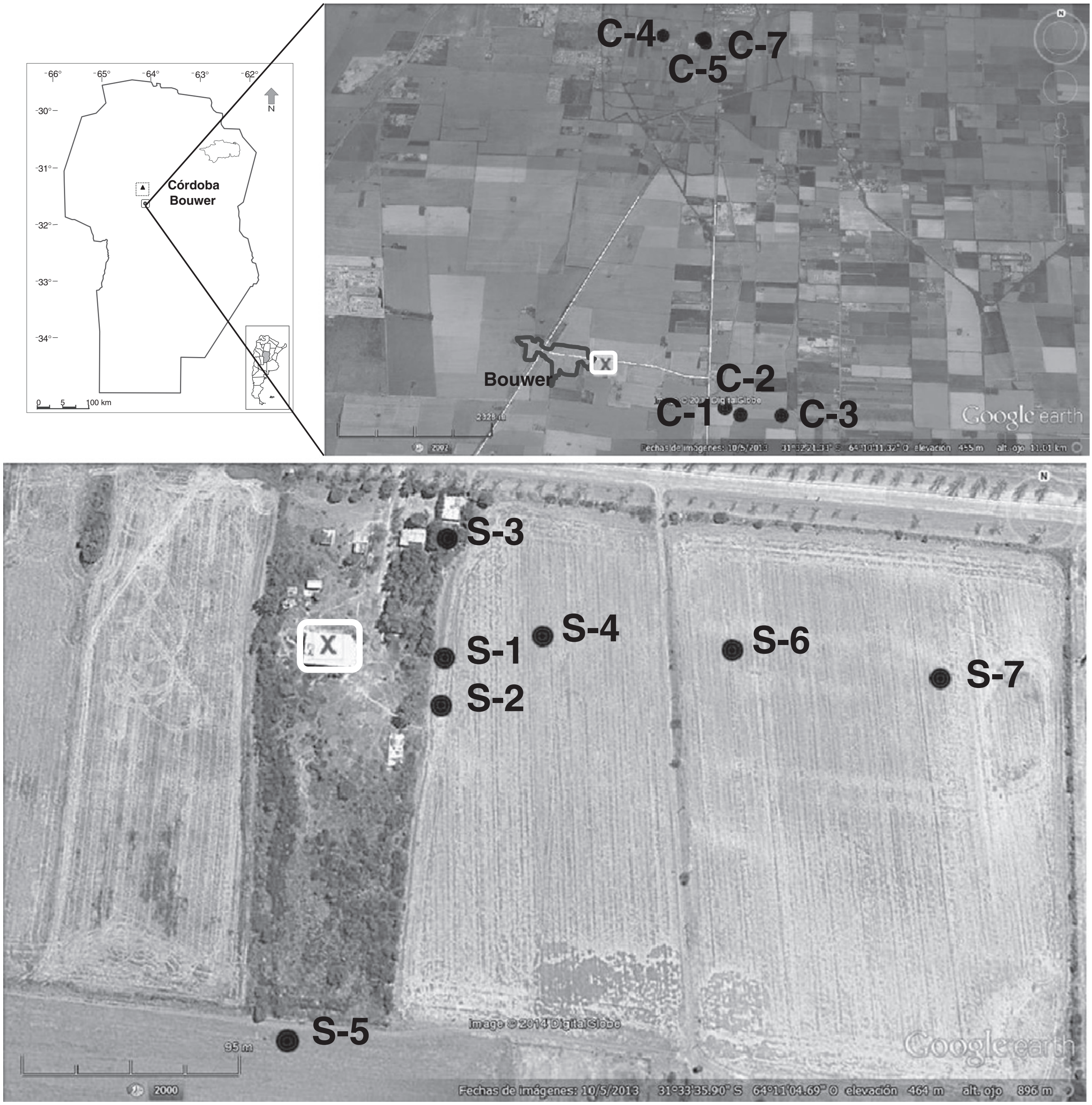

Fig. 1. Topsoil and soybean sampling area in Córdoba (Argentina). Sampling sites: Control area (C-1, C-2, C-3, C-4, C-5, C-6, C-7) and Smelter area (S-1, S-2, S-3, S-4, S-5, S-6, S-7). References: X Localization of former battery recycling plant.

Levene test for equality of variances) and graphically (residual vs. fitted values, box plots, and steam leaf plots). As not all measured data showed a normal distribution, they were analyzed with the non-parametric procedure of the Kruskal–Wallis test.

The Spearman correlation matrix was used to identify the relationships between soil variables (pH, EC and %MO) and heavy metal content in soil for both fractions (exchangeable and pseudototal) in order to determine the parameters that best indicated the availability of metals in soils. This method was also used to evaluate possible relationships among the metal exchangeable concentrations in soil, morphological variables, seed quality parameters and heavy metal content in soybean organs.

The statistical analysis was performed with the software InfoStat, Version 2012.

2.5.2. Risk assessment

The risk to human health resulting from consumption of soybean grown at the different sites was calculated by employing the estimated dietary intake (EDI μg kg^{-1} day^{-1} bw), target hazard quotients (THQ) and hazard index (HI) as described by Zheng et al. (2007) and US EPA (1989). If either TQH or HI exceeds unity, a high risk of non-carcinogenic effects is implied.

For the present study, Chinese, European and Argentine inhabitants were considered to be potential consumers, taking into account that

Table 1
Median (minimum–maximum values) and results of Kruskal–Wallis test of exchangeable and pseudototal Pb and Zn concentrations (in μg g^{-1} DW) of topsoils measured in the study area.

Area	Soil fraction	Metal	
		Pb	Zn
Smelter	Exch	193.34 (18.23–640.71)^{a}	5.50 (4.40–26.30)^{a}
Control	Exch	5.64 (4.01–9.07)^{b}	5.00 (3.50–8.80)^{a}
p		***	*ns*
Smelter	Pst	235.85 (23.49–1050.72)^{a}	30.9 (20.00–51.50)^{a}
Control	Pst	8.63 (6.85–9.93)^{b}	26.60 (23.90–29.20)^{b}
p		***	*

Values in each column followed by the same letter do not differ significantly at $p < 0.05$. (ns, not significant, $^{*}p < 0.05$, $^{**}p < 0.01$, $^{***}p < 0.001$). Abbreviations: Exch, exchangeable soil fraction; Pst, (pseudototal soil fraction).

Argentina exports soybean and its products mainly to China and the countries of the EU, for more details please refer the study of Salazar et al. (2012).

3. Results

3.1. Analysis of heavy metals, pH, EC and %OM in topsoils

Descriptive statistics and the results of the Kruskal–Wallis test of exchangeable and pseudototal Pb and Zn concentrations of topsoils are shown in Table 1. Lead values above the limits for agricultural land use of soil quality (threshold: 375 mg kg^{-1} DW) were found in the “smelter” area (Argentinean legislation, 1992; CCME, 2001), being significantly higher than the values of both soil fractions (exchangeable and pseudototal) close to the smelter. Although Zn values in the study area were within the limits corresponding to agricultural soils (Lavado, 2006), the pseudototal concentrations were significantly higher in the vicinity of the former smelter lead.

Regarding Spearman's correlation coefficients between soil parameters (pH, EC and %OM) and metal concentrations, a slightly but significant correlation was found for the OM percentage with exchangeable and pseudototal Pb in soils (Pb_{Exch} −0.53, p = 0.06; Pb_{Pst} −0.55, p = 0.05). Furthermore, a significant correlation existed between EC and Zn_{Exch} in soil (0.51, p = 0.06).

3.2. Heavy metal concentrations in roots, stems, seeds and pods

Table 2 shows the descriptive statistics and results of the Kruskal–Wallis test for Pb and Zn concentrations in root, stem, pod and seed of soybeans at the maturity stage in the study area.

Regarding Pb, the concentrations in most organs were significantly higher at sites close to the smelter area, whereas the Zn accumulation was significantly higher only for stems and seeds.

It is noteworthy that significant differences among organs for Pb accumulation were observed in the “control” area following this decreasing order: pods > seeds > stems > roots, whereas for Zn significant differences in both “smelter” and “control” areas were found as follow: seed > pods > roots > stems. Regarding Zn the highest concentration was found in seeds at sites close to the smelter.

Table 3
Spearman correlation coefficients between soybean quality parameters (biomass, number of seeds per plant, weight of 1000 seeds and germination potential), metal content in soybean seeds and exchangeable Pb concentrations in soils (μg g^{-1} DW).

	Pb_{Exch}	Pb_{seeds}	Zn_{seeds}
Stem biomass			0.65*
Pods biomass	−0.55**		
Seeds biomass	−0.55**		
No. seeds/plant		−0.71***	−0.68**
Weight of 1000 seeds		−0.71***	−0.75**
Germination potential		−0.49*	
Pb_{Exch}		0.65**	
Zn_{seeds}	0.65**	0.67**	

Abbreviations: Exch, exchangeable soil fraction; Pst, pseudototal soil fraction; Pb seeds, accumulation of lead in seeds; Zn_{seeds}, accumulation of zinc in seeds.

* $p < 0.1$.
** $p < 0.05$.
*** $p < 0.01$.

3.3. Soybean quality analyses and toxicological risk associated with seed consumption

In Table 3, the Spearman correlation coefficients are presented, which reveal significant values among soybean quality parameters, metal content of seeds and exchangeable soils. Negative correlations between Pb_{Exch} in soils and biomass of pods and seeds were found. In addition, the Pb content in seeds was negatively correlated with the number of seeds per plant, weight of 1000 seeds and germination potential. Furthermore, Pb content in seeds was positively correlated with the Pb_{Exch} in soils. In contrast, Zn content in seeds only correlated positively with stem biomass, soil Pb_{Exch} and content of Pb in seeds, whereas Zn content in seeds showed a negative correlation with the number of seeds per plant and weight of 1000 seeds.

The THQ and HI values for Pb and Zn, corresponding to an individual Chinese, European or Argentine consumer did not show values greater than one for any case (data not shown).

4. Discussion

4.1. Chemical analysis of topsoils

Taking into account the heavy metal concentrations in soil, it is important to note that lead levels exceeded the limits of soil quality for agricultural land use (threshold: 375 mg kg^{-1} DW) at sites corresponding to the “smelter” area (Argentinean legislation, 1992; CCME, 2001), being significantly higher for both soil fractions. Although the Zn values in the study area were within the limits corresponding to agricultural soils (Lavado, 2006), the pseudototal concentrations were significantly higher in the vicinity of the former lead smelter. These results are

Table 2
Median (minimum–maximum values) and results of Kruskal–Wallis test of Pb and Zn concentrations (in μg g^{-1} DW) in roots, stems, pods and seeds of *Glycine max* in the study area.

Metal	Area	Organ				
		Root	Stem	Pod	Seed	*p**
Pb	Smelter	2.03 (0.37–34.97)^{a}	1.90 (1.12–20.33)^{a}	2.35 (1.50–5.54)^{a}	1.70 (1.52–1.75)^{a}	*ns*
	Control	0.15 (0.01–0.31)^{b}	1.03 (0.86–1.42)^{b}	2.74 (2.51–3.06)^{a}	1.33 (1.20–1.41)^{b}	***
p		*	**	*ns*	***	
Zn	Smelter	5.10 (4.04–5.96)^{a}	3.22 (2.35–4.36)^{a}	6.84 (4.47–13.55)^{a}	30.81 (28.88–32.40)^{a}	***
	Control	4.80 (4.17–6.38)^{a}	2.10 (1.83–2.53)^{b}	4.86 (2.85–6.40)^{a}	23.99 (22.42–26.75)^{b}	***
p		*ns*	**	*ns*	***	

Values in each column followed by the same letter do not differ significantly at $p < 0.05$. (ns, not significant, $^{*}p < 0.05$, $^{**}p < 0.01$, $^{***}p < 0.001$). Abbreviations: p^{*}, significance level among soybean organs for each area and metal.

similar to those reported by Salazar et al. (2012) and Salazar and Pignata (2014) at sites located nearby to the former lead smelter, who also mentioned not only an increase in Pb concentrations but also of other metals associated with this metal such as Zn.

Regarding the chemical and physical soil parameters, only significant associations were observed among OM, EC and heavy metals in soils. It has been widely reported that both organic matter and electrical conductivity are parameters closely related to the metal mobility in soils (Kabata-Pendias, 2004; Matos et al., 2001), with organic matter in soils playing an important role in the availability of metals, since together with clay this determines most of the cation exchange capacity (CEC), a key parameter related with sorption and desorption of nutrients and contaminants in soils (Kashem and Singh, 2001). On the other hand, the parameter EC measures the availability of the soil solution to transmit an electrical current, which takes place through the moisture-filled pores between soil particles and depends on the chemical species of metals (Seifi et al., 2010).

4.2. Chemical analysis in soybeans and toxicological risk

As regard to the Pb and Zn concentrations in soybeans corresponding to sites near to the former lead smelter, an effective translocation and accumulation of Pb, and to a lesser extent Zn, were observed in different organs of soybean. Is important to note, that all the Pb values in seeds were above the permitted maximum levels of 0.2 μg g^{-1} Pb DW, which is the level given by the EU directive relating to maximum levels of certain contaminants in foodstuffs (EU, 2006). However, in the Argentinean legislation, as the limits for lead in foods are set at 2 μg g^{-1} Pb DW, then the lead concentrations in seeds from this study were with permitted values according to this legislation (CAA, 2006). Regarding Zn, its concentrations in seeds did not exceed the maximum permitted levels of 100 μg g^{-1} Zn DW according to CAA (2006) and were within the normal values quoted for soybean in Argentina (Lavado, 2006; Salazar et al., 2012). These results are in agreement with those reported by Salazar et al. (2012) for soybean crops at different sites in Córdoba, with these authors also having reported an association between elevated levels of lead in soils and crops with an increase in the Zn content, which has been observed in other studies (de Souza Silva, 2006; Salazar and Pignata, 2014). Moreover, this behavior may be related to that reported by Goldstein et al. (2006), who showed an increase of antioxidant system enzymes such as the superoxide dismutase, which uses Zn as an electron carrier in polluted soil as a response to stress toxicity.

In contrast, results on the differential accumulation of metals in soybean organs revealed the highest levels in seed and pods, which confirm the results of other authors who mentioned that this crop accumulated potentially more heavy metals than other plants (Lavado, 2006; MAFFJ, 2002; Rodriguez et al., 2011a; Salazar et al., 2012; Zhao et al., 2014).

Regarding the soybean quality analyses, this finding clearly shows the negative effect of lead on seed quality parameters. For Zn, the results show an association between this metal and lead in sites near the smelter, which was also associated with a decrease in the quality of the seeds. Once again, this indicates synergistic behavior between lead and zinc, as mentioned above.

Concerning the toxicological risk associated with the consumption of soybean grown in the study area, our results did not show any potential non-cancer risk for heavy metals to consumers. However, taking into account that all seeds had lead levels above the limits established by international legislation, it is advisable to perform a continuous monitoring of the toxicological risk associated with consumption of this crop.

5. Conclusions

The metal concentrations (Pb and Zn) in soybean crops grown close to the former lead smelter showed high levels of these metals in soil, which were above the maximum permitted values of Pb in agricultural soils. Moreover, the Pb concentrations in soybean in the study area exceeded the maximum values according to European legislation, revealing a toxicological risk in these soils. However, it is important to highlight that consumption of these seeds does not present a potential non-cancer risk from heavy metals.

The seed quality parameters were negatively influenced by the exchangeable lead concentration in soils from the former smelter area, as well as by the accumulation of this metal in seeds. An interesting result was found with respect to the accumulation of Zn in plant organs, which confirmed that the accumulation was higher in seeds and was negatively correlated with seed quality parameters, a behavior that needs to be studied in order to understand the chemical processes occurring between metals and their influence on productivity and quality of crops.

Acknowledgments

This work was partially supported by the Agencia Nacional de Promoción Científica y Tecnológica (FONCyT) and Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET). The authors M. J. Salazar and J. H. Rodriguez were supported by the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET). The author M. J. Salazar is a PhD student in Biological Sciences at the National University of Córdoba. The author L. Steffan was supported by the German Academic Exchange Service (DAAD) through a scholarship.

Special thanks to F. J. Morales, Bouwer smelter neighbors (M. R. Pavani and S. Herrera), to land owner and mayor of Bouwer (J. Lupi), and to Dr. P. Hobson (native speaker) for language revision.

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