Scientific Papers. Series A. Agronomy, Vol. LXII, No. 1, 2019
ISSN 2285-5785; ISSN CD-ROM 2285-5793; ISSN Online 2285-5807; ISSN-L 2285-5785

CHEMICAL COMPOSITION AND YIELD OF SWISS CHARD AS INFLUENCED BY METALLURGICAL SLAG AND FISH FERTILIZER ADDITION TO MARGINAL SOIL

Aleksandra STANOJKOVIĆ-SEBIĆ[1], Zoran DINIĆ[1], Stevan ČANAK[2], Jelena MAKSIMOVIĆ[1], Radmila PIVIĆ[1]

[1]Institute of Soil Science, 7 Teodora Drajzera Street, 11000, Belgrade, Serbia
[2]State University of Novi Pazar, Department of Chemical-Technological Sciences, 36300, Novi Pazar, Serbia

Corresponding author email: astanojkovic@yahoo.com

Abstract

The paper aimed to present the effects of Ca - containing metallurgical slag (MS) and liquid fish (LF) fertilizer appliance on yield and chemical composition of aerial parts of Swiss chard cultivated on marginal eutric cambisol type of soil. The study was performed in semi-controlled glasshouse conditions, and the effects of MS was compared to those of commercial lime materials - ground limestone and hydrated lime, in combination with and without standard mineral and LF fertilizers. The results of the paper indicate that all Ca-materials studied, including MS, along with the studied fertilizers, showed positive effects on the content of main and beneficial biogenic macroelements in chards biomass and its yield. There is a statistically significant tendency of an increase in the content of P, K and C in tested herb in the treatment with LF fertilizer in relation to other treatments. The concentration of trace metals such as Fe and Cd was within the safety limits and allowed concentrations in all the treatments in spite of significant Fe content in MS, which is a highly desirable outcome.

***Key words**: Swiss chard, Eutric Cambisol, chemical properties, metallurgical slag, mineral and organic fertilizers.*

INTRODUCTION

Certain soil properties often change with time, making soils useful relative age indicators. Cambisols combine soils with at least an incipient subsurface soil formation. Transformation of parent material is evident from structure formation and mostly brownish discoloration, increasing clay percentage, and/or carbonate removal. Decarbonation is often followed by leaching (French: *lessive*, washing), which generally presents the translocation of claysized particles in suspension from E to Bt soil horizons (Schaetzl & Anderson, 2005) and is, therefore, an important prerequisite for soil acidification.

Cambisols generally make good agricultural land and are used intensively (IUSS Working Group WRB, 2006). Intensification in their use, in the manner of mineral fertilizers overuse, causes their transformation into marginal soils.

Amelioration of the marginal soils adverse properties, such as low pH, is the first step in creating favorable soil conditions for productive plant growth. Crops vary in their ability to tolerate an acidic soil. In general, Swiss chard (*Beta vulgaris* var. *cicla*), belongs to those vegetables that grow well in a soil of pH around 6.5-6.8 and acidic conditions will stunt its growth. Thus, a necessary lime should be applied. The application of traditional alkaline liming materials such as limestone, dolomite and burnt lime to acid soils for the amelioration of acidity and consequently for improving the crop production is a common practice (Troeh & Thompson, 2005; National Slag Association, 2011; Huang et al., 2012). However, the alkaline properties of metallurgical slag and the need for its sustainable and environmentally acceptable disposal options (Lopez et al., 1995) have prompted its use as a liming material on acid agricultural soils.

Metallurgical slag mainly consists of SiO_2, CaO, Fe_2O_3, FeO, Al_2O_3, MgO, MnO, P_2O_5 and several complex minerals (Motz & Geiseler, 2001). The liming materials in metallurgical slag comprise water-soluble and less water-soluble Ca and Mg compounds. Free Ca in slag reacts rapidly with water to form $Ca(OH)_2$. The $Ca(OH)_2$ will react rapidly with soil acidity.

Anderson (1991) reported yield increases of the certain crops such as sugar cane with calcium silicate slag use. White et al. (1937) reported on field trials in Pennsylvania that crop yields of corn, wheat, oats, buckwheat and soybeans with metallurgical slag use were as good or better than an equivalent amount of limestone. In addition to the liming materials, metallurgical slag contains various concentrations of plant nutrients, such P, S, Mn, Fe, and Mo. Some slags may contain elevated concentrations of trace metals such as Fe, Cd, Cr, Cu, Pb, Mo, Ni and Zn. All of these metals occur naturally in soil, and many are essential plant nutrients. Their concentrations vary in slags from different sources. If concentrations in the slag are similar to soil concentrations, they present no problem. If they are present at substantially higher concentrations in the slag than in the soil, repeated application of the slag could significantly increase soil metal concentrations. This possibly could lead to plant toxicity, increased plant uptake and transfer of metals to animals or humans, or to other environmental problems. Nevertheless, the bioavailability of these metals in slags is very low (National Slag Association, 2001).

As a by-product of an industrial process, metallurgical slag offers considerable cost advantages over commercial limestone. Along with other lime materials (ground slag stone, saturated slag etc.) present in Serbia, metallurgical slag from steel factory (Smederevo, Serbia) can be of great importance.

As in steel industry, there is a great problem with manure waste in aquaculture industry. In recent years this industry had to develop various management strategies to reduce the environmental impacts of aquaculture manure waste. In this regard, to evaluate the potential of aquaculture solid waste for use as a fertilizer, the aquaculture industry and regulatory agencies require analytical data regarding the concentrations of various plant nutrients found in the waste (Naylor et al., 1999).

The aim of this research was to investigate the effect of Ca-containing metallurgical slag, a by-product from steel factory (Smederevo, Serbia), on yield and chemical composition of the aerial parts of chard. The effects of metallurgical slag were compared to those of other lime materials (ground limestone and hydrated lime) in combination with and without standard mineral and organic (liquid fish) fertilizers.

MATERIALS AND METHODS

The research was carried out in pot experiments under semi-controlled conditions in the glasshouse of the Institute of Soil Science (Belgrade, Serbia), during 2015. In the experiments the comparison of the effect of metallurgical slag (MS) with other lime materials (ground limestone and hydrated lime) in combination with and without mineral NPK (N: P: K = 15%: 15%: 15%) and organic (liquid fish - LF) fertilizers were studied. The ground limestone (calcium carbonate or calcite, $CaCO_3$) contains 60% of carbonate. Hydrated lime (slaked lime, $Ca(OH)_2$) reacts very rapidly and has a TNV (Total Neutralizing Value) of 135, thus 740 kg of hydrated lime is equivalent to one ton of ground limestone i.e. the TNV = 135 (Ristow et al., 2010).

The experiment was undertaken with 1.4 kg pot^{-1} of Eutric Cambisol (WRB, 2014), a type of marginal soil from Central Serbia region that has very low pH and poor physical and biological properties (Pivić et al., 2011). The following designed treatments were carried out in three replicates: T1 - control (untreated soil); T2 - NPK mineral fertilizer; T3 - $CaCO_3$; T4 - $Ca(OH)_2$; T5 - MS; T6 - LF fertilizer; T7 - NPK mineral fertilizer + $CaCO_3$; T8 - NPK mineral fertilizer + $Ca(OH)_2$; T9 - NPK mineral fertilizer + MS.

Before sewing the chard, the amount of fertilizers and slag was measured according to the experimental design and mixed with soil (calculated as for 1 ha): composite NPK fertilizer (15: 15: 15) = 500 kg ha^{-1}; LF fertilizer = 170 kg ha^{-1}; $CaCO_3$ = 4 t ha^{-1}; $Ca(OH)_2$ = 2,8 t ha^{-1}; MS = 4 t ha^{-1}. All three Ca-materials with granulation of 0.2 mm were used in the experiment.

Chemical properties and elemental composition of the plowed layer of Eutric Cambisol used in this study (Table 1) were analyzed and determined in our previous studies (Pivić et al., 2011; Stanojković et al., 2011). Accordingly, the soil is characterized by acid reaction, with pH in 1M KCl 4.98, then, potential acidity (Y) and relatively low saturation of CEC, medium to high content of nitrogen, low content of soluble phosphorus, and it is well supplied with available potassium and trace elements - iron, zinc and copper. As for toxic metal cadmium, its concentrations are below the MPV (maximum permissible value).

Table 1. Chemical properties of the studied soil (Pivić et al., 2011; Stanojković et al., 2011)

Chemical parameter	Mean	PLV/MPV* (mg kg^{-1})
pH in 1M KCl	4.98	-
The sum of bases - S (cmol kg^{-1})	21.98	-
Potential acidity - Y′	11.50	-
Cation exchange capacity - CEC (cmol kg^{-1})	29.46	-
Base saturation -V (%)	74.62	-
Total N (mg kg^{-1})	0.28	-
Available P (mg kg^{-1})	79.8	-
Available K (mg kg^{-1})	21.8	-
Available Fe (mg kg^{-1})	63	>25
Available Zn (mg kg^{-1})	2.2	>6
Available Cu (mg kg^{-1})	4.1	>2.5
Available Cd (mg kg^{-1})	0.1	0.8

*PLV - provision limit value for Fe, Zn and Cu (Ankerman & Large, 1977); MPV - maximum permissible value for Cd (OGRS, 2018).

In Serbia, eutric cambisols are mostly medium-heavy soils, with a marked texture difference through the profile. Chemical properties vary depending on the intensity of use, degree of erosion, chemical properties of the parent material, as well as the level of development (Hadžić et al., 2002).
Table 2 displays the chemical composition of metallurgical slag (MS) applied, which was in detail determined in our previous studies (Pivić et al., 2011; Stanojković et al., 2011).

Table 2. Chemical composition of MS (Pivić et al., 2011; Stanojković et al., 2011)

Parameter	Mean value
pH in H_2O	12.48
Total Ca (mg kg^{-1})	26.20
Total CaO (mg kg^{-1})	36.60
Total $CaCO_3$ (mg kg^{-1})	65.80
Available Ca (mg kg^{-1})	17.18
Total Mg (mg kg^{-1})	0.41
Available Mg (mg kg^{-1})	0.07
Total P (mg kg^{-1}, in HNO_3)	0.64
Total P (mg kg^{-1}, in 2% citric acid)	0.61
Total Fe (mg kg^{-1})	15.34
Available Fe (mg kg^{-1})	3.38
Total Mn (mg kg^{-1})	1.80
Available Mn (mg kg^{-1})	3.12
Total Zn (mg kg^{-1})	14.60
Total Cu (mg kg^{-1})	228.8

Accordingly, this material has very alkaline reaction (pH in H_2O = 12.50), with the content of calcium in oxide forms (CaO) from 33-45 mg kg^{-1}, of which about 50% is easily soluble in 1 M ammonium acetate; content of the total magnesium is about 0.40 mg kg^{-1} and it was mainly in forms of MgO (0.07 mg kg^{-1}); total phosphorous contained in the material is about 0.60 mg kg^{-1}, where nearly all the amount is in available forms for plants; content of the total iron is high (about 15 mg kg^{-1}), with noticeable lower amounts of its soluble forms; manganese is present in total amount of about 1.8 mg kg^{-1}, but with noticeable low amounts of soluble forms; zinc is contained in lower amounts (10-20 mg kg^{-1}), while the content of copper is a little higher (about 200 mg kg^{-1}).
The settleable faecal fish waste, used as liquid fertilizer in this research, was obtained from the farm growing rainbow trout (*Oncorhynchus mykiss*) in village Krupac, municipality of Pirot, Serbia. Chemical composition of the liquid fish (LF) fertilizer included the following analysis: total nitrogen (N), carbon (C) and sulphur (S) were determined on elemental CNS analyzer Vario EL III (Nelson and Sommers, 1996); available phosphorus (P) was determined by spectrophotometer and potassium (K) by flame emission photometry, using AL-method (Đurđević, 2014a), after they were heated to boiling with the mixture of concentrated sulfuric and perchloric acids.
Swiss chard seedlings were grown according to the standard growing methods from March, 31st until July, 27th in 2015, when all studied relevant parameters of the plant growth were measured/analyzed. Biomass from each experimental variant and replicates was taken, air-dried and weighed, after which it was dried for 2 hours at 105°C and weighed again. The following chemical parameters of the aerial plant parts were analyzed: contents of nitrogen (N), carbon (C) and sulphur (S) were determined on elemental CNS analyzer Vario EL III (Nelson and Sommers, 1996); phosphorus (P) and potassium (K) concentrations were determined by "wet" combustion, i.e. they were heated to boiling with the mixture of concentrated sulfuric and perchloric acids, after which, in the obtained solution, P was determined by spectrophotometer with molybdate (Đurđević, 2014b), and K - by flame emission photometry (Đurđević, 2014c); in the determination of investigated trace biogenic elements - iron (Fe), zinc (Zn) and copper (Cu), as well as cadmium (Cd) as the toxic heavy metal, plant material was converted to a solution

by "dry" combustion, i.e., first by heating for several hours at 550ºC and then by treating the obtained ash with hydrochloric acid, after which these elements were determined by atomic absorption spectrometry - AAS (Wright & Stuczynski, 1996).

The evaluation of an influence of studied treatments on the analyzed chemical composition of the plant material was carried out using the analysis of variance (SPSS 20.0, Chicago, USA), followed by Duncan's Multiple Range Test (DMRT). Significant differences between means were tested by the LSD test at P = 0.05.

RESULTS AND DISCUSSIONS

By analyzing the content of the main chemical constituents of faecal fish waste in this study, it was determined its moderate to high quality for application as an organic fertilizer, containing 3.3 mg kg^{-1} of nitrogen, 36.5 mg kg^{-1} of carbon, 0.36 mg kg^{-1} of sulphur, 10.2 mg 100 g^{-1} of available phosphorus and 0.12 mg 100 g^{-1} of available potassium (Table 3).

Table 3. Chemical composition of the liquid fish (LF) fertilizer

Parameter	Average value
Total N (mg kg^{-1})	3.33
Total C (mg kg^{-1})	36.5
Total S (mg kg^{-1})	0.36
Available P_2O_5 (mg 100 g^{-1})	10.2
Available K_2O (mg 100 g^{-1})	0.12

According to the certain previous studies (Olson, 1992; Westerman et al., 1993) fish fertilizers tend to be highly variable in their chemical content, which is also the case with other manures. The various results demonstrated a wide variability in the general chemical composition of fish manure, although its macronutrients composition is of primary interest, given the end use of the manure as an agricultural fertilizer. As stated by Olson (1992), fish manure contains moderate amounts of essential plant nutrients in dry matter (2.83 mg kg^{-1} N; 2.54 mg kg^{-1} P; 0.10 mg kg^{-1} K; 6.99 mg kg^{-1} Ca; 0.53 mg kg^{-1} Mg), which is similar to the results of the current study, with an exception of phosphorus (the content was much higher in the present study - 10.2 mg kg^{-1}). Nevertheless, as suggested by Naylor et al. (1999), it is difficult to compare the values from the present study with those from others because of the differences in conditions under which the solids were produced, separated, stored and collected.

The results of the main and beneficial biogenic macroelements content in aerial parts of the tested vegetable (Table 4) show the statistically significant differences between the treatments at P<0.05, that are due to a higher accumulation of some elements and their mobilization from natural soil reserves primarily, as well as influenced by the additional LF fertilizer amendment and lime materials in combination with mineral ferilizer. However, these treatments had positive effect on N, P, K, C and S contents in relation to the control. There is a statistically significant tendency of an increase in the content of P, K and C in tested plant material in the treatment with LF fertilizer in relation to other treatments.

Improved organic and mineral nutrition in combination with lime materials including MS would explain the promotion of root and plant growth which led to promotion of biomass yield. The data on yield of the Swiss chard dry biomass were in accordance with chemical parameters, meaning that the yield was significantly higher in variants which included LF fertilizer and NPK mineral fertilizer in combination with MS and lime material in the form of Ca(OH) (Table 4).

As stated by Riesen and Feller (2005), the nature of applied treatments and their combinations have a great impact on trace metals accumulation, their mobility and storing capacity in plant tissues. Some trace elements may pose a toxicity threat if present at elevated levels as their availability and mobility increases under acidic conditions (Pawłowski, 1997).

The concentration of trace metals in Swiss chard aerial parts showed that there are statistically significant differences between different treatments at P<0.05 (Table 4). With an exception of plants from LF fertilizer treatment, it was determined elevated and critical concentrations of Fe in all other studied variants plants, although these concentrations were below the toxic value (Table 5). Nevertheless, there was not found higher accumulation of Fe in tested plants in the treatments where metallurgical slag was applied in spite of its significant content in this liming material. The content of Cu was in the range of normal and critical concentrations in chard plants from all variants studied except from control, where the content of Cu in chard was a little above the toxic value of 20 mg kg^{-1} per dry biomass (Table 4). The content of Zn and Cd in plants from all variants were in the range of normal and critical concentrations, but below the toxic (Table 5), which is a highly desirable outcome since Cd is a highly mobile element and can be easily translocated to the aerial plant parts (Sipter et al., 2008). The obtained results of Pajević et al. (2018) indicate that heavy metal accumulation significantly depends not only on soil quality, but also on plant species and in accordance, translocation of heavy metal ions from roots to aboveground plant parts. Different distribution of heavy metals within the plant was also previously reported by Al Jassir et al. (2005).

The edible parts of leafy green vegetables, such as Swiss chard, showed higher potential to accumulate heavy metals in comparison to storage organs and fruits (Sharma et al., 2008), which could explain elevated concentrations of the studied trace elements in this plant species.

Table 4. Available macroelements in Swiss chard and the yield of dry biomass depending on the treatment applied

Treatments	Macroelements (mg kg^{-1} of dry biomass)*					Yield (g pot^{-1})
	N	P	K	C	S	
T1 - control	2.17 ± 0.04^{i}	0.27 ± 0.04^{h}	3.59 ± 0.01^{f}	36.77 ± 0.05^{e}	0.75 ± 0.05^{d}	9.09 ± 0.10^{b}
T2 - NPK	3.81 ± 0.03^{b}	0.31 ± 0.01^{e}	4.03 ± 0.12^{c}	36.48 ± 0.07^{f}	1.07 ± 0.04^{a}	9.34 ± 0.12^{b}
T3 - $CaCO_3$	2.75 ± 0.06^{g}	0.37 ± 0.02^{cd}	3.83 ± 0.06^{d}	37.33 ± 0.37^{d}	0.96 ± 0.01^{b}	9.08 ± 0.09^{b}
T4 - $Ca(OH)_2$	3.07 ± 0.05^{e}	0.35 ± 0.01^{d}	3.83 ± 0.03^{d}	38.27 ± 0.39^{c}	1.03 ± 0.03^{a}	9.10 ± 0.12^{b}
T5 - MS	2.62 ± 0.02^{h}	0.33 ± 0.03^{de}	3.83 ± 0.01^{d}	38.21 ± 0.10^{c}	0.97 ± 0.02^{b}	9.26 ± 0.13^{b}
T6 - LF fertilizer	2.90 ± 0.05^{f}	0.49 ± 0.01^{a}	4.42 ± 0.09^{a}	39.75 ± 0.04^{a}	1.04 ± 0.01^{a}	9.72 ± 0.08^{a}
T7 - NPK fertilizer + $CaCO_3$	3.20 ± 0.02^{d}	0.34 ± 0.02^{de}	3.70 ± 0.01^{e}	37.40 ± 0.10^{d}	1.07 ± 0.02^{a}	9.13 ± 0.13^{b}
T8 - NPK fertilizer + $Ca(OH)_2$	4.23 ± 0.07^{a}	0.44 ± 0.02^{b}	4.13 ± 0.02^{b}	38.83 ± 0.16^{b}	0.81 ± 0.03^{c}	9.76 ± 0.20^{a}
T9 - NPK fertilizer + MS	3.32 ± 0.08^{c}	0.40 ± 0.02^{c}	3.38 ± 0.02^{g}	38.56 ± 0.11^{bc}	1.07 ± 0.02^{a}	9.81 ± 0.18^{a}
P value	***	***	***	***	***	***
LSD (0.05)	0.105	0.034	0.066	0.449	0.045	0.226

*means ± standard deviation; LSD - least significant difference; value followed by the same letter in a column is not significantly different at P< 0.05.

Table 5. Trace elements in Swiss chard biomass depending on the treatment applied

Treatments	Trace metals (mg kg^{-1} of dry biomass)*			
	Fe	Zn	Cu	Cd
T1 - control	302.33 ± 2.08^{c}	183.78 ± 1.55^{a}	22.61 ± 0.03^{a}	3.74 ± 0.03^{a}
T2 - NPK	465.33 ± 17.93^{b}	129.95 ± 8.21^{b}	13.50 ± 0.18^{d}	3.25 ± 0.05^{b}
T3 - $CaCO_3$	259.33 ± 5.03^{d}	76.27 ± 8.76^{ef}	13.46 ± 0.16^{d}	1.52 ± 0.03^{h}
T4 - $Ca(OH)_2$	236.33 ± 12.50^{d}	85.55 ± 4.50^{de}	15.25 ± 0.16^{b}	1.93 ± 0.04^{f}
T5 - MS	325.67 ± 2.52^{c}	67.49 ± 7.79^{f}	11.61 ± 0.14^{e}	2.04 ± 0.06^{e}
T6 - LF fertilizer	123.33 ± 9.45^{e}	91.88 ± 5.41^{cd}	11.33 ± 0.10^{f}	2.58 ± 0.01^{c}
T7 - NPK fertilizer + $CaCO_3$	528.67 ± 16.50^{a}	30.83 ± 2.93^{g}	7.39 ± 0.15^{h}	1.72 ± 0.02^{g}
T8 - NPK fertilizer + $Ca(OH)_2$	545.00 ± 36.01^{a}	41.96 ± 7.17^{g}	14.56 ± 0.04^{c}	1.31 ± 0.01^{i}
T9 - NPK fertilizer + MS	309.67 ± 14.22^{c}	100.00 ± 10.33^{c}	10.01 ± 0.01^{g}	2.41 ± 0.09^{d}
P value	***	***	***	***
LSD (0.05)	17.864	5.318	0.111	0.057
Reference value				
Normal	50[1]	15[3]	3[3]	<0.1-1[3]
Critical	250[1]	150[2]	15[2]	5[2]
Toxic	600[2]	200[2]	20[2]	10[2]

*means ± standard deviation; LSD - least significant difference; value followed by the same letter in a column is not significantly different at P< 0.05; Literature source: [1]Schulze et al. (2005), [2]Kastori et al. (1997), [3]Kloke et al. (1984).

CONCLUSIONS

Fertilizer management is of great importance in vegetable production. The results of the paper indicate that all Ca-materials studied, including metallurgical slag, along with the studied mineral and liquid fish fertilizers, showed positive effects on the content of main and beneficial biogenic macroelements in aerial biomass of Swiss chard. There is a statistically significant tendency of an increase in the content of P, K and C in tested plants in the variant with liquid fish fertilizer in relation to other treatments. Similar to the content of macroelements, the biomass yield was significantly higher in variants which included liquid fish fertilizer and NPK mineral fertilizer in combination with metalurgical slag and lime material [particularly in the Ca(OH) form]. The content of trace elements in Swiss chard plants was mainly in the range of normal and critical concentrations, except for Cu from control plants, where its content was a little above the toxic value of 20 mg kg^{-1} per dry biomass (Kastori et al., 1997). Nevertheless, there was not found higher accumulation of Fe in tested plants in the treatments where metallurgical slag was applied in spite of its significant content in this liming material. Generally, it was estimated that the studied metallurgical slag of the standardized chemical composition can be added to marginal soils toward their fertility amelioration/improving without adverse effects. It should be noted that liquid fish fertilizer of the stated chemical composition its self showed an excellent effect on all parameters tested and could be a part of an effective alternative to chemical fertilization in vegetable production under semi-controlled conditions.

ACKNOWLEDGEMENTS

This research work was carried out with the support of Ministry of Education, Science and Technological Development of the Republic of Serbia and also was financed from Project TR-37006.

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