

Phytoavailability of Toxic Heavy Metals and Productivity in Wheat Cultivated Under Residual Effect of Fertilization in Soybean Culture

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Abstract Achieving high productivity in agriculture is increasingly needed and requested; however, this activity should be performed in a sustainable and rational way. The use of micronutrients in the fertilization of the most diverse cultures is becoming a common practice on farms, but it is important to conduct studies in relation to fertilizers used for this supplement, including raw materials with which they are produced. Therefore, this study aimed to evaluate the phytoavailability of nutrients and toxic heavy metals Cd, Pb, and Cr; productivity; and yield components in wheat sown in soil with residue of N/P₂O₅/K₂O+Zn-based fertilizer applied in previous crop. Treatments consisted of residual fertilization of five forms arranged in two doses (D1=300 kg ha⁻¹ and D2=600 kg ha⁻¹). The five types of fertilization were composed of formulated N/P₂O₅/K₂O and the variation of different Zn sources. In the assessment of phytoavailability were determined levels of K, Ca, Mg, Cu, Mn, Zn, Fe, Cd, Pb, and Cr in wheat leaves. The results show that the residual effect of fertilization was not enough for there being difference between treatments at both doses used; however, it was found that the fertilizers used to Zn supply provided residual

effect, providing significant levels of Pb and Cr for wheat plants.

Keywords Environmental contamination · Residual fertilization · Toxic heavy metals · *Triticum aestivum* · Zinc sources

1 Introduction

Wheat (*Triticum aestivum*) is a plant from the Middle East (Asia), where it is grown to more than 5,000 years, being of great importance for Babylonians and Egyptians. It presents as one of the main cereals grown on our planet, occupying the largest acreage in the world (about 20% of the total arable area). The main world producers of wheat are Russia, Ukraine, USA, China, India, and France; according to Brazilian research institutions, the current production of this crop is around 500 million tons/year (SEAGRI 2010; Fornasieri Filho 2008; Embrapa 2010).

In Brazil, wheat production is concentrated in southern and central-south regions, with Rio Grande do Sul, Parana, and Sao Paulo as the main producing states, with the southern region accounting for 90% of Brazilian production. The average wheat import by Brazil in the last five seasons was 5.5 million tonnes to a demand of 8 million (SEAGRI 2010).

The crop management has become a major factor in grain yield in the tech field systems, where it is common the nutritional imbalance in soil, especially

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of micronutrients. This factor has been increasing interest in studies about doses and sources, as micronutrients are very important to maintaining self-sustaining systems. Nevertheless, due to the intensive land use and utilization of improved productive varieties and more demanding in relation to nutrition, there is need for better monitoring of levels of micronutrients in agricultural soils in relation to crop management, even for small amounts (Oliveira et al. 2001). Micronutrient deficiency in agricultural soils is an increasing concern, with a tendency to accentuate in the near future. Cultivation in low fertility soils, liming, and increased productivity are factors that have favored the increase in micronutrient deficiencies (Gonçalves Jr. 2000).

In 2006, technicians of the Supervision Department of the Ministry of Agriculture and Supply of Parana (SEAB 2009) stated in their analysis that 30% of fertilizer found in Parana shops do not meet the required standard, and the rates of nutrient obtained in the analysis are below those that products ensure on their labels. Due to this alert, there are initiatives to start testing if the inputs can also be contaminated by toxic heavy metals harmful to the environment which would contaminate soil, food, water, and consequently human health (Ribas 2007).

Currently, some formulators companies of fertilizers in Brazil are increasingly offering the domestic market products containing micronutrients, especially Zn. Most of these products offered have evocative names such as *Extra*, *Top*, *Full Power*, *Turbo*, *Premium*, and others, with the intention of differentiation in terms of performance in field and consequently higher prices.

Also in the Brazilian legislation, the guarantee and official methods of analysis refer to the total content of micronutrients (Brazil, Ministry of Agriculture 1993). This enables to market several industrial by-products containing micronutrients with total levels required by legislation, but they can be composed of low solubility when are not listed in the legislation. An example is the marketing of metal Zn under the label of zinc oxide (Alcarde and Vale 2003).

Once present in soil, air, or water, whether by natural occurrence or by human action, the toxic heavy metal can enter the food chain and when reaching high concentrations in plants, animals, and humans causes toxicity problems, decreasing productivity in the case of plants and animals and causing

disease in humans, which may yet culminate in death (Melo et al. 2007).

The knowledge of residual effect of fertilizers containing micronutrients is of fundamental importance for defining the range of doses and reapplication of them. This is a complex matter involving not only sources used but also the doses, application methods, export rates by crops, management of crop residues, soil types and production systems (conventional agriculture and tillage), among others (Lopes 1999).

In general, products with lower water solubility, such as colemanite and ulexite, have higher residual effect. With respect to copper, there is evidence that the reversal of sources for this metal to unavailable forms to plants is low, with ranges for new Cu applications exceeding 5 years depending on the sensitivity of cultures and deficiency severity. The residual effect of fertilization with molybdenum depends on MoO_4^{-2} reactions with soil constituents, amount of Mo leached, and export rates by crops. For zinc, studies show that doses between 25 and 30 kg ha⁻¹ applied may correct deficiencies for several years due to the slow Zn reversal to the unavailable form to plants (Lopes 1999).

In the search for results related to micronutrient fertilization and its residual effect, this study was performed with the aim of evaluating the residual effect of micronutrients fertilization for the soybean crop on the yield components and wheat productivity as well as to evaluate the phytoavailability of the toxic heavy metals cadmium, lead, and chromium in the leaves of wheat plants.

2 Material and Methods

2.1 Experimental Site

The experiment was installed in Palotina, state of Parana, during the winter season of 2008, located at 24°18' S, 53°55' W and 310 m of altitude. The soil was classified as Hapludox (RED) (Embrapa 2006) with clay texture. The climate is tropical hot and humid (Cfa), with average annual temperature of 21.3°C, 16°C minimum, and 28.6°C maximum. The experiment was conducted in field, cropland area with no-till system in the straw, with soybean crop (*Glycine max* L.) variety NK-412 113 previous to the experiment.

Table 1 Soil chemical features at the beginning of the experiment in the areas with recommended dose (D1) and double dose (D2)

Area	pH	OM g ;dm ⁻³	P mg dm ⁻³	K cmol _c .dm ⁻³	Ca	Mg	Al	V %	Al
D1	4.60	24.91	48.67	1.37	2.79	1.10	0.30	51.00	5.52
D2	4.78	21.61	47.80	0.88	2.65	1.32	0.25	49.00	4.98

D1 recommended dose area, D2 double recommended dose area

2.2 Experimental Design and Treatments

The experimental design was in the randomized blocks and factorial scheme 6×2 with three replications. The plots of treatments for wheat cultivation were arranged to coincide exactly with those of the previous crop (soybean), once its fertilization residue was used.

Fertilization treatments for soybean crop were composed of the fertilizer N/P₂O₅/K₂O at 2:20:18 formulation supplemented with 0.3% Zn in form of granules applied at the base, for such four sources of different brands of commercial fertilizer were used for Zn supplement. Two doses of fertilizer based on soil test for fertility (Tables 1 and 2) were used, following the recommendations of Embrapa (2006). Thus, doses were defined as one time the recommended dose and two times the recommendation, considering 300 kg of formulated N/P₂O₅/K₂O (2:20:18) per hectare as the recommended dose, and hence, the double is 600 kg of N/P₂O₅/K₂O (2:20:18) per hectare. In addition to the treatments with fertilizer, a treatment without applying any fertilizer was used, which is considered as “control.”

In all treatments with N/P₂O₅/K₂O, sources of nutrients were urea for N, simple super phosphate, and triple super phosphate for phosphorus and potassium chloride for K. Below are shown all conditions used in the fertilization of soybeans:

T1=300 kg NPK—formula 02-20-18 with 0.3% brand A Zn

T2=300 kg NPK—formula 02-20-18 with 0.3% brand B Zn

T3=300 kg NPK—formula 02-20-18 with 0.3% brand C Zn

T4=300 kg NPK—formula 02-20-18 with 0.3% brand D Zn

T5=300 kg NPK—formula 02-20-18 without Zn

T6=control without fertilization

T7=600 kg NPK—formula 02-20-18 with 0.3% brand A Zn

T8=600 kg NPK—formula 02-20-18 with 0.3% brand B Zn

T9=600 kg NPK—formula 02-20-18 with 0.3% brand C Zn

T10=600 kg NPK—formula 02-20-18 with 0.3% brand D Zn

T11=600 kg NPK—formula 02-20-18 without Zn

T12=control without fertilization

2.3 Deployment and Conduct of the Experiment

To determine the soil’s initial condition and fertilizer recommendation, samples were collected at 0–20 cm depth at three different points (sub-samples), inside the useful plot already determined for soybean crop, and then they are then mixed up obtaining a composed sample sent for analysis. Chemical analysis was performed at the Laboratory of Environmental and Instrumental Chemistry in Western Parana State University using the official methodology of the State of Parana for soil chemical analysis, proposed by Pavan et al. (1992), and the results are presented in Tables 1 and 2.

It was further performed the chemical characterization of fertilizers used in the soybean crops, determining their levels of nutrients and toxic heavy metals. The extraction of K, Ca and Mg, Fe, Zn, Cd, Pb, and Cr was carried out by perchloric digestion (AOAC 2005), and then it was performed their

Table 2 Average values of toxic heavy metals in soil of the areas with recommended dose (D1) and double dose (D2)

Area	Cu µg g ⁻¹	Mn	Zn	Fe	Cd	Pb	Cr
D1	17.29	219.67	6.60	27.38	5.77	27.39	13.11
D2	15.72	266.50	3.86	37.27	5.27	21.11	31.27

D1 recommended dose area, D2 double recommended dose area

Table 3 Levels of nutrients and toxic heavy metals in fertilizers used in the crop planting previous to wheat

Fertilizers	P $\mu\text{g g}^{-1}$	K	Ca	Mg	Fe	Zn	Cd	Pb	Cr
A	14.79	12.83	68.33	5.09	1,185.58	1,349.68	5.52	23.02	21.44
B	14.55	12.97	68.00	5.37	1,430.57	1,321.80	5.52	22.89	21.79
C	14.76	12.95	67.58	4.96	1,356.38	1,302.41	5.52	22.99	21.48
D	23.50	32.17	56.13	8.07	8,700.00	3,313.33	5.33	23.33	23.33
E	15.23	12.72	69.82	4.80	892.02	1,206.82	5.51	23.00	21.16

determination by atomic absorption spectrometry (AAS) flame method (Welz and Sperling 1999). For the P element, it was used extraction by sulfur digestion (AOAC 2005) and determination by ultraviolet/visible spectroscopy (UV–VIS). Results obtained in the fertilizer's chemical analysis are shown in Table 3.

The wheat planting was carried out at the end of April 2008, with the designated area for the experiment being handled in accordance with appropriate actions. With the purpose of removing weeds, it was applied the *Glyphosate*[®] (at a dose of 3.00 Lha⁻¹) herbicide for area desiccation. Afterward, sowing was performed with a precision seed drill at 3 cm depth and deposition of 60 seeds per linear meter, and it should be repeated that fertilizer was not used at wheat sowing.

The wheat cultivar used in the experiment was IPR-130, developed by Agronomic Institute of Paraná (IAPAR 2009), with medium maturity, type improver bread, and low stature. The entire process of conducting experimental cultivation was as close as possible the conditions used in commercial fields, i.e., with the use of certified seed, chemical control of weeds, pests, and diseases.

Table 4 Analysis of variance for yield components and wheat productivity

VS	Mean squares			
	FD	HW	1,000 grains	Productivity
Block	2	0.38 NS	0.34 NS	144,990.61 NS
Dose (<i>D</i>)	1	0.45 NS	1.22 NS	26,910.21 NS
Treatment (<i>T</i>)	5	0.31 NS	0.55 NS	41,496.19 NS
<i>D</i> × <i>T</i>	5	1.22 NS	0.35 NS	199,414.00 NS
Residue	22	1.45 NS	0.80 NS	137,231.75 NS
CV (%)		1.63	2.83	14.63

VS variation source, FD freedom degrees, NS not significant at 5% probability by the *F* (Fisher) test, HW hectoliter weight, 1,000 grains mass of 1,000 grains

For post-emergent weed control, it was applied the *Metsulfuron*[®] (at a dose of 4.13 gha⁻¹) herbicide. For insect control, it was applied the *Chlorpyrifos*[®] (at a dose of 0.750 Lha⁻¹) insecticide. For disease control, it was applied the *pyraclostrobin* + *epoxiconazole*[®] (at a dose of 0.500 Lha⁻¹) fungicide.

2.4 Collection of Leaf Samples and Crop Harvest

In July 2008, at 72 days after emergence (AE), when plants were at the phenological growth stage 10 (early ear), wheat plants leaf samples of the experiment were performed. In each useful plot were collected 30 leaves between 1st and 4th expanded leaf from the plant apex (Malavolta 1994). For determination of nutrients (K, Ca, Mg, Cu, Mn, Zn, Fe) and toxic heavy metals (Cd, Pb, and Cr) in the structure of wheat plant, it was used the perchloric digestion method (AOAC 2005) and the determination performed by AAS flame method (Welz and Sperling 1999). The P was determined by sulfuric acid digestion (AOAC 2005) and used the UV–VIS technique.

Table 5 Analysis of variance for contents of P, K, Ca, and Mg in leaf tissue of wheat plants

VS	Mean squares				
	FD	P	K	Ca	Mg
Block	2	0.04 NS	1.54 NS	1.52 NS	0.05 NS
Dose (<i>D</i>)	1	0.92 NS	1.89 NS	0.00 NS	0.02 NS
Treatment (<i>T</i>)	5	0.33 NS	2.48 NS	2.16 NS	0.04 NS
<i>D</i> × <i>T</i>	5	0.47 NS	1.20 NS	3.35 NS	0.23 NS
Residue	22	0.34 NS	3.71 NS	2.48 NS	0.13 NS
CV (%)		24.77	7.62	17.01	11.32

VS variation source, FD freedom degrees, NS not significant at 5% probability by the *F* (Fisher) test

Table 6 Analysis of variance for contents of Cu, Mn, Zn, Fe, Cd, Pb, and Cr in leaf tissue of wheat plants

VS variation source, NS not significant at 5% probability by the *F* (Fisher) test, ND not detected by the EAA flame

VS	Mean squares						
	Cu	Mn	Zn	Fe	Cd	Pb	Cr
Block	0.44 NS	142.11 NS	0.52 NS	385.33 NS	ND NS	14.77 NS	28.77 NS
Dose (<i>D</i>)	0.02 NS	51.36 NS	18.77 NS	3,006.7 NS	ND NS	0.44 NS	0.11 NS
Treatment (<i>T</i>)	0.56 NS	802.89 NS	2.11 NS	1,598.3 NS	ND NS	2.97 NS	17.31 NS
<i>D</i> × <i>T</i>	0.42 NS	350.62 NS	3.57 NS	4,081.8 NS	ND NS	4.37 NS	54.91 NS
Residue	0.44 NS	631.29 NS	7.89 NS	2,215.9 NS	ND NS	4.41 NS	25.56 NS
CV (%)	11.48	17.86	15.65	32.33	0.00	108.05	54.5

The crop harvest occurred in September 2008 with 128 days AE. It was performed manually picking up all the plants in the useful plot (3.0 m²) by evaluating the following components: mass of 1,000 grains (1,000 grains), hectoliter weight (HW), and productivity (15% humidity).

All experimental data were subjected to analysis of variance and means compared by the Tukey test at 5% probability. Statistical analysis was performed using the statistical program Sisvar 5.0 (Ferreira 2003).

3 Results and Discussion

Table 4 presents mean squares of the variance analysis for yield components and wheat productivity. It can be observed that there was no significant effect ($P>0.05$) for any of yield components and wheat productivity, showing that doses used in previous crop (soybean) did not provide sufficient residual effect to increase yield components and wheat productivity.

According to the Ministry of Agriculture and Supply of Paraná (SEAB 2009), 2,111 kg ha⁻¹ average wheat productivity was achieved in western Parana in the crop of 2008, showing that even accounting only with the

Table 7 Metals Cu, Mn, Zn, Fe, Cd, Pb, and Cr concentrations in the leaves of wheat plants in function of the two fertilization doses of soybean culture

Area	Cu μg g ⁻¹	Mn	Zn	Fe	Cd	Pb	Cr
D1	5.83	139.50	17.22	136.44	ND	2.06	9.22
D2	5.78	141.89	18.67	154.72	ND	1.83	9.33

D1 recommended dose area, D2 double recommended dose area, ND not detected by AAS flame method

residual fertilizer from the previous crop, yields obtained in the experiment (2,558.80 kg ha⁻¹) are slightly above the regional average. The average values of components HW and mass of 1,000 grains (1,000 grains) obtained in treatments (74.21 kg hl⁻¹ and 31.47 g, respectively) are very close to the average values indicated by IAPAR (2009) for the cultivar that are 77 kg hl⁻¹ and 35 g, showing that values obtained from the residual fertilizer can be considered satisfactory.

Tables 5 and 6 show the mean squares of the analysis of variance to the contents of nutrients, micronutrients, and toxic heavy metals in wheat plant tissue. Tables 4 and 5 show that no significant effect ($P>0.05$) was observed for levels of P, K, Ca, Mg, Cu, Mn, Zn, Fe, Cd, Pb, and Cr in wheat leaf tissue.

The different Zn sources studied did not differ in their residual effect on the wheat crop, and this residual effect was still insufficient for occurring higher means between the different doses and treatments in the concentrations of P, K, Ca, Mg, Cu, Mn, Zn, Fe, Cd, Pb, and Cr. For a better view of the results, Table 7 shows the concentrations of metals found in the leaves of wheat plants at the two fertilization doses of soybean culture.

There were no Cd concentrations in wheat leaf tissue by the AAS (flame mode), but it cannot be

Table 8 Normal and critical concentrations of toxic Cd, Pb, and Cr in plant's leaf tissue

Element	Normal range mg kg ⁻¹	Critical range
Cd	0.1–2.4	5–30
Pb	0.2–20	30–300
Cr	0.03–14	15–30

Kabata-Pendias and Pendias (1992)

affirmed that this element is not present in the leaf tissue and maybe at concentrations below the detection limit of this atomization method. The failure to detect this element may indicate that the largest portion of this metal, which was present in the soil before wheat crop establishment, was probably percolate to deeper layers and/or leached into other areas.

According to Mortvedt (2001), some leafy vegetables can absorb significant amounts of Cd, Cr, Ni, and Pb, but these metals in general are not translocated to grains, which may indicate that small amounts of Cd remained in the soil and perhaps were not translocated to wheat shoots. According to Dudka et al. (1994), Cd is not toxic to plants; however, it is a heavy metal that deserves concern because it can accumulate in plants at levels that can be toxic to animals and humans. According to these authors, Cd concentrations 25 times above the control treatment did not affect wheat plants; however, wheat resulting from this experiment could be toxic for consumption.

In an experiment conducted by Wang et al. (2002), significant linear correlations between concentrations of the heavy metals Cd, Cr, and Pb in wheat plants and concentrations determined in soil were obtained. Being still found greater Cd accumulation in wheat grains, which could pose a risk of food contamination in the deployment of crops in soils contaminated with these toxic heavy metals.

The application of fertilizer with micronutrients in the previous crop (soybean) showed an effective availability of Pb and Cr for wheat plants in both fertilization conditions used (recommended fertilization and double recommended dose).

Pb contents obtained in leaf tissue remained within the range considered as normal for levels of this element in plants (Table 8), which ranges from 0.2 to 20 mg kg⁻¹ (Kabata-Pendias and Pendias 1992). However, some Cr values obtained are high enough for its setting within the range considered critical (Table 8), ranging between 15 and 30 mg kg⁻¹ (Kabata-Pendias and Pendias 1992).

Among the various adverse effects associated with the presence of heavy metals in soil, it can be highlighted the possibility of its adsorption by plants with subsequent entry into the food chain. The capacity of accumulation of heavy metals by soils, which could affect their quality in the future, is another concern for which has not, to date, a conclusive answer (Ferreira et al. 2001).

4 Conclusion

After completion of this experiment, it can be stated that different fertilizers used for Zn supply to soybean crop showed no difference in their residual effect on the wheat crop, being it also insufficient for occurring higher average between the different doses of P, K, Ca, Mg, Cu, Mn, Zn, Fe, Cd, Pb, and Cr in the leaf tissues. However, the application of these fertilizers showed an effective availability of residual Pb and Cr for wheat plants in both fertilization conditions used.

The availability of heavy metals toxic to wheat plants by residual soil fertilization is a worrying fact, since it demonstrates that these harmful elements persist in soil for more than one agricultural crop maybe promoting soil contamination and therefore the environment if using fertilizers produced from sources contaminated by toxic heavy metals.

More researches must be conducted with the aim of investigating the products being marketed under the label of fertilizers as well as the source of their raw materials. Agriculture must be practiced with good sense, while respecting the sustainability and the contamination limits of the entire ecosystem; otherwise, the damage may be unavoidable.

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