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CONTAMINATION LEVEL OF *TRITICUM VULGARE* L. CULTIVATED ON SOILS AROUND A METALLURGICAL AREA IN GALATI, ROMANIA

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Abstract

Wheat (*Triticum vulgare* L.) is one of the most cultivated plants in the Galati-Braila region, where after the latest statistical data, quantities of 4000-5000 kg/ ha/year have been obtained. The present study aims to investigate the contamination level of the wheat edible parts due to industrial activity. This aspect is of great interest for human nutrition, especially as the studied area is located in the air mass circulating zone that trains the toxic particles emitted by the Galati steel plant. An impact on the quality of agricultural production, regarding the contamination with toxic elements, may also have the defective application of chemical fertilizers, which in quantities not complying with plant needs and soil properties may lead to the loading of agricultural products with harmful elements. In order to determine the transfer level of contaminants (heavy metals) in grains, the concentrations of Cr and Zn both in soil and wheat were determined by specific techniques, such as High-Resolution Continuum Source Atomic Absorption Spectrometry (HR-CS AAS) applied at INPOLDE research center, ReForm multidisciplinary platform, "Dunarea de Jos" University of Galati. Analytical results showed very high concentrations in soil for total Cr (117.10-383.10 mg/kg), exceeding approximately 13 times the maximum admissible limit (30 mg/kg), and for total Zn (63.31-136.59 mg/kg), exceeding sensitively the reference limit (100 mg/kg). Zn is known for its important role in the normal course of physiological processes in plants, but which in high concentrations can cause significant crop decline. Chromium is one of the most toxic elements which, if released in the soil solution, mostly under particular pH conditions, can be translocated into the plant tissues. The investigated grains shows low concentrations of Cr and Zn. The bioaccumulation factor recorded values lower than 1, which means that the wheat grains do not accumulate these elements in excess, under this region climate and the given soil condition.

Keywords: *Triticum vulgare* L., Cr, Zn, contamination, bioaccumulation, HR-AAS technique.

1. INTRODUCTION

Recent archaeological discoveries have shown that wheat has been cultivated in the Carpathian-Danubian-Pontic space since ancient times, being discovered grains of a species that is no longer cultivated (*Triticum diccocum* L.). Nowadays grain is one of the world's leading foods, with some of the best nutritional properties, and one of the most cultivated plants in the world, occupying the second place after rice [1]. In 2018, world's wheat production recorded 734.74 million tons [2], occupying the second place after the production of corn.

According to the data provided by the National Institute of Statistics, in 2018, an area of 2109 thousand hectares in Romania was cultivated with wheat. Production has increased significantly compared to the previous year, with preliminary data indicating a quantity of 10130 thousand tons [3].

The demographic explosion of the last decades that generated the expansion of agricultural land had a major impact not only on the structure of agricultural crops, but also on the quantities obtained and the quality of production. Under these conditions, the need to know the chemical composition of edible parts of wheat is imperative to avoid contamination or occurrence of imbalances in the diet of humans and animals. Agricultural plots close to industrial areas, main roads or any source of pollution or potentially polluting should be carefully monitored. The role of micro- and macroelements is well known for the optimal development of the physiological processes that take place at the level of the vegetal organs, as well as of the other living organisms [4-7]. But if they were in excess or in deficit? Each of them can bring considerable harm to agricultural productions, on the one hand, and to the end-beneficiaries, humans and animals, on the other hand, through toxicity caused by excess or insufficient nutrient intake through deficiency.

Recent research has shown the importance of knowing the level of heavy metals in cereals, especially as, along with other contaminants, they are associated with a particular impact on the environment and human health [8, 9]. Investigating the nutrients or toxic elements levels in plants requires a thorough research into the environmental conditions in which they develop, as each contributes to a certain extent in assimilating them in lower or higher quantities.

The two elements investigated in this work, Cr and Zn, are known for the benefits they bring to the human body and the plants, whether administered or disposed of in optimal doses, but especially for the disturbances to the biological systems when the concentrations exceed the limits established by the international authorities [10, 11].

2. EXPERIMENTAL

2.1. Sampling area position and characterization

The study area is located in the south-eastern region of Romania, in the vicinity of the industrial platform in the western part of Galati town, where a steel industrial complex has been operating for more than 50 years (Fig. 1).

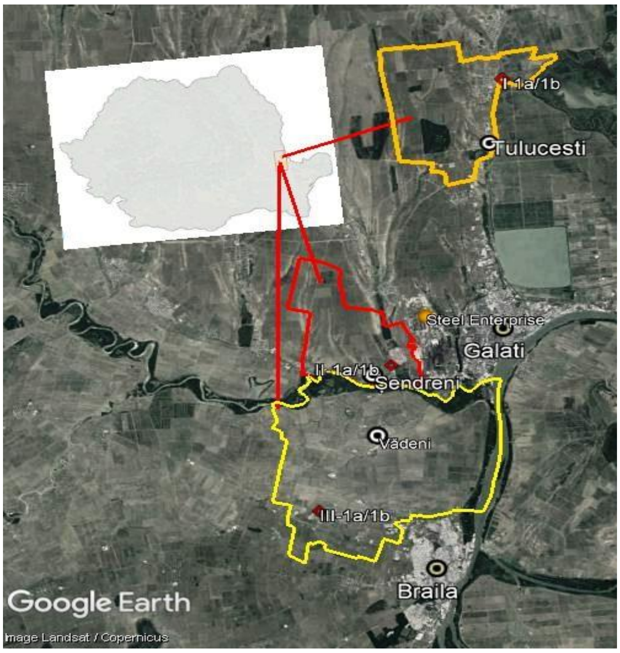

Fig. 1. Target area location, Galati and Braila counties, SE Romania

Soil and plant samples were taken from the arable plots of the Sendreni (Galati county) and Vadeni (Braila county) located in the west and southwest of the Galati Steel Works. In order to quantify the level of pollution with heavy metals, a control area considered non-polluted, located in the north of the industrial platform (Tulucesti commune, Galati county) was chosen.

Sendreni and Tulucesti territories are geomorphologically located in the High Covurlui Plain, characterized by a relief of low hills with low-moderately slopes. The interfluves have NNV-SSE dominant orientation, conforming to geological strains and are fragmented by valleys with symmetrical slopes, slightly branched, indicating the youthfulness of the area's relief. The Vadeni territory is located in the Braila Plain (Romanian Plain), with altitudes not exceeding 5-6 m in the study area. The two mentioned relief units are separated by the Siret Corridor, which marks a sub-area to the neighboring regions.

The soils were formed on North-Dobrogean geological structures, covered by quaternary loess and loessoid deposits of different granulometry.

The climatic characteristics highlight an excessive temperate-continental climate, characterized by temperatures ranging from 10.7ºC, in the Galati area, to 11.1 ºC near the city of Braila. The average annual precipitation ranges between 485.7 mm/ year (Galati) and 440 mm/ year (Braila) and fall largely in the summer season, they have a downfall character and a high potential for removal of fertile particles from the soil surface.

The characteristic vegetation is that of silvostepe and stepe antropically modified, represented by *Quercus pedunculiflora L., Quercus pubescens L., Crataegus monogyna L., Cotinus coggygria L., Sambucus nigra L., Prunus spinosa L., Rosa canina L*. etc. In the meadow area the vegetation is represented by hygro-mesophilic species such as *Agrostis stolonifera L., Alopecurus pratensis L., Deschampsia caespitosa L., Festuca arundinacea L., F. pratensis L., Plantago altissima L., Rumex confertus L., Carex vulpina L* .etc.

The depth at which the water can be intercepted on interfluves varies from over 10 m, not influencing pedogenic processes, to about 1-1.5 m in the alluvial area, generating complex physico-chemical processes through oscillations on the vertical during the year.

Representative soils are slightly-moderately alkaline, sand to loamy sand, with low or medium concentrations of $CaCO_3$ and organic matter. The soils are base saturated and unsalted.

The brief presentation of the main pedogenetic factors is meant to establish a correlation between the morpho-pedo-phyto-climatic conditions of the researched area and the accumulation, migration and disposal of toxic elements in the soil and from soil to the vegetal organs of the crop plants intended for the population and animals nutrition alike.

2.2 Sampling and samples treatment

Prior to the field trip, topographical plans at 1: 25000 scale and the satellite images of the investigated area were studied. The soil samples were taken from agricultural plots cultivated with wheat, where 30x30x30 cm pits were dug in each sampling site (Figs. 2 and 3 - Tulucesti, Figs. 4 and 5 - Sendreni, Figs. 6 and 7 - Vadeni). The samples were taken from the physiological layer 0-30 cm, separated on the sections 0-5 cm and 5-30 cm, as stipulated by Order 756/1997. Together with the soil samples, about 100 wheat plants, not mechanically injured or affected by disease or pests, were randomly harvested on each plot (Fig. 8). It is very important to mention that sampled wheat was harvested at maturity.

Soil sample preparation for analysis consisted in the removal of visible decomposed organic matter, air-drying, grinding and sieving through a 0.125 μm nylon sieve and storage in optimum temperature and humidity conditions in polyethylene bags until the analytic phase of the research (Fig. 9).

Fig. 2. Soil sampling, I-1a/1b site, Tulucesti territory

Fig. 3. Triticum vulgare L. I-1 sampling site, Tulucesti territory

Fig. 4. Soil sampling, II-1a/1b site, Sendreni territory

Fig. 5. Triticum vulgare L. II-1 sampling site, Sendreni territory

Fig. 6. Soil sampling, III-1a/1b site, Vadeni territory

Fig. 7. Triticum vulgare L. III-1 sampling site, Vadeni territory

The plants were decontaminated shortly after they have been collected by quickly washing with tap water and rinsed with distilled water in order to remove any particles that could influence the results of subsequent analyses. After that, they were separated by sections (Fig. 10 a, b, c), air-dried, grounded in a mortar and placed in paper containers (Fig. 9).

Fig. 8. Triticum vulgare L. samples before decontamination procedure

Fig. 9. Plant samples storage

Fig. 10. Triticum vulgare L. leaves and grains: a- Tulucesti samples, b-Sendreni samples, c-Vadeni samples

2.3 Soil and wheat samples analysis

Prior to determining the concentration of microelements in the soil and wheat samples, the elements were extracted by wet digestion, the combination of reagents used for the two types of samples being different, given the specificity of each of them. The digestion procedure was carried out for both soil and plants in two phases: at first the samples were treated with reagents and then the actual extraction of microelements was performed. The used quantities for samples and reagents are shown in Table 1. Soil and plant samples were digested separately using different programs.

Table 1. Quantities of reagents and sample for metals extraction

Type of analyte	Quantity (g)	Reagent
Soil	1	7.5 mL 37% HCl 2.5 mL 69% HNO_3 1 mL 48% HF
Plant (leaves & grains)	0.3	6 mL 69% HNO_3 3 mL 35 % H_2O_2

Table 2. Operating conditions of HR-CS AAS ContrAA 700 Spectrometer for each technique

	Element	**Wavelength (nm)**	**Fuel flow (L/h)**	**Burner height (mm)**	**Flame type**
Flame	Cr	357.8687	100	8	air-acetylene
	Zn	213.8570	50	6	air-acetylene
Graphite furnace	**Element**	**Wavelength (nm)**	**Pyrolysis temperature (ºC)**	**Atomization temperature (ºC)**	**Ramp rate for atomization (ºC/s)**
	Cr	357.8687	1300	2500	1500
	Zn	213.8570	300	1300	1500

The solution was filtered and brought to 50 ml volumetric flask with distilled water. Cr and Zn concentrations were measured by High-Resolution Continuum Source Atomic Absorption Spectrometry (HR-CS AAS), at INPOLDE research center, ReForm platform, “Dunarea de Jos” University of Galati. A ContrAA 700 spectrometer (Analytik Jena, Germany) was employed. Soil samples were analyzed by flame technique, the results being expressed in mg/kg, while vegetal samples were investigated by the graphite furnace techniques, the concentration of microelements being of the order of μg/kg. The device operating conditions for each technique are shown in Table 2.

3. RESULTS AND DISCUSSION

3.1 Microelements concentration in soil and plants

The concentration of Cr and Zn in soil and wheat grains and leaves are reported in Table 3 and Table 4, respectively.

Table 3. Soil contamination level with Cr and Zn (mg/kg)

Element	Tulucesti		Sendreni		Vadeni	
	T-1a (0-5 cm)	T-1b (5-30 cm)	S-1a (0-5 cm)	S-1b (5-30 cm)	V-1a (0-5 cm)	V-1b (5-30 cm)
Cr	**383.10** ± 5.38*	**148.90** ± 1.80	**191.00** ± 5.87	**183.50** ± 2.84	**117.10** ± 1.04	**123.40** ± 2.35
Zn	**136.59** ± 1.23	**122.69** ± 2.25	69.37 ± 2.03	63.31 ± 1.81	73.10 ± 0.36	73.57 ± 0.85

*values that exceed the maximum admissible limits stipulated by Romanian legislation [12] (30 mg/kg for Cr and 100 mg/kg for Zn)

The results revealed high concentration of Cr for all investigated soils (Fig. 11), exceeding about 13 times the maximum values accepted (MVA) by legislation for normal levels, even for the Tulucesti reference area, which makes us assuming that the Iron and Steel Works of Galati activity is not the main factor that might cause these high concentrations, but also the use of fertilizers, pesticides or even the geological abundance of the area. These issues will be clarified through future studies. In terms of Zn soil supply, it exceed the limits admitted only for samples taken from the reference area (Fig. 12), values that are attributed to fertilizers or pesticides. The Zn concentrations recorded for Tulucesti area exceed the Romania average value (87 mg/kg) reported by [13], while for the other samples the results are below this value. In [14] it is reported an average value of Cr concentration in the world's top soil of 59.5 mg/kg and for Zn of 70 mg/kg. At the same time, the concentrations of both elements exceed the values of the European median and the world median mentioned by [15] and [16].

In relation to the results reported by [15-17] for various samples taken from agricultural soils adjacent to different industrial areas in Romania, which exceed the normal reference values but are below the alert threshold for sensitive (agricultural) use, the concentrations of Cr in the soil samples investigated by us are higher. All Cr levels are above the alert threshold for sensitive use (100 mg /kg [12]), except the T-1a sample where the level of Cr exceeds the intervention threshold for agricultural use (300 mg /kg [12]).

The content of Zn shows similar values of those obtained by [17] near the steel industry of Galati (Sendreni-Vadeni area). The samples taken from Tulucesti territory show values between the normal levels (100 mg/kg [12]) and the alert threshold for sensitive use (300 mg/kg [12]).

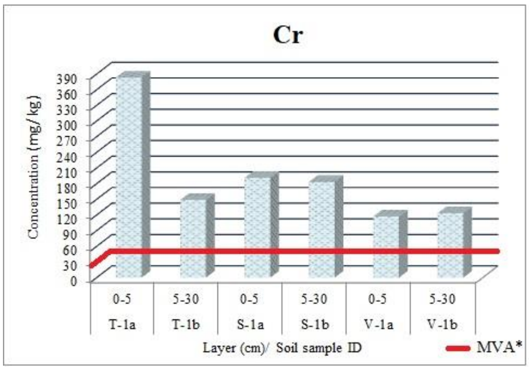

Fig. 11. Cr concentration in soil

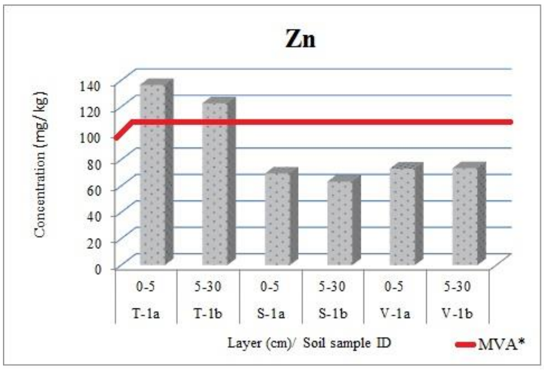

Fig. 12. Zn concentration in soil

Table 4. Wheat grains and leaves Cr and Zn concentration

Element	Tulucesti	Sendreni	Vadeni

(µg/kg)	WL-T	WG-T	WL-S	WG-S	WL-V	WG-V
Cr	769.27 ± 75.39	785.51 ± 54.20	3592.32 ± 134.67	402.41 ± 17.71	1921.91 ± 67.27	632.11 ± 17.70
Zn	78696.00 ± 1.34	81906.00 ± 0.49	53286.00 ± 2.08	60116.00 ± 1.98	44236.00 ± 0.44	64076.00 ± 0.90

Cr concentration records values from 769.27 µg/kg to 3592.32 µg/kg for wheat leaves and from 402.41 µg/kg to 785.51 µg/kg for wheat grains (Figure 13). Zn levels are highlighted by values from 44236.00 µg/kg to 78696.00 µg/kg for wheat leaves and from 60116.00 µg/kg to 81906.00 µg/kg for wheat grains (Figure 14). Analyzed grains show low concentrations of Cr and Zn, which are below the safety limit provided by [8,18] (2.3 mg/kg for Cr and 99.4 mg/kg for Zn). Although the concentration of Zn in edible parts of wheat is much higher than that of Cr, this has no negative impact on wheat, as the concentrations do not exceed 150-500 mg/kg, values which are considered critical for plants [4,19].

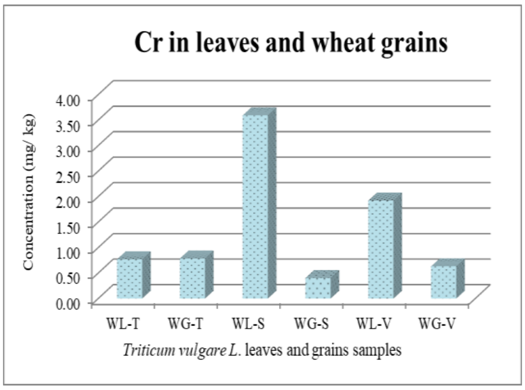

Fig. 13. Cr level in leaves and wheat grains

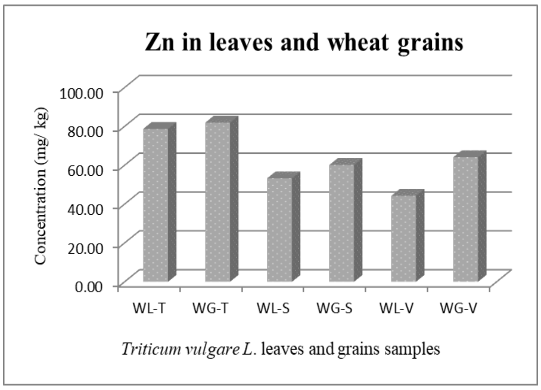

Fig. 14. Zn level in leaves and wheat grains

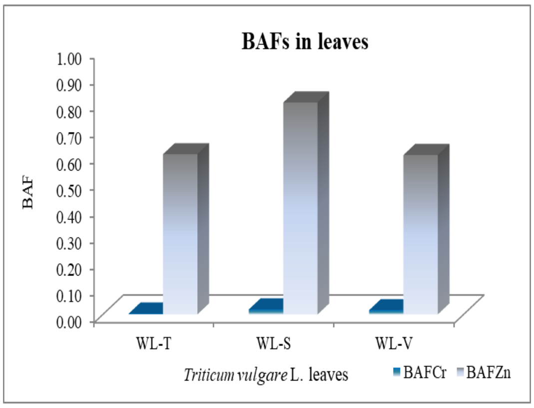

Fig. 15. Bioaccumulation factors (BAFs) of Cr and Zn in Triticum vulgare L. leaves

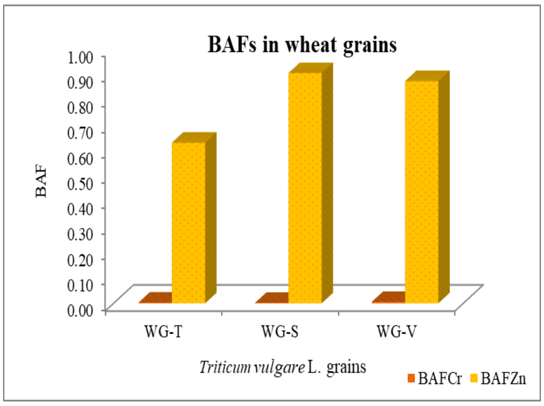

Fig. 16. Bioaccumulation factors (BAFs) of Cr and Zn in Triticum vulgare L. grains

3.2 Cr and Zn bioaccumulation in wheat leaves and grains

The bioaccumulation factor expresses the accumulation rate of an element from one of the environment's components (water, air, soil, etc.) to vegetative compartments of plants. As it can be seen from Figs. 15 and 16, the bioaccumulation factors (BAFs), both for Cr and Zn, do not exceed the value 1, which means that wheat did not accumulate these elements in excess, under this climate and given soil conditions. Another observation is that wheat accumulates more Zn than Cr, both in leaf (Fig. 15) and grain (Fig. 16).

4. CONCLUSIONS

The main purpose of this study was to investigate Cr and Zn levels in soil and cultivated wheat. The results obtained by High-Resolution Continuum Source Atomic Absorption Spectrometry revealed that in soil the concentrations of the above mentioned elements exceed the limit imposed by the regulations. For wheat leaf and grain samples there were no results that would pose a potential contamination through the food chain. However, careful monitoring of all components of the environment and better soil management is required, so that crop plants will not be contaminated in the future according to the soil-plant transfer relationship, especially because crop rotation is routinely conducted annually, and the level of bioaccumulation of toxic or potentially toxic elements is species-dependent.

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