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EFFECT OF FERTILIZERS ON HEAVY METAL RESIDUES IN AGRICULTURAL SOILS

UTICAJ ĐUBRIVA NA SADRŽAJ TEŠKIH METALA U POLJOPRIVREDNOM ZEMLJIŠTU

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Abstract: *The use of fertilizers is an integral part of agricultural production nowadays, as it has beneficial effects on the yield of agricultural products and the functioning of the agricultural sector. Nevertheless, their unregulated use can lead to serious harmful effects on the environment and human health. The aim of this research is to measure the residual amounts of selected elements in agricultural soils, aggregated due to the use of fertilizers during the vegetation season and to predict the potential for contamination of agricultural soils. The applied dose of fertilizers has resulted in the accumulation of heavy metals in the soil, but their quantities were within the allowed threshold values.*

Key words: *fertilizers, heavy metals, residues, contamination, soil*

Apstrakt: *Primena đubriva je u današnje vreme sastavni deo proizvodnje jer unapređuje poljoprivredni sektor i prinos gajenih biljaka. Međutim, njihova nekontrolisana primena može dovesti do ozbiljnih štetnih efekata na životnu sredinu i zdravlje ljudi. Cilj ovog istraživanja je bio da se izmere zaostale količine pojedinih elemenata u zemljištu usled primene đubriva tokom vegetacije useva i da se na osnovu toga predvidi mogućnost zagađenja poljoprivrednog zemljišta. Primenjena doza đubriva je uticala na akumulaciju metala u zemljištu i njihov sadržaj je bio u graničnim vrednostima.*

Ključne reči: *đubriva, teški metali, ostaci, kontaminacija, zemljište*

1. INTRODUCTION

Good agricultural practices nowadays imply an integral approach to growing crops, an increased use of nonchemical measures and the production of healthy and safe food, with no harmful effects on human and animal health and the environment. The main goal of every agricultural production is to ensure the highest yields and economic benefits. Benefits and downsides of conventional agricultural production have been analyzed for a decade now, leading agricultural production towards a more organic approach to food production. Nevertheless, organic production is not always

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a source of the best quality food. The fact is that food produced in this way is safer, as it contains less nitrates and pesticides. On the other hand, organically produced food also contains lower amounts of proteins, and its higher amount of minerals and vitamins does not give it an advantage over conventionally produced food [1-2]. An advantage of these organically produced products is certainly a higher content of secondary metabolites forming part of the defense mechanisms of plants, animals, and humans [2]. Due to the conflicting facts, practical results, and analysis, in this case it is often debatable whether the goal justifies the cause?

One of the aspects of successful production is also the application of fertilizers. Although their application strengthens the agricultural sector, their effects should not be seen only through the prism of increased crop yields, as their effects on the environment and human health should also be considered. In the times of climate change, analyses have shown that commercial fertilizers increase CO_2 emissions, global warming, soil contamination, and the contamination and eutrophication of surface and groundwaters [3-4]. Also, a study [5] has shown that a reduced use of fertilizers would lower the emission of harmful gases by 20%. In general, an inadequate application of fertilizers affects the agricultural soils directly, and climate change, human, livestock, and game health indirectly. Furthermore, research has shown that plants absorb only about 50% from nitrogen-based fertilizers, while the remaining amount goes into groundwaters or the atmosphere in the form of N_2O gas [6-7]. An uncontrolled use of nitrogen and phosphorus-based fertilizers is especially harmful, as it leads to anion build up in the soil [8]. Also, high concentrations of nitrates in tap water can lead to cancer development, while resulting in lower concentrations of oxygen in the rivers and increased concentrations of salt in the ground, thus increasing alkalization of agricultural soils. Nevertheless, despite all of the above, agricultural production is unimaginable without fertilizers. [9] have done research in Germany which has shown that a reduced application of nitrogen fertilizers reduces wheat yields by up to 50%, the producers' revenues by up to 40%, while the wheat price increased (up to 5%), as did the investments in the production (by about 12%). Fertilizers contain macro and micro elements essential for the crop. However, their on presence content in the environment and food, due to their uncontrolled application, can reach toxic levels. Each state has defined limits on the maximum allowable concentrations of these elements in food, water, soil, and air.

The aim of this research was to measure the amounts of nickel, zinc, and manganese that remain in the soils after the application of fertilizers during the vegetation season, and to predict the potential for contamination of agricultural soils based on this.

2. MATERIAL AND METHODS

Trials were conducted in 2021 in laboratory conditions. Residues of chemical elements in the soil were tested after the application of synthetic fertilizers. Fertilizers were applied at quantities of 1.5 ml/100 ml of water (with 3 l/ha as the recommended dose) 25 days after plant emergence. Seeds were planted in 1 L volume pots in the following treatment combinations: monocultures - *Avena fatua* (AV), *Abutilon teophrasti* (AB), wheat (PŠ) and corn (KK) and their combinations KK *vs.* AB, KK *vs.* AV, AB *vs.* AV, PŠ *vs.* AV, PŠ *vs.* AB. Plants (pots) were watered when needed and kept in controlled conditions: light/dark 12/12 h, T = 25/22 ºC. Analysis of heavy metal contents were done 20 days after removing the plants, following the Meeting the Challenges of Soil Analysis with the Avio 200 ICP-OES methodology (Author: Nick Spivey PerkinElmer, Inc. Shelton, CT). From each pot (treatment) 1 g of finely ground soil was extracted (in three replicates). Soil degradation was done using 20 ml of concentrated nitric acid for 1 hour at 80°C, after which 5 ml of hydrogen-peroxide were added and the sample was heated for 30 min at 60-70°C, resoaked in 5 ml of hydrochloric acid and heated for 1 h. After cooling, distilled water was added up to 100 ml of volume and the filtered content was used in the analysis of heavy metal contents. The calibration curve was obtained from the mixture of heavy metals and microelements. Adequately diluted working solutions were on prepared (in the range of 0.05 mg/kg to 2 mg/kg) based on which the calibration curves were produced. The content of heavy metals and microelements in the soil samples are given in mg/kg of the soil. All the results were compared by analysis of variance (LSD test) and t-test of independent samples.

3. RESULTS AND DISCUSSION

The presence of metals in the soil in quantities higher than the allowed represents a potential environmental risk, with possible harmful effects on human and animal health. Heavy metals can reach the soil, and consequently the food chain, through the application of different fertilizers, industry, traffic, and pesticide use. Microelements from fertilizers are often a source of heavy metals and their uncontrolled use or facilitates their deposition. In the instances when their concentration is high, plants can absorb large amounts of these compounds, which reach human and animal organisms through the food chain. [10] state that accumulated quantities of these metals are often not toxic for plants, even though they can be for people and animals (e.g. cadmium). This study has shown that applied fertilizers have resulted in higher quantities of copper, zinc, nickel, and molybdenum in the soil (with the exception of nickel after the application of F3 fertilizers). Average values of heavy metal and microelement content in soil samples following the application of fertilizers are shown in Table 1, with results of statistical analysis given in Table 3.
Based on the analysis of average content of tested elements the following was shown: 1) when grown in monoculture, zinc was present in all samples following the application of both tested fertilizers, copper was also present in all samples (except for KK) after the application of both fertilizers, while manganese was detected only in PŠ after the application of F2 fertilizer and 2) when grown in combination treatments: zinc was detected in all samples, except in the KK *vs* AB combination after the application of F3 fertilizer, copper was present in KK *vs* AV and PŠ *vs* AV combinations after the application of F3 fertilizer, nickel in KK *vs* AV and PŠ *vs* AV combinations after the application of F2 fertilizer and in KK *vs* AB, AV *vs* AB, and AV *vs* PŠ combinations after the application of F3 fertilizer, while manganese was registered in AB *vs* AV and PŠ *vs* AV combinations after the application of F3 fertilizer (Table 1). No consistency in the deposition of certain metals in the soil was observed depending on the plant species, which leads us to conclude that the tested fertilizers (Table 2) are the source of the detected elements.

Table 1. Average values of heavy metal and microelement content (mg/kg soil) in soil samples

plants	fertilizer	Nickel	Copper	Zinc	Manganese
soil	control	0.099	17.498	9.843	59.356
KK	F2	≤	≤	10.835	≤
KK	F3	48.530	≤	20.628	≤
PŠ	F2	≤	23.228	28.212	62.406
PŠ	F3	0.993	24.133	29.695	≤
AV	F2	≤	19.796	20.596	≤
AV	F3	2.495	22.359	25.354	≤
AB	F2	1.832	18.635	24.052	≤
AB	F3	3.283	27.159	29.745	≤
KK vs AV	F2	3.479	24.749	38.962	≤
KK vs AV	F3	≤	≤	13.300	≤
KK vs AB	F2	≤	≤	12.987	≤
KK vs AB	F3	2.098	≤	≤	≤
AB vs AV	F2	≤	≤	19.503	≤
AB vs AV	F3	6.640	21.705	28.543	64.717
PŠ vs AV	F2	9.728	20.846	26.405	≤
PŠ vs AV	F3	12.896	25.692	29.791	62.881

KK-corn, AV-*Avena fatua*, AB-*Abutilon teophrasti*, PŠ-wheat, ≤ - lower of equal to the amount in the control (with no plants or fertilizers applied) soil sample.

All the detected quantities were below the threshold of the maximum allowable concentrations (MAC). From the aspect of safe food production these tests have shown that the application of fertilizers in recommended doses is safe, although a potential environmental risk is always present.

Table 2. Macro and micro elements in the tested fertilizers (based on the product declaration)

	F2	F3
Polyphenolic (hydroxy) acids	-	-
Nitrogen	0,2%	16-24 %
Phosphorus	0,4%	12 %
Potassium	0,02%	36 %
Iron	220 mg/l	0,01-0,04 %
Magnesium	550 mg/l	1,9 %
Zinc	49 mg/l	0,01-0,02 %
Copper	35 mg/l	0,009-0,01 %
Boron, Calcium, Molybdenum, Cobalt, Nickel	10 mg/l	-
Boron	-	0,02 %
Calcium	-	14 %
Molybdenum	-	0,001-0,002 %
Manganese	54 mg/l	0,009-0,03 %

Statistical data analysis has shown that the differences between treatments were statistically significant for: the zinc content in all the samples compared to the control (except for KK *vs* AB), copper content in all the samples from the monoculture treatments after the application of both fertilizers and after the application of the F2 fertilizer in KK *vs* AV and PŠ *vs* AV combinations and the F3 fertilizer in AB *vs* AV and PŠ *vs* AV combination treatments, nickel content in KK *vs* AV and PŠ *vs* AV combination treatments after the application of the F2 fertilizer and in KK *vs* AB and AB *vs* AV combinations after the application of the F3 fertilizer, and manganese content only after the application of the F3 fertilizer in AV *vs* PŠ and AV *vs* AB combination treatments (Table 3).

Table 3. Statistical analysis of the heavy metal contents (mg/kg soil) and microelements in the samples of soil treated by fertilizers compared to the control (LSD test)

K *vs* sample	fertilizer	Ni	Cu	Zn	Mn
KK	F2	-	-	**	-
KK	F3	**	-	**	-
PŠ	F2	-	**	**	**
PŠ	F3	**	**	**	-
AV	F2	-	**	**	-
AV	F3	**	**	**	-
AB	F2	**	**	**	-
AB	F3	**	**	**	
KK vs AV	F2	**	**	**	-
KK vs AV	F3	-	-	**	-
KK vs AB	F2	-	-	**	-
KK vs AB	F3	**	-	-	-
AB vs AV	F2	-	-	**	-
AB vs AV	F3	**	**	**	**
PŠ vs AV	F2	**	**	**	-
PŠ vs AV	F3	-	**	**	**

K - control, p<0,01**, KK - corn, PŠ - wheat, AB - *Abutilon theophrasti*, AV - *Avena fatua*, Zn - zinc, Ni - nickel, Mn - manganese, Cu - copper

It is well known that some weed species can accumulate certain chemical elements and serve as bioaccumulators to improve the environment. [11] analyzed plant material of the weed species *Abutilon theophrasti* grown on contaminated soils (lead 1004.3 mg/kg, copper 711.5 mg/kg and zinc 1234.2 mg/kg) and detected the following amounts of lead 38.7 mg/kg, copper 32.5 mg/kg and zinc

56.1 mg/kg. [12] determined hyperaccumulation of lead by the weed species *Avena fatua*. Hyperaccumulation as a phytoremediation method can be very useful, but when this accumulation happens in plants intended for dietary consumption, it can present a significant health risk. The trials have shown that wheat plants are capable of easily absorbing zinc, nickel, and copper, while the absorption of lead and chromium is more difficult [13]. The rhizosphere of corn was also detected to contain numerous macro and micro elements: copper 16.34 mg/kg soil, 6.997 mg/kg lead, 0.19 mg/kg cadmium, and 69.77 mg/kg zinc, while at the end of the vegetation season corn seeds contain 0.341 mg/kg mass of lead and 0.342 mg/kg mass of zinc. Similar was detected by [14]. These studies indicate a risk for human health [15]. Consequently, it is very important to create a balance when applying fertilizers on the fields in order to maintain a healthy and clean environment. This confirms the fact that the application of fertilizers must be done only after conducting an analysis of the soil quality.

4. CONCLUSION

The applied dose of fertilizers has resulted in the accumulation of heavy metals in the soil and their contents were within the acceptable limits. In order to avoid the harmful effects of fertilizers and their pollutants, it is necessary to select for hybrids/varieties which are characterized by a highly efficient use of the available nutrients. Also, studies should focus on the development of fertilizers containing minimal amounts of contaminants, highlighting the need for the application of organic fertilizers and optimizing fertilizer doses for specific crops, ensuring minimal losses. Contamination of soils and water by fertilizers can also be reduced to a minimum by applying different control measures, such as phytoremediation, wastewater treatment, raising awareness, and developing appropriate national legislation.

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