THE EFFECT OF SOIL SELENIUM FERTILIZATION TREATMENT ON THE CONTENT OF SOME IONS (Cd, Fe, Zn and Se) AND YIELD OF TWO CORN HYBRIDS

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ABSTRACT

The concentration and form of some metals and metalloids in soil is governed by many chemical and physical properties of soil as pH, redox, Fe, Al ions and soil composition. The paper studied presents influence of chemical soil properties, environment conditions and selenium fertilization rate applied on ions status of zinc, cadmium, selenium and iron in soil and plant material, as well as specific adsorption of these ions in two different maize hybrids. The study was conducted at the farm Vita-Vi Višići (Čapljina). The experiment design was a completely randomized design with two hybrids, four different fertilization treatments in four replications. The experimental area was implemented standard agricultural management practices of preparation, tillage, fertilization, application of protective agents. Hybrid NP Pako is selected in order to achieve a high yield, and M34 hybrid for quality yield. The test results and statistical analysis revealed no significant difference in the yield of hybrids combined with different fertilization treatments. Accumulation of selenium, zinc, cadmium and iron in upper ground plant part of maize was not affected by fertilization treatments or selected hybrid. The highest yield was achieved by hybrid M34 Pioneer of 37.6 t $ha^{-1}$and the highest yield was obtained in application of third fertilization treatment 20 kg $NaSeO_4ha^{-1}$, but without statistically significant differences comparing to other hybrid or applied treatments. The highest content of selenium in the plant was found in hybrid NP PAKO 0.06 mg Se kg^{-1} of dry matter of maize applying the fourth liquid fertilization treatment (20 kg $Na_2SeO_4ha^{-1}$) but also without statistically significant difference comparing to other hybrid or fertilization treatment. Content of zinc, cadmium and iron in soil or plant material had not shown significant differences due to the applied fertilization or used maize hybrids, but some fluctuations were observed. Selenium

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fertilization did not have a limiting effect on the formation of the yield and tested elements, but its mobility and availability in soil and plant depends also on other factors as soil properties and climatic conditions of growing season.

Keywords: *selenium fertilization, maize hybrid, metals, metalloids, soil properties*

INTRODUCTION

In the past decades, European crop production including the southeastern European (SEE) countries has largely focused on securing food and feed production and maximizing yield in terms of biomass production per hectare. To meet the growing food demand due to ever increasing population, food policy was focused toward the consumption of food rich in calories and proteins. The consumption of food rich in micronutrients (minerals, vitamins, secondary metabolites) hasn't increased proportionally. Today 40% of the world population suffers from micronutrient deficiencies. Also on other hand soil pollution by heavy metals has become a critical environmental concern due to its potential adverse ecological effects.

Trace elements (TE) contents in soils can be locally rather high and are still increasing owing to many human activities, resulting in risk to human health and the environment. The total metal load on agricultural soils is the sum of metal input from atmospheric deposition, and input from the addition of fertilizers (mainly phosphate fertilizers), metal-containing pesticides, biosolids (for example sewage sludge, industrial wastes), emissions and wastewater (Adriano, 2001; Kabata-Pendias and Pendias, 1992). On the other hand, (TE) deficiency in plants has been found in regions of SEE countries. For example Zn and Fe deficiency in eastern part of Croatia (Jug *et al*., 2008), Cu deficiency in pasture and blood of sheep at Niksici Plateau (B&H) (Muratović *et al*., 2005), and selenium (Se) deficiency in almost whole SEE region (Maksimovic *et al*., 1992; Antunović *et al*., 2005; Muratović *et al*., 2007) have been observed. The soil-plant barrier limits transmission of many trace elements through the food chain, although Cd (an important human health concern) can bypass the soil-plant barrier. Results from many studies that support these key concepts provide a basis of our understanding of the relationship between trace element chemistry and soil chemical properties.

The paper objective was to enhance the bioavailability trace elements in soils and check the uptake level of Fe, Zn, Se and Cd in upper ground parts of maize to provide solutions for increasing their content by 2 to 3- fold in fodder crops.

MATERIAL AND METHODS

Experimental Site

Field trials experiments with different fertilization treatments of maize were set on Farm Vita VI, Višići, Čapljina. Two types of silage maize hybrids were selected according to the duration of vegetation stages one from FAO group 490 and other FAO group 380, NP Pako Singenta and M34 Pioneer. During vegetation season 2012 trials was set up on the experimental area of 1120 m^2 using a complete randomized block design statistical model. The experiment included three fertilization treatments and control treatments in four replications. The basic plot size was 20 m^2. On base of the soil analysis it was recommended to apply basic fertilization of 140 kg N ha^{-1}, 70 kg $P_2O_5ha^{-1}$ and 130 kg K_2O ha^{-1}. Basic NPK fertilization was same for all treatments and other treatments included control, 10 kg Na_2SeO_4 ha^{-1}; 20 kg Na_2SeO_4 ha^{-1} (these treatments were incorporated in soil in spring) and fourth treatment 20 kg $Na_2SeO_4ha^{-1}$ (liquid soil application in the phase of intensive growth along with additional nitrogen fertilizers).

Sample collection and chemical analysis

After the harvest of five randomly selected maize hybrids per plot in middle rows the whole plant material was weight, chopped, dried and prepared for chemical analyses. The plant material samples were analyzed after microwave digestion using 9 mL 65% (v/v) HNO_3 and 2 mL 30% (v/v) H_2O_2 (Kingstone and Jassie, 1986). Concentration of trace element Se was determined by inductively coupled plasma IICP), optical emission spectrometry (OES) technique.

Four average soil samples were collected from experimental site. The soil samples were prepared for analyses by drying and milling and basic chemical analyses were done: soil pH_{H2O} and pH_{KCl} (ISO 10390), soil organic matter by sulfochromic oxidation (ISO 14235), plant available phosphorus and potassium extracted by ammonium-lactate (Egner *et al*., 1960). Determination of trace elements selenium was extracted by aqua regia (ISO 11466) and the fraction extracted by aqua regia was considered as soil total content. Trace elements concentrations were determined using a Perkin Elmer Optima 5300 DV Inductively Coupled Plasma Optic Emission Spectrometer (ICP-OES).

Weather conditions on experimental sites

During vegetation seasons weather conditions were observed (average precipitation and average air-temperature) and are shown in Table 1.

Table 1. Weather condition on experimental site in trail with bio fortification of silage maize by selenium

Year		May	June	July	August	September	Total (L/m^2)	Mean (°C)
Višići (Mostar), B&H								
2012	Pecip. L/m^2	96.1	28.3	1.8	0.4	151.8	278.4	
	Max. °C	30.5	37	39	41	35.5		36.6
	Min.°C	7.2	12	16.5	13.5	6.5		11.1
	Humidity (%)	74	69	49	49	62		60.7

Data for summer of 2012 show extremely dry weather, with 0.4 l/m^2 of precipitation in August and it had affected on lower yields of green matter. Average minimal and maximal temperatures for maize growing period from May to September varied from 11.1°C till 36.6°C. Relative humidity for this five month of maize growth has also varied from 74 to 49%.

Data analysis

Data used for this paper work arise for selenium fertilization of maize and reflection on absorption on selenium, iron, zinc and cadmium and the aim of the research was primarily to provide a practical and basic knowledge of agronomic technologies and physiology of selenium and other metals in maize plant. The main investigation was to evaluate the bioavailability of selenium, content of trace element in maize plant and yield, as this could be reflected on the health and productivity of people and animals.

Obtained values were analyzed by ANOVA for find the differences in total selenium content, iron, zinc, cadmium in plant material for two types of maize hybrids fertilized with increasing rates of selenium fertilizer. For statistical data processing the GenStat 7 software (Laws Agricultural Trust, Rothamsted Experimental Station) was used.

RESULTS

Results of the analysis of agrochemical properties of soil from the site Višići indicate mild acid (in 1M KCl) to neutral (in H_2O) soil reaction, good humus which is moderate supplied with phosphorus and potassium (Table 2).

Table 2. The basic agrochemical soil properties on experimental locations

Location name Farm Višići	Soil sampling depth	pH		Humus (%)	Potassium mg K_2O/100 g	Phosphorus mg P_2O_5/100 g
		H_20	KCl			
1	0-30	6.56	5.69	3.95	32.2	16.9
2	0-30	6.84	5.91	3.65	31.6	14.3
3	0-30	6.49	5.34	3.08	18.1	13.7
4	0-30	6.36	5.19	3.52	28.5	16.2

Soil selenium content varied from 0.6047-0.9854 mg per kg of soil at our experimental site while Fe soil content varied from 28320-31800 mg per kg of soil. Cadmium content has varied 0.6130-0.6634 mg per kg of soil and zinc content varied form 89.89-103.40 mg per kg of soil (Table 3).

Table 3. Trace element analysis of soil samples on experimental site

Location name Farm Višići	Soil sampling depth	Fe (mg kg^{-1})	Zn (mg kg^{-1})	Cd (mg kg^{-1})	Se (mg kg^{-1})
1	0-30	30980	99.76	0.6284	0.8879
2	0-30	28320	89.89	0.6130	0.9854
3	0-30	31380	99.41	0.6634	0.6471
4	0-30	31800	103.40	0.6556	0.6047

Soil type on experimental site is Fluvisol at elevation of 0 m. Fluvisols are found typically on level topography that is flooded periodically by surface waters or rising groundwater, as in river flood plains and deltas and in coastal lowlands. These soils exhibit a stratified profile that reflects their depositional history or an irregular layering of humus and mineral sediments in which the content of organic carbon decreases with depth.

According to the presented results in Table 4 there no differences between the fertilization treatments for tested elements iron, cadmium, zinc, selenium and yield. These results means that applied selenium fertilizers in different doses has not provide differences in result of measured parameters. Even without significant differences yield was highest by application of soil selenium doses 10 kg and 20 kg Na_2SeO_4 ha^{-1} while control was lowest. Cadmium, iron and zinc content variation has not been in relation to applied fertilization but selenium in plant material has shown slight increments as selenium treatment has increased.

Table 4. Difference in obtain average values for some elements and yield regarding the applied four fertilization treatments for the vegetation season 2012 for two type of maize hybrid

Variants	Control	10 kg Na_2SeO_4 ha^{-1}	20 kg Na_2SeO_4 ha^{-1}	20 kg Na_2SeO_4 ha^{-1} liquid applic.+additional fert.	LSD=0.05
Cd mg kg^{-1}	0.0539	0.0548	0.0535	0.0431	0.02
Fe mg kg^{-1}	81.1	84.6	68.4	74.9	15.35
Zn mg kg^{-1}	54.1	62.6	57.7	59.2	12.94
Se mg kg^{-1}	0.0467	0.0516	0.0502	0.0602	0.01
Yield t ha^{-1}	29.3	37.2	37.6	35.6	4.01
Significance	NS	NS	NS	NS	

NS-no significant differences between fertilization treatments

As the there is no significant differences for fertilization treatments for tested parameters two type of maize hybrids had also showed no difference for the same traits. Without significant differences the M 34 Pioneer cultivar has shown 15% higher yield than cultivar NP PAKO Syngenta. For named trace elements slight increment was visible for cultivar NP PAKO Syngenta comparing to M34 Pioneer (Table 5).

Table 5. Difference in obtain average values for some elements and yield regarding the selected maize hybrids for the vegetation season 2012

Variants	Yield t ha^{-1}	Cd mg kg^{-1}	Fe mg kg^{-1}	Zn mg kg^{-1}	Se mg kg^{-1}	Significance
M34	37.6	0.0509	74.6	56.2	0.0499	NS
NP PAKO	32.2	0.0517	79.9	60.6	0.0545	NS
LSD=0.05	8.33	0.01	10.85	9.15	0.008	

NS-no significant differences between fertilization treatment

Regarding the correlation between trace elements and yield some positive relation has been found (Table 6). This means that increment one of trait is strongly or medium followed by other measured traits or that correlation is not found. Iron had strong positive correlation with cadmium and zinc and moderate correlation with selenium and yield. Cadmium had strong positive correlation with iron and zinc, modern positive correlation with selenium and no correlation with yield. Zinc had strong positive correlation with iron and selenium, and moderate correlation with cadmium but no correlation with yield. Selenium has also positive affected trace elements included in trial, but no correlation has been found with yield.

Table 6. Correlation coefficients between tested traits

	Cd mg kg^{-1}	**Zn mg kg^{-1}**	**Se mg kg^{-1}**	**Yield t ha^{-1} FW**
Fe mg kg^{-1}	0.51**	0.52**	0.35*	0.35*
Cd mg kg^{-1}		0.36*	0.22*	-0.06^{ns}
Zn mg kg^{-1}			0.50**	-0.11^{ns}
Se mg kg^{-1}				-0.002^{ns}

** Strong to very strong correlation; *weak to medium weak correlation; ns-no correlation

DISCUSSION

Balanced nutrition of the plants is one of the main factors that affect the yield and quality of the plants. Significant impact of applied selenium fertilization on tested trace element and yield has not been found but some correlation relation between elements explains connection between them in combinations with chemical component of experimental soil and weather condition. According to Chaney (1988) the climate strongly influences soil types; these two factors largely control element (metals and metalloids) mobility and availability. Heavy metals and metalloids can be involved in a series of complex chemical and biological interactions. The most important factors which affect their mobility are pH, sorbent nature, presence and concentration of organic and inorganic ligands, including humic and fulvic acids, root exudates and nutrients (Violante *et al.*, 2010). Accumulation of metal ions and metalloids in different compartments of the biosphere, and their possible mobilization under environmentally changing conditions induce a perturbation of both the structure and function of the ecosystem and might cause adverse health effects to biota (Fedotov and Mirò, 2008). Anthropogenic processes include inputs of heavy metals through use of fertilizers, organic manures, and industrial and municipal wastes, irrigation, and wet and/or dry deposits. These processes contribute with variable amounts of heavy metals to the agro-ecosystem (Violante *et al.*, 2010).

In alkaline, well-drained soils, selenium tends to form selenates (Se^{+6}) which are highly available to plants and may sometimes lead to their accumulation at toxic levels. Although soil reaction plays a major role in determining Se solubility and availability, its influence lessens as the contents of clay and organic matter in the soil increase. Regarding the high content organic matter and clay soil particulates on our experimental site could affect the solubility and availability of selenium and its interaction with other TE's elements. But in acid and more poorly-drained soils, a ferric iron-selenite complex may form, which is only slightly available to plants (Gustafsson and Johnsson, 1992). Acid pH soil reaction on experimental site and moderate content of iron in soil could provide forming the iron-selenite complex or the low effect of fertilization on selenium content in soil and plant material could be provided by very low applied fertilization amount of Na_2SeO_4 per basic plot.

Although most soils contain adequate total iron, amounts that are available to plants might be inadequate dependent in various soil factors such as very high or low soil temperature, high humidity, poor soil aeration and compaction, high pH, HCO_3^- and $CaCO_3$ contents. Beside the bad physical properties of the soil Fe chlorosis is also related with PO_4^- and NO_3^- anions and other heavy metal concentrations such as Zn, Cd, Mn, Co, Cu and Ni (Basar, 2000; Lucena, 2000).The typical iron concentrations in soils range from 0.2% to 55% (20.000 to 550.000 mg kg^{-1}) (Bodek *et al*,. 1988) and concentrations can vary significantly even within localized areas due to soil types and the presence of other sources. According to our results variation of iron content at experimental site around 0.3% was moderate. Iron can occur in either the divalent (ferrous or Fe^{+2}) or trivalent (ferric or Fe^{+3}) states under typical environmental conditions. Iron is absorbed by plants as the ferrous ion (Fe^{+2}) which is necessary for the formation of chlorophyll and functions in some of the enzymes of the plant's respiratory system (Schneider *et al*., 1968).

Soil pH reaction, aeration and organic matter affect iron availability. The concentrations of iron in soil solution decrease sharply as the soil pH increase with minimum around pH 7.4-8.5. Poor soil aeration caused by flooding or compaction can increase or decrease iron availability depending on other soil conditions (Schulte, 2004). According to the same author the reduction in fixation and precipitation results in higher concentration of iron remaining in the soil solution available for root absorption. Iron plant analysis interpretation for maize impute deficiency iron at <10 mg kg^{-1}; low content 10-50 mg kg^{-1} and sufficient from 51-250 mg kg^{-1}. If we look at iron soil content at experimental site the moderate supply had result in sufficient content of iron in maize plant material showing the values of 74.6-79.9 mg per kg. Regarding not only the iron soil content but also low pH values that favors sufficient uptake level of iron in plant material. The formation of solid organic matter reduces the mobile forms of iron and its absorption by plants (Kabata-Pendias and Pendias, 1992), even our soil were rich in organic matter, nitrogen and phosphorus and potassium content this was not limiting factor for iron availability to soil or plant. Iron is very abundant element in Earth's crust and exists mainly as ferric oxides and hydroxides in soil under aerobic conditions. On floated land with very high underground water and love altitude during the rainy years as was experimental year with maize Fe (III) oxides undergo reductive dissolution and Fe (II) concentration is increased in soil solution (Neubauer *et al*., 2007). The biogeochemical transformation of Fe is very important as it affects not only solubility and speciation of Fe, but also bioavailability and toxicity of other metal contaminants such as cadmium (Cd) in soil (Neubauer *et al*., 2007).

Regarding the Cd in soils available for plant uptake and subsequent human uptake presents in the environmental poses a significant health risk. Cadmium is nonessential heavy metal that does not have any metabolic use (Samantaray and Rout, 1997). Generally zinc application decrease Cd uptake and accumulation in plants (McLaughin *et al*., 1994). Cadmium is of great environmental concern because it is highly toxic to plants and animals and it is highly mobile in the terrestrial environment. Atmospheric input and the use of phosphate fertilizers are the major sources of Cd for total plant concentration of agricultural crops. Low-molecular-weight organic acids present in the rhizosphere soil influenced the solubilisation of particulate-bound Cd into soil solution and accumulation by plant (Cieslinski *et al*., 1998). According to the Pavlikova *et al*. (2007) the content of cadmium at luvisol had ranged 0.287±0.107 mg $kg^{-1}$and on chernozem 8.101±4.799 mg kg^{-1} for maize experiment planted in pot. Regarding the Cd content at fluvisol from experimental site soil content is very low around 0.6 mg kg^{-1} and also there was a low content in plant material of maize 0.05 mg per kg without difference in selected cultivars. In anoxic environments, nearly all particulate cadmium is complexed by insoluble organic matter or bound to sulfide minerals (Kersten, 1988). Cadmium concentrations in non-polluted soils increase with clay concentration, but are generally lower than 1 μg g^{-1} dry soil (Mengel *et al*., 2001). Cadmium is concentrated in the topsoil, where it is associated with organic matter.

Hart *et al*. (2002) obtained the competitive interaction between Cd and Zn for uptake to the existence of a common transport system on plasma membranes. The effects of zinc application on Cd uptake and accumulation in plant are not consistent. Hart *et al*., (2002) found in durum and bread wheat that decreases in Cd uptake by roots with increasing Zn treatment is possibly due to a competition between Zn and Cd for uptake. Cadmium toxicity in plants become more severe under Zn deficient condition and this effect was not related to increasing Cd concentration in plant (Adiloglu *et al*., 2005). It is important to mention that the zinc and iron are in antagonistic relations, and high level of iron in the soil reduces the absorption of other metals by plants (Goletić, 2005). Uptake of zinc by the plants can be inhibited by the high iron content in the plant (Kovačević *et al*., 2004). In general, Zn in soil could varied between 10-300 mg Zn kg^{-1} (Kiekens, 1995). However, total Zn in soil is not good enough indicator of amount of Zn readily to uptake by plants. Total concentrations of metals in soils are a poor indicator of metal toxicity since metals exist in different solid-phase forms that can vary greatly in terms of their bioavailability (Huang and Gobran, 2005).

CONCLUSIONS

Fertilization with different selenium rate has not affected the yield or the selected hybrid had significant differences in yield. Also, fertilization with different selenium rate has not provide significant effect on Fe, Zn, Cd and Se in plant material or the hybrids showed significant differences between them.

Some strong positive correlation has occurred between Fe vs. Cd; Fe vs. Zn; Fe vs. Se and some moderate positive correlations were between Cd vs. Zn; Cd vs. Se and Zn vs. Se indicating the relations between them.

TE's element reactivity and bioavailability depends not only on its total content in soil but also on its chemical form in soil. For further research speciation of TE in soli could provide better defining influence of soil condition on their reactivity and bioavailability and identify the species that are more available for plants and microorganisms.

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