CHEMICAL COMPOSITION AND YIELD OF WHITE MUSTARD AS AFFECTED BY INORGANIC, ORGANIC AND METALLURGICAL SLAG AMENDMENTS IN ACID SOIL

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Abstract
White mustard (*Sinapis alba* L.), is a quick-growing long-day annual which prefers light well-drained soil with neutral pH, but the plant tolerates moderately acid and alkaline soils ranging from 5.5 to 8.3. Thus, highly acidic soil conditions could stunt its growth and a necessary lime should be applied. The aim of this study was to determine the effect of Ca - containing metallurgical slag usage, sampled from steel factory area, as well as the effects of commercial lime material and fertilizers, on macro and trace elements content in aerial biomass of white mustard, grown on Stagnosol (a soil with high acidity), through greenhouse vegetative experiments, in 2019. The effects of metallurgical slag were compared to those of commercial lime material ($CaCO_3$) in combination without and with standard inorganic NPK and organic (NPK nutrient of animal origin) fertilizers. P was determined by spectrophotometer, K - by flame emission photometry, and N - using elemental CNS analyzer. In the determination of Fe, Zn, Cu and Cd, ICP-AES was used. Used lime materials, along with metallurgical slag, particularly in combination with organic fertilizer, showed positive effects on elemental composition of white mustard and its yield. The high and toxic concentrations of trace elements in herb comparing to untreated soil were not significantly increased and were within the permissible levels in plants in all the variants in spite of their higher content in metallurgical slag. Based on the results obtained in present study, high potential has been estimated in the application of the studied alkaline metallurgical slag, particularly when combined with organic and inorganic fertilizers, to acid soils toward amelioration their fertility without adverse effects.
Keywords: Metallurgical slag, commercial lime material, inorganic and organic fertilizers, *Sinapis alba*, Stagnosol.

Introduction
Acid soils are widespread and limit plant production all over the World. They cover approximately 30-40% of arable soils and more than 70% of potential arable soils [1]. A similar situation exists in the Republic of Serbia, where long-term research showed that there are over 60% of acidic soils, and that their productivity is increasingly becoming a limiting factor in plant production. It is considered that the constant increase in their surface area is the result of intensive production technology, uncontrolled use of inorganic fertilizers, the impact of acid rain, as well as the lack of organic fertilizers usage [2]. Crops vary greatly in their soil affinity and ability to tolerate low pH. White mustard (*Sinapis alba* L.) is an annual plant with a strong root system with numerous root hairs that contribute to drought resistance. It is grown for its young leaves with a sharp smell, which are used raw in salads, but also for its aromatic seeds, from which mustard is obtained by a special technological process. Commonly, wild plants grow in the fields, but they are also cultivated [3]. There are no special plant requirements for the soil if it is properly fertilized. White mustard grows best in light well-drained soil with neutral pH, although it can tolerate moderately acid and alkaline soils ranging from 5.5 to 8.3 [4], reacting very well to limestone. It is not recommended to grow on halomorphic soils, although extremely acidic soil conditions could significantly reduce or impede

its growth and development [5]. Thus, a necessary lime should be applied. The use of traditional commercial alkaline liming materials to acid soils for the amelioration of acidity consequently improving crop production is a common practice [6]. Along with these materials present in Serbia and regarding its alkaline nature, metallurgical slag, sampled from steel factory area, can be of great importance. Although the significant quantities of metallurgical slag are generated as waste material every day from steel industries, its physicochemical property offers a high potential for its utilization in agriculture. As metallurgical slag contains fertilizer components such as CaO, SiO_2 and MgO, its alkaline property remedies soil acidity [7]. In addition to these three components, it also contains components such as FeO, MnO and P_2O_5, so it has been used for a broad range of agricultural purposes. White et al. [8] reported on field trials in Pennsylvania that crop yields of corn, wheat, oats, buckwheat and soybeans with metallurgical slag application were as good or better than an equivalent amount of limestone. Huang et al. [6] stated that converter slag is used to produce siliceous and phosphorus fertilizer, as well as micronutrient fertilizer, in Germany, USA, France and Japan. Some slags may contain elevated levels of trace metals such as Fe, Cd, Cr, Cu, Pb, Mo, Ni and Zn, that occur naturally in soil, and many of them are essential plant nutritive in low concentrations. Although there are varying concentrations of trace elements in metallurgical slags, their bioavailability is very low [7].
The aim of this research was to investigate the effect of Ca-containing metallurgical slag, a by-product from steel factory, on yield and chemical composition (N, P, K, Fe, Zn, Cu, Cd) of the aerial biomass of white mustard, grown on Stagnosol (a soil with high acidity) and performed in semi-controlled greenhouse conditions. The effects of metallurgical slag were compared to those of commercial lime material ($CaCO_3$) in combination without and with standard inorganic NPK and organic (NPK nutrient of animal origin) fertilizers.

Experimental

The research was performed in Institute of Soil Science in greenhouse vegetative experiments using plastic pots, from the first decade of May to the second decade of July, in 2019. Each pot was filled with 3 kg pot^{-1} of homogenized soil - Stagnosol [9], brought from an experimental field of Institute - Varna, near Šabac town. In every plastic pot ten white mustard seeds were sown.
Chemical characteristics of Stagnosol plowed layer, used in present research, were determined in our previous study [2]. Accordingly, the soil is characterized by very acid soil reaction, low content of available P, then, it is well supplied with available K, medium provided with total N, Cu and Zn, and very highly provided with Fe. Content of toxic heavy metal Cd was low and far from the maximum limiting value of 0.8 mg kg^{-1} [10].
In the experiments the comparison of metallurgical slag (MS) effects in relation to the effects of lime material (calcite - $CaCO_3$, containing 60% of carbonate), and in combination with and without inorganic NPK [composite NPK (15:15:15)] and commercial organic (solid NPK 4:3:4 nutrient of animal origin - Nervosol Complex, NC) fertilizers, were studied. The following seven designed variants were carried out in three replications: control (untreated soil) - V1; $CaCO_3$ - V2; NPK inorganic fertilizer + $CaCO_3$ - V3; NC + $CaCO_3$ - V4; MS - V5; NPK inorganic fertilizer + MS - V6; NC fertilizer + MS - V7. Before sewing the mustard, the amount of fertilizers, lime and slag was measured according to the experimental design and mixed with soil (calculated as for 1 ha): NPK fertilizer (15:15:15) = 500 kg ha^{-1}; NC fertilizer = 170 kg ha^{-1}; $CaCO_3$ = 4 t ha^{-1}; MS = 4 t ha^{-1} (same as the amount of $CaCO_3$). Both MS and $CaCO_3$ with granulation of 0.2 mm were used in the experiment.
The samples of metallurgical slag used in present study were taken during spring 2009 from different deposition sites of Steel factory – Smederevo, Serbia (previously US Steel, now Hesteel Serbia), located approximately 60 km South-East from Belgrade. Chemical composition of MS applied (Table 1) was determined in our previous study [2]. Accordingly, this material has very

alkaline reaction, with the content of calcium in oxide forms (CaO) from 33-45%, of which about 50% is easily soluble in 1 M ammonium acetate; content of the total magnesium was mainly in forms of MgO, while nearly all the amount of P is in available forms for plants; contents of the total Fe and Mn are high, but with lower amounts of their soluble forms; Zn is contained in lower amounts, while the content of Cu is a little higher.

Table 1. Chemical composition of MS [2].

Parameter	Mean ± STDV	Parameter	Mean ± STDV
pH in H_2O	12.48±0.04	Total P (%)	0.61±0.10
Total Ca (%)	26.20±3.48	Total Fe (%)	15.34±0.79
Total CaO (%)	36.60±4.83	Available Fe (mg kg $^{-1}$)	3.38±0.96
Total $CaCO_3$ (%)	65.80±8.64	Total Mn (%)	1.80±0.15
Available Ca (%)	17.18±1.98	Available Mn (mg kg $^{-1}$)	3.12±1.04
Total Mg (%)	0.41±0.04	Total Zn (%)	14.60±5.59
Available Mg (%)	0.70±0.02	Total Cu (%)	228.8±15.4

Organic fertilizer used is a solid NPK 4:3:4 nutrient of animal origin, commercially called Nervosol Complex (NC). According to its main chemical composition, it consists of 4% of total N, 4% of organic N, 3% of P (P_2O_5 form), 4% of K (K_2O form), and 30% of organic C [11].

The aerial biomass of white mustard plants was taken shortly before their final phases of growth from each experimental variant and replicate in experimental pots. Biomass was then air-dried and the yield of plants was measured and expressed in g pot^{-1}, after which it was dried for 2 hours at 105^{o}C and weighed again for chemical analyses, using gravimetric method for determination of dry matter content of plant tissue [12]. The content of N was determined on elemental CNS analyzer Vario EL III [13]. The content of P was determined by spectrophotometer with molybdate [14], and the content of K - by flame emission photometry [15]. In the determination of trace elements - Fe, Zn and Cu, as well as the toxic heavy metal Cd, inductively coupled plasma-atomic emission spectrometry (ICP-AES) was used, after microwave oven extraction and moisture content [16].

The effects of V1-V7 experimental variants on the studied chemical parameters and yield of the plants were evaluated using the SPSS analysis of variance, followed by Duncan's Multiple Range Test (DMRT). Significant differences between means were tested by the LSD test at P = 0.05.

Results and discussion

Certain types of soil, acid particularly, require the periodic application of soil conditioners such as commercial liming materials to provide aeration, increase moisture retention, and promote root permeation and growth. In several experiments in European countries it was determined the ability of metallurgical slag to raise the pH of acid soils [7, 17]. The optimum pH range in soil for growth of most crops in soil is between 5.5 and 7.0, within which most plant nutritives are available [18].

Table 2 shows that the macroelements content in white mustard aerial parts statistically significantly differs (*P**) between the variants for P and K at P<0.05, and no significantly differs (NSD) for N. Nevertheless, there is a noticeably tendency of an increase in the content of N, P and K in tested plant material in the variants that included NC fertilizer and NPK inorganic fertilizer, respectively, in combination with MS (V6 and V7), in relation to other variants. In relation to the untreated soil (V1), all studied variants from V2 to V7 showed positive effects both on increase of yield and valuable chemical composition of white mustard. Improved organic and mineral nutrition in combination with MS would explain the promotion of white mustard biomass growth which led to the promotion of its yield. The data on yield of white mustard were in accordance with chemical ones, meaning that the yield was highly significantly higher (*P****) at P<0.05 in variants V6 and V7 (Table 2).

Table 2. Effect of tested variants on macroelements content in mustard dry biomass and its yield*

Variants	Macroelements			Yield (g pot^{-1})
	N (%)	P (mg kg^{-1})	K (mg kg^{-1})	
V1 - control (untreated soil)	3.28±0.09^{ab}	0.49±0.03^{cd}	2.98±0.51^{c}	4.09±0.10^{b}
V2 - $CaCO_3$	3.35±0.11^{ab}	0.64±0.09^{ab}	3.35±0.37^{abc}	4.15±0.13^{b}
V3 - NPK mineral fertilizer + $CaCO_3$	3.37±0.32^{a}	0.58±0.04^{abcd}	3.72±0.24^{ab}	4.28±0.13^{b}
V4 - NC + $CaCO_3$	3.36±0.35^{a}	0.57±0.08^{bcd}	3.69±0.32^{ab}	5.09±0.12^{b}
V5 - MS	3.34±0.11^{b}	0.51±0.07^{d}	3.02±0.29^{c}	5.09±0.09^{b}
V6 - NPK mineral fertilizer + MS	3.67±0.17^{a}	0.65±0.05^{abc}	3.77±0.41^{ab}	5.57±0.20^{a}
V7 - NC fertilizer + MS	3.69±0.17^{a}	0.66±0.03^{a}	3.90±0.30^{a}	5.62±0.18^{a}
P value	NSD	*	*	***
LSD (0.05)	0.448	0.106	0.558	0.237

*means ± STDEV; LSD - least significant difference; NSD - no significant difference at P=0.05; *, **, *** - statistical significant differences at P<0.05, P<0.01 and P<0.001, respectively; values followed by the same letter in a column are not significantly different at P<0.05.

Table 3. Effect of tested variants on the trace elements content in mustard dry biomass

Variants	Trace elements (means ± STDEV), in mg kg^{-1}			
	Fe	Zn	Cu	Cd
V1 - control (untreated soil)	108.11±2.11^{a}	59.59±2.24^{de}	7.79±0.32^{d}	0.27±0.08^{b}
V2 - $CaCO_3$	118.62±7.48^{a}	71.24±8.93^{c}	8.58±0.64^{c}	0.38±0.09^{ab}
V3 - NPK mineral fertilizer + $CaCO_3$	125.08±25.98^{a}	74.57±3.81^{abc}	9.21±0.55^{abc}	0.36±0.07^{ab}
V4 - NC + $CaCO_3$	108.50±1.56^{a}	47.69±2.03^{e}	9.16±0.34^{abc}	0.34±0.08^{ac}
V5 - MS	117.13±3.66^{a}	78.79±3.13^{a}	9.36±0.27^{a}	0.43±0.05^{a}
V6 - NPK mineral fertilizer + MS	117.33±13.71^{a}	71.94±4.53^{bc}	9.15±0.31^{abc}	0.38±0.07^{ab}
V7 - NC fertilizer + MS	112.64±8.29^{a}	67.45±5.93^{cd}	9.24±0.42^{ab}	0.31±0.06^{ab}
P value	NSD	***	***	NSD
LSD (0.05)	19.103	7.611	0.528	0.142
Reference value				
Normal	50[1]	15[3]	3[3]	<0.1-1[3]
Critical	250[1]	150[2]	15[2]	5[2]
MPL	600[2]	200[2]	20[2]	10[2]

LSD - least significant difference; NSD - no significant difference at P=0.05; *, **, *** - statistical significant differences at P<0.05, P<0.01 and P<0.001, respectively; values followed by the same letter in a column are not significantly different at P<0.05; MPL - maximum permissible levels; literature source: [1][19], [2][20], [3][21].

Table 3 shows that the trace elements content in white mustard aerial parts statistically highly significantly differs (*P****) between different variants at P<0.05 for Zn and Cu, and no significantly differs (NSD) for Fe and Cd. Moreover, there was not found higher accumulation of Fe in plants in the variants where MS was applied in spite of Fe significant content in it. According to the reference values [21], the content of Cd was within the safety limits and permissible levels in all the variants, which is a highly desirable outcome. The present results of the trace elements content confirm the statements of several authors [22, 23]. The nature of tested treatments and their combinations have an impact on trace elements accumulation, their mobility and storing capacity in plant tissues [22]. Some of them may pose a toxicity threat if present at elevated levels as their availability and mobility increases under acidic conditions [23].

Conclusion

All tested treated variants showed positive effects both on increase of yield and chemical composition of white mustard in relation to the control, particularly when $CaCO_3$ and metallurgical slag are combined with inorganic and organic fertilizer. Comparing to control, trace elements were not significantly increased in spite of their higher content in studied metallurgical slag. Through experiments in greenhouse pot conditions, as well as using various laboratory accredited analysis, application of metallurgical slag has shown some of the potential benefits and made it a favourable potential material for liming the acid soils.

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References

[1] H.R. Von Uexkuell, E. Mutert, Plant Soil 171 (1995) 1.
[2] R. Pivić, A. Stanojković, S. Maksimović, D. Stevanović, Fresenius Environ. Bull. 20 (2011) 875.
[3] https://www.agroklub.rs/sortna-lista/uljarice-predivo-bilje/bela-slacica-87/
[4] S. Snapp, K. Date, K. Cichy, K. O'Neil, Extension Bulletin E-2956, Department of Crop and Soil Sciences, Michigan State University, 2006.
[5] https://agrosmart.net/2016/12/22/tehnologija-odgoja-bele-slacice/
[6] Y. Huang, X. Guoping, C. Huigao, W. Junshi, W. Yinfeng, C. Hui, Procedia Environ. Sci. 16 (2012) 791.
[7] National Slag Association, http://www.nationalslag.org/tech/ag_guide909.pdf, 2011.
[8] J.W. White, F.J. Holben, C.D. Jeffries, Mustards-A Brassica Cover Crop for Michigan, Penn State Bulletin AES 341 (1937).
[9] WRB, World Soil Resources Reports, 106, FAO, Rome, Italy, 2014.
[10] OGRS, Regulation on Limit Values of Pollutants, Harmful and Dangerous Substances in Soil. "Sl. glasnik RS", 30/2018 and 64/2019, 2019.
[11] N. Đurić, B. Kresović, Đ. Glamočlija, Systems of Conventional and Organic Production of Field Crops, Grafos Internacional, Pančevo, Serbia, 2015.
[12] R.O. Miller, in: Y. Kalra (Ed.), Handbook of Reference Methods for Plant Analysis, CRC Press, Taylor & Francis Group, Boca Raton, Florida, 1998, pp. 51.
[13] D.W. Nelson, L.E. Sommers, in: D.L. Sparks (Ed.), Methods of Soil Analysis, Part 3, SSSA, Madison, Wisconsin, 1996, pp. 961.
[14] B. Đurđević, in: D. Miklavčić (Ed.), Manual in Plant Nutrition, Faculty of Agriculture, Osijek, Croatia, 2014a, pp. 60.
[15] B. Đurđević in: D. Miklavčić (Ed.), Manual in Plant Nutrition, Faculty of Agriculture, Osijek, Croatia, 2014b, pp. 62.
[16] Y.P. Kalra, Handbook of Reference Methods for Plant Analysis. CRC Press, Taylor & Francis Group, Boca Raton, Florida, 1998.
[17] M. Rodriguez, F.A. Lopez, M. Pinto, N. Balcazar, G. Besga, J. Agron. 86 (1994) 904.
[18] R. Prasad, J.F. Power, Soil Fertility Management for Sustainable Agriculture. CRC Press, Lewis Publishers, Florida, 1997.
[19] E-D. Schulze, E. Beck, K. Müller-Hohenstein, D. Lawlor, K. Lawlor, G. Lawlor, Plant Ecology, Springer-Verlag, Berlin, Heidelberg, Germany, 2005.
[20] R. Kastori, N. Petrović, I. Arsenijević-Maksimović, in: R. Kastori (Ed.), Heavy Metals in the Environment, Institute of Field and Vegetable Crops, Novi Sad, Serbia, 1997, pp. 196.
[21] A. Kloke, D.R. Sauerbeck, H. Vetter, In: J.O. Nriagu (Ed.), Changing Metal Cycles and Human Health, Springer-Verlag, Berlin, Heidelberg, New York, Tokyo, 1984, pp.113.
[22] O. Riesen, U. Feller, J. Plant Nutr. 28 (2005) 421.
[23] L. Pawlowski, Ecol. Eng. 8 (1997) 271.