Biblid: 1821-4487 (2013) 17; 1; p 43-46
UDK: 591.145:658.2

Original Scientific Paper
Originalni naučni rad

TOXIC AND ESSENTIAL ELEMENTS IN AGRICULTURAL SOIL AND WHEAT
TOKSIČNI I ESENCIJALNI ELEMENTI U POLJOPRIVREDNOM ZEMLJIŠTU I PŠENICI

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ABSTRACT

The research was conducted with the aim of examining the presence of toxic elements (Pb, Cd, As and Hg) and essential elements (Zn, Cu, Fe i Mn) ions in selected agricultural soil and wheat samples by ICP mass spectrometry. An overall toxic element index was calculated by taking into account each element assay, which contributed with the same weight into final result.Correlation between toxic microelements contents in soil and wheat was monitored. Correlation analysis, ANOVA and F-test were applied for statistical evaluation of obtained results. The calculated mean and median levels of contamination were compared with the recommended or regulated maximum levels according to the European Commission and the national legislation.

***Key words**: microelements, land, wheat, ICP mass spectrometry.*

REZIME

Istraživanje je sprovedeno sa ciljem ispitivanja prisustva toksičnih elemenata (Pb, Cd, As i Hg) kao i esencijalnih elemenata (Zn, Cu, Fe i Mn) na odabranim uzorcima poljoprivrednog zemljišta i pšenice primenom ICP masene spektrometrije. Praćena je korelacija između sadržaja toksičnih mikroelemenata u zemljištu i pšenici. Analiza korelacije, ANOVA i F- test upotrebljeni su za statističku evaluaciju dobijenih rezultata. Izračunate srednje vrednosti nivoa zagađenja su upoređene sa maksimalno preporučenim ili propisanim koncentracijama prema pravilniku Evropske komisije i nacionalnom pravilniku.

***Ključne reči**: mikroelementi, zemljište, pšenica, ICP masena spektrometrija.*

INTRODUCTION

In the period when toxic elements entered the soil from natural sources, their importance was not much considered. However, with the development of industry and increased use of chemicals in agriculture the problem of toxic elements presence in soil-plant-humans continuum has become more frequent.

The land of Banat and Bačka is an exceptional farming area from the point of view of its natural potential, so monitoring of the land quality is required in order to preserve this natural treasure, i.e. production of healthy food and obtaining high and stable yield.

Wheat is one of the most important and most commonly grown cereals in the world. The importance of wheat is stressed by the fact that it occupies the largest areas in the world agricultural production. Wheat grain contains vitamins, mineral matters and fibres as wll as greater quantity of proteins than other cereals, so as a result, wheat and wheat-based products are recommended for daily consumption.

Wheat grains transport significant quantities of impurities due to the specific anatomical structure of atoms which enables concentration of pollutants originating from various sources on their surface; thus, in the last few decades, wheat-based products have received considerable attention in view of their potential role in transporting of microelements into the human diet *(Škrbić et al., 2007)*.

Therefore, there is international concern about human intake of microelements. There are three groups of mineral elements interesting to food technologists and scientists and nutritionists *(Carbonell-Barrachina et al., 2002)*: those essential in the diets of humans (Cu, Ca, Fe, Mg,etc.); those essential to one or more species and plants but not currently known to be essential for humans (As, Cd, Ni, etc.); and those known only for their toxicity or therapeutic use (Al, Ba, Hg).

According to the current Regulation on the quantities of pesticide, metals, metalloids and other toxic substances, drugs, anabolic and other substances that could be present in foodstuffs *(Serbian Regulations, 1992)* the maximum allowed Pb, Cd, Hg and As concentrations in wheat are 0.4; 0.1; 0.05 and 1 mg/kg of dry matter respectively. The maximum allowed concentrations of some elements in soil according to the Regulation on the maximum levels of dangerous and harmful substances found in soil and irrigation water and methods of their testing *(Serbian Regulations, 1994)* are shown in Table 1.

Table 1. The maximum allowed concentrations of some elements in soil

Elements	MAC in soil mg/kg of soil
Cadmium	3
Lead	100
Mercury	2
Arsenic	25
Copper	100
Zinc	300

Overviews of toxic microelements content in wheat grain and agricultural land have been published in many countries *(Lin Jai et al., 2010, Hussain et al., 2011, Škrbić et al. 2007, Ayari et al., 2010)*. Monitoring and determination of microelements content in wheat and in land are extremely important for evaluation and prevention of contamination with these elements. The objective of this research is to test the presence of toxic elements (Pb, Cd, As and Hg) and essential elements (Zn, Cu, Fe i Mn) ions in selected agricultural land parcels and wheat in Banat and Bačka and to study correlations between elements content in land and wheat. In order to enable more comprehensive comparison between investigated samples toxic elements index (TEI) and essential microelements index (EMI), assigning equal weight to all

TEIs and EMIs assays applied has been introduced. Correlation analysis, ANOVA and F-test were applied to show relations between applied assays.

MATERIAL AND METOD

Material

An average land sample was taken from ten selected parcels, in Banat Perlez, Elemir, Melenci, Kumane, Novi Bečej, Kikinda, Banatski Monoštor, Čoka) and Bačka (Senta, Tornjoš), where wheat will be grown. The average land sample consists of 20-25 individual land samples which are mixed up to obtain an average sample. Individual samples were taken with a spade to an approximate depth of 0-30 cm. Three samples were taken from each parcel right next to a busy road. The wheat was harvested from every parcel. The total of 30 samples of land and 30 samples of wheat were analyzed.

Preparation and analysis of samples

The land samples were prepared in accordance with the EPA METHOD 3051A- Microwave assisted acid digestion of sediments, sludges, soil and oils while determination was performed in accordance with EPA 6020A: 2007 Inductively coupled plasma- mass spectrometry. Pb, Cd, Hg, As, Zn, Cu, Fe and Mn in land were determined by weighing 0.5 g of sample using analytical balance, then 9 ml $_{cc}$ HNO_3 and 3 ml HCl were added and finally digestion was performed in Multiwave 3000 (Anton Paar). After digestion the destroyed sample was quantitatively transferred into a 50 ml normal flask, 50μl of internal standard Rh of 10 mg/l concentration were added and the container was filled with ultra-clean water up to the graduation line. The content of elements was determined by ICP mass spectrometry (Elan 9000, DRC-e).

The wheat samples were prepared in accordance with the BS EN 15763: 2009 Foodstuffs- Determination of arsenic, cadmium, mercury and lead in foodstuffs by inductively coupled plasma mass spectrometry (ICP-MS) after pressure digestion in the following way: prior to weighing on the analytical balance the wheat samples were ground in the water-cooled mill (1095KNIFTEC Sample Mill) and homogenized. 7 ml $_{cc}$ HNO_3 were then added into the weighed sample (0.5 g) and then digestion was performed in Multiwave 3000 (Anton Paar). After digestion the destroyed sample was quantitatively transferred into a 50 ml normal flask, 50μl of internal standard Rh of 10 mg/l concentration were added and the container was filled with ultra-clean water up to the graduation line. The content of elements was determined by ICP mass spectrometry (Nexion 300 X, Perkin Elmer).

Toxic elements index (TEI) and essential microelements index (EMI)

Central tendency is the most widely used to compare the toxic elements and essential microelements content of complex samples determined using multiple assays, where samples are ranked based on the mean value and standard deviation of the assays used. Since the units and the scale of the data from various assays are different, the data in each data set should be transformed into standard scores, dimensionless quantity derived by subtracting the mean from the raw data divided by the standard deviation, according to following equation (for both TEI and EMI):

$$\text{Standard score} = (x - \mu)/\sigma \quad (1)$$

where x represents the raw data, μ the mean, and σ the standard deviation. The standard scores of a sample for different assays when averaged give a single unitless value termed as: toxic elements index (TEI), for toxic elements (Pb, Cd, As and Hg) and essential microelements index (EMI), for essential elements (Zn, Cu, Fe i Mn), which is a specific combination of data from different chemical assays with no unit limitation and no variance among methods.

Statistical analysis

All experiments were performed with 8 repetitions. Descriptive statistical analyses for calculating the means and the standard error of the mean were performed using StatSoft Statistica 10 software. All obtained results were expressed as the mean ± standard deviation (SD). The evaluation of correlation matrix, one-way analysis of variance (ANOVA), and F-test of obtained results were performed using StatSoft Statistica 10 software.

RESULTS AND DISCUSSION

The one-way ANOVA test has been calculated for toxic elements and essential microelements content in wheat kernel, accompanied by the F-test. According to F-test comparison between effects, Mn content (F=3000.6) has been found to be the more influential variable than Zn (F=2773.4) or Fe (F=1609.0), significant at $p<0.01$ level, 95% confidence limit. Table 2 shows the discriptive statistics concerning both toxic elements and essential microelements data of wheat kernel for different distances from the main road. Maximum allowed concentration proscribed by the European Commission (1997) are 0.2 mg/kg Cd in wheat grain, 0.1-0.2 mg/kg Pb in cereals, while Hg and As must not be present in food. If maximum concentrations of lead in wheat grain (Table 2) are compared to the values prescribed in Codex Standard 193-1995, it is obvious that the content of lead is increased in samples taken from land next to a road According to *Ludajić and Filipović (2009)* the Cd ion content in samples of wheat grown in Central Banat in the period 2003-2007 was 0,065 mg/kg. The obtained values of Cd ion content (Table 2) indicate that more intensive application of phosphorous fertilizers and manure is necessary. The content of biogenic elements in grain was between usual upper and lower limits. For instance, maximum allowed Cu and Zn contents in wheat in Bulgaria *(Bojinova et al., 1996)* are 10 and 40 mg/kg of dry matter respectively, while they have not been defined in our regulations yet. Somewhat increased Zn content in wheat (Kikinda) is probably a result of its presence in soil near Metal Foundry " Kikinda" and of sedimentation of this metal in the air since zinc is used as an additive in lubricants so it may come from the traffic.

Table 2. Discriptive statistics data for toxic element and essential microelements content (mg/kg) in wheat grain at different distances from the road

Name	Distance	Toxic elements				Essential microelements			
		Pb	Cd	Hg	As	Zn	Cu	Fe	Mn
mean	0m	0.169	0.116	0.007	0.019	20.532	3.221	36.558	52.992
	100m	0.142	0.113	0.007	0.017	22.193	2.990	34.963	47.996
	200m	0.118	0.112	0.008	0.013	20.795	2.992	35.771	51.607
SD	0m	0.045	0.006	0.002	0.011	4.357	0.603	4.942	6.114
	100m	0.039	0.004	0.002	0.010	10.032	0.838	7.621	12.511
	200m	0.004	0.003	0.003	0.003	4.631	0.520	6.631	7.694
min	0m	0.112	0.103	0.003	0.012	12.083	2.269	29.913	44.081
	100m	0.116	0.108	0.003	0.011	12.198	1.794	27.170	30.639
	200m	0.114	0.108	0.003	0.009	14.720	2.166	25.416	40.225
max	0m	0.225	0.128	0.009	0.048	26.128	4.035	46.821	63.274
	100m	0.220	0.118	0.009	0.043	48.528	4.741	51.524	69.823
	200m	0.125	0.118	0.012	0.018	28.145	3.775	49.840	65.248

ANOVA has been calculated for toxic element and essential microelements content in soil. According to F-test comparison between effects, Mn content (F=78640.0) has been found to be the more influential variable for than Zn (F=2885.4) or Fe (F=2699.02), significant at $p<0.01$ level, 95% confidence limit. These results were expected, because Mn content span the greater range of values, i. e. shows the greatest variation between different observations. TEI and EMI score results, calculated using Eqn. (1), for wheat kernel at different distance from the main road is presented on Fig. 1. Positive scores on Fig. 1 show increased toxic element and essential microelements content, and these values belong to larger towns.

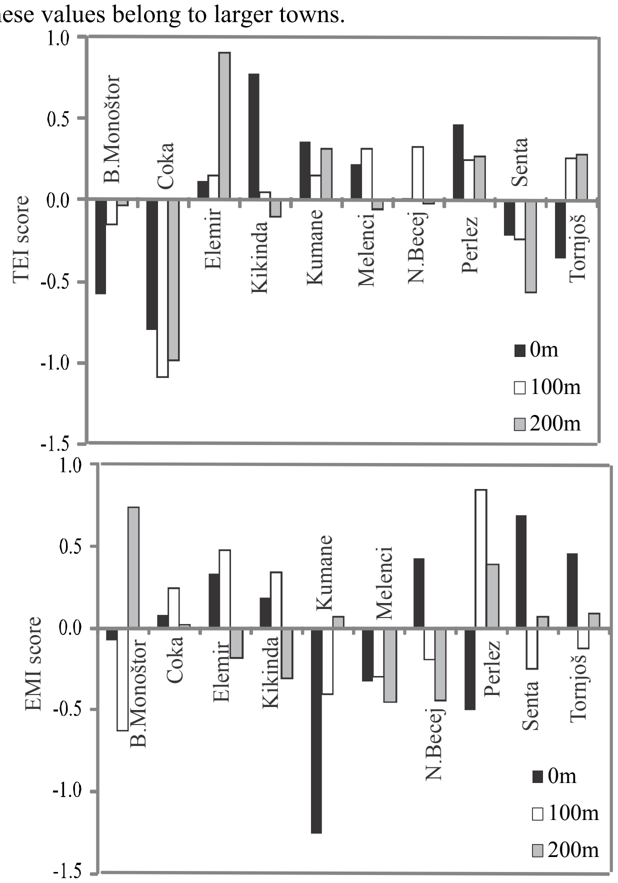

Fig. 1. TEI and EMI score results for wheat kernel at different distance from the main road

ANOVA has been also calculated, together with F-test for toxic element and essential microelements content in soil. According to F-test comparison between effects, Mn content (F=78640.0) has been found to be the more influential variable for final result, then Zn (F=2885.4) or Fe (F=2699.02), significant at $p<0.01$ level, 95% confidence limit.

TEI and EMI score results, calculated using Eqn. (1), for soil is presented on Fig. 2. Positive scores on Fig. 2 show increased toxic element and essential microelements content, and these values belong to denser populated areas.

Table 3. Discriptive statistics data for toxic element and essential microelements content (mg/kg) in soil

Name	Toxic elements				Essential microelements			
	Pb	Cd	Hg	As	Zn	Cu	Fe	Mn
mean	17.398	0.164	0.012	10.696	58.574	21.795	24214.038	592.396
SD	3.397	0.015	0.001	1.712	13.859	4.740	3860.615	86.653
min	11.205	0.131	0.011	7.036	37.570	13.936	18088.250	417.825
max	22.205	0.180	0.016	13.043	80.333	31.603	31584.750	748.450

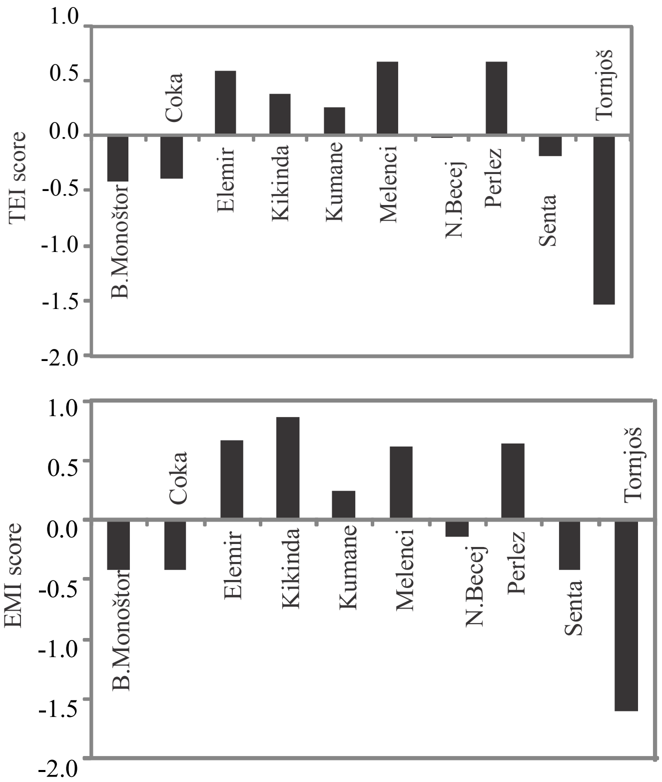

Fig. 2. TEI and EMI score results for soil

The data in Table 4 show a correlation between toxic element and essential microelements assays in soil and wheat grain samples, distanced 0, 100 and 200 m, from the main road. These data showed that Pb, and Hg, as well as Zn content content in wheat kernel are independent from these metal content in soil. Cd content on 0 m is influenced of Cd content in soil at $p<0.05$ significant level, and at $p<0.10$ statistically significant level on 200 m from the main road.

The data show a correlation of Cd content in wheat grain in relation to its content in soil which indicates that wheat adopts Cd from the soil. Cd enters agricultural land via applied phosphorus fertilizers.

Table 4. Pearson's correlation coefficients between toxic element and essential microelements assays in soil and wheat grain samples (0; 100 and 200 m from the road), with statistical significance expressed as p-level values, written in small parentheses

Distance	Toxic elements				Essential microelements			
	Pb	Cd	Hg	As	Zn	Cu	Fe	Mn
0 m	0.432	0.655*	0.267	-0.075	-0.526	0.019	-0.117	0.259
	(0.212)	(0.040)	(0.456)	(0.837)	(0.119)	(0.958)	(0.748)	(0.470)
100 m	-0.077	0.112	0.071	-0.151	0.478	-0.745*	0.633*	0.726*
	(0.833)	(0.758)	(0.845)	(0.677)	(0.162)	(0.014)	(0.049)	(0.017)
200 m	-0.299	0.629**	-0.084	-0.661*	-0.394	-0.254	-0.391	0.242
	(0.402)	(0.051)	(0.817)	(0.037)	(0.259)	(0.479)	(0.264)	(0.501)

* Significant at $p<0.05$ level, ** Significant at $p<0.10$ level,

CONCLUSION

Based on the results of the analysis of toxic element and essential microelements in wheat and land, it could be concluded that:

- ANOVA test and F-test for Mn content (F=3000.6) showed a more influential variable in comparison with other elements, meaning that samples taken in different locations differ significantly due to Mn influence. As for Fe and Zn, F is 1609.0 and 2773.4 respectively. These findings confirm that Mn, Fe and Zn assays are more accurate compared to other applied assays. According to ANOVA and F-test at $p<0.01$ level, 95% confidence limit used for elements content analysis in soil, it was found that Mn content (F=78640.0) was a more influential variable for final result, followed by Zn (F=2885.4) or Fe (F=2699.02).

- Pearson table shows correlation between chemical elements in wheat grain compared to the content of analyzed elements in soil. It was found that there is correlation between Cd content in wheat and soil, which indicates that this element entered the wheat via the soil.

- A regular quality control of wheat in different agro-ecological conditions is necessary. It will provide production of healthy and safe foodstuffs and prevent the presence of toxic elements in the food chain.

- Healthy foodstuffs can be produced in this land with high and stable yield provided that controlled and rational agricultural technique is used.

ACKNOWLEDGEMENT: These results are part of the project supported by the Ministry of Education and Science of the Republic of Serbia, TR 31055 and TR 46005.

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Received: 22.02.2013. Accepted: 01.04.2013.