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THE EFFECT OF NATURAL ZEOLITES AND ORGANIC FERTILISERS ON THE CHARACTERISTICS OF DEGRADED SOILS AND YIELD OF CROPS GROWN IN WESTERN SERBIA

I. P. GLISIC[1], T. M. MILOSEVIC[1]*, I. S. GLISIC[2] AND N. T. MILOSEVIC[2]

[1]*Faculty of Agronomy, Department of Horticulture, 32000 Cacak, Cara Dusana 34, Serbia*
[2]*Fruit Research Institute, Department of Fruit Growing Technology, 32000 Cacak, Kralja Petra I/9, Serbia*

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ABSTRACT

Soils with unfavourable characteristics (pronounced acidity, disturbed structure, compaction, exhaustion, tiredness, etc.) cover a considerable area of Serbia. Specific crops, the fruit ones in particular, are being grown on these soils, yielding, however, considerably lower yields. The paper presents results of two-year studies on the effect of natural zeolites, organic fertiliser—cattle manure and mineral NPK fertiliser (15:15:15) on soil properties and fruit yield and fruit properties of strawberry and blackberry plants grown on shallow eroded vertisol.

The results have shown that the chemical properties of the soil improved with the natural zeolite 'Agrozel' (1 kg m^{-2}) + Manure (1 kg m^{-2}) treatment—resulting in a 0·94-unit acidity decrease and a 0·58% humus content increase at a 0–20 cm soil depth. Positive but less pronounced changes were also detected at greater soil depths. The strawberry and blackberry cultivation in these soils using the above substances gave rise to a yield increase. In the second year of study, strawberry and blackberry yields increased by 13·15% and 6·27%, respectively. Basic chemical properties of strawberry and blackberry fruits (soluble solids and total acid contents) were not significantly affected by zeolite and organic fertiliser additions to the soil.

KEY WORDS: degraded soil; zeolites; manure; strawberry; blackberry; Serbia

INTRODUCTION

Rapid economic development and advanced technologies have caused increase in the contamination and degradation of soil which is a basic substrate for crop cultivation and food production. At the same time, world population growth has brought about both food consumption increase and soil area decrease (Ovuka, 2000; Ramankutty *et al*., 2002; Lepers *et al*., 2005). Soil structure deterioration, soil disturbance, frequent accumulation of heavy metals and other hazardous substances, destruction of beneficial soil macro- and microorganisms and alteration of soil chemical properties are induced partly by the effect of nature, abundant precipitations, acid rains and erosion (Kirkby *et al.*, 2000; Lal, 2001; Evans, 2002; Andry *et al.*, 2007) but mostly by human activities (the uncontrolled use of mineral fertilisers and pesticides (Chen *et al*., 1999; Di *et al*., 2001; Popov *et al*., 2005; Hartemink, 2006)). Not only do such soils have reduced fertility, but they also carry risks of producing food of unsuitable quality and questionable safety.

Regeneration of such soils is a long-term process which may, only with the effect of nature, take more than 20 years (Ruecker *et al*., 1998; Tiag *et al*., 2000).

The use of different organic and inorganic fertilisers can induce different changes in soil chemical properties and different results in crop cultivation on these soils (Singh *et al*., 1997; Turk *et al*., 2006; Riley *et al*., 2008).

*Correspondence to: T. M. Milosevic, Faculty of Agronomy, Department of Horticulture, Cara Dusana 34, 32000 Cacak, Serbia.
E-mail: tomom@tfc.kg.ac.yu

The basic objective of the study was to examine the effect of natural zeolite and organic fertiliser (cattle manure) additions to shallow eroded vertisol soil having poor physico-chemical properties on the chemical properties of the soil and, hence, the fruit yield and basic fruit chemical properties of the strawberry and blackberry plants grown on this soil.

The Study Area

The trial research was conducted in the village of Gornja Gorevnica, 10 km northwest from the town of Cacak located on the border of Central and Western Serbia. This is mainly an upland area, with an average altitude of about 400 m, characterised by temperate continental climate.

Basic climatic parameters during the growing season (April–October) for the Cacak area for the years of study (2002 and 2003) and the 30-year average (1961–1990) are presented in Table I.

In the first research year (2002), the average temperature for the growing season (April–October) was 0·9°C higher than the long-term mean. Extremely low precipitations in the first part of the growing season (74 mm m^{-2} during April and May) were determined in the second research year (2003), resulting in the total precipitation amount in the growing season being 45·2 mm lower than the long-term average. However, the amount of precipitation in August (blackberry ripening time) was high (86·7 mm), being considerably higher than the long-term average of 59·5 mm for August.

Soil and Land Use

The examinations were conducted on shallow eroded vertisol or 'smolnitza', as it is called in Romania and Bulgaria (USDA Soil Taxonomy, 1999). This soil type covers 780 000 ha, accounting for 8·93% of the total land area in Serbia (Protic *et al*., 2003). It is generally distributed in Central and Western Serbia. Furthermore, the soils predominating in Central and Western Serbia (vertisol and cambisol) are characterised by significantly pronounced acidity (Protic *et al*., 2003).

The soil chemical properties examined prior to trial establishment are presented in Table II.

A Pye glass electrode pH—meter—potentiometer (W.G. Pye, Cambridge) was used to measure the pH value (in 0·01 M KCl). The humus content was determined by oxidation with the $KMnO_4$ solution (according to Kotzman), and total nitrogen content by the Kjeldahl method. Available P and K were determined by extraction with Al solution, and P and K by colorimetry with molybdate and flame photometry, respectively (Egner *et al*., 1960).

The results of the soil chemical analysis showed that the soil had acid reaction (pH = 4·86–5·07) and a 0·98–2·92% humus content. The contents of phosphorus and potassium ranged from 24·0 to 68·0 mg kg^{-1} and from 160·0 to 321·5 mg kg^{-1}, respectively.

Table I. Weather characteristics (Cacak Weather Bureau*)

Precipitation (mm) and mean air temperatures (°C)								Total	Mean
Months	Apr	May	Jun	Jul	Aug	Sep	Oct		
The 2002 growing season									
mm	60·3	60·4	102·5	95·6	46·3	50·8	55·3	471·6	—
°C	11·8	17·3	19·2	20·7	20·9	17·3	16·6	—	17·6
The 2003 growing season									
mm	43·2	30·8	70·5	56·8	86·7	79·8	50·3	418·1	—
°C	12·2	17·5	19·4	21·2	20·3	17·2	11·9	—	17·1
The long-term means (30 years: 1961–1990)									
mm	57·8	88·6	98·2	76·0	59·5	56·5	47·8	463·6	—
°C	11·5	16·2	19·5	20·9	20·5	16·9	11·8	—	16·7

*10 km (NW-direction) air-distance to the experimental field.

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Table II. Soil chemical properties prior to trial establishment

Soil depth (cm)	pH	Content (%)		AL-method (mg kg^{-1})	
		Humus	Total N	P_2O_5	K_2O
00–20	5·07	2·92	0·14	68·0	263·0
20–40	4·88	1·12	0·06	24·0	321·5
40–60	4·86	0·98	0·05	29·5	160·0

MATERIAL AND METHODS

The experimental orchards of the Senga Sengana strawberry and Thornfree blackberry cultivars were established on the soil with the above characteristics. The elementary plot size was 20 m^2 (20 × 1 m). The trial was set up in four replications. The soil treatments involving the application of both the compound 15:15:15 NPK mineral fertiliser and the natural material (Agrozel type of zeolite and organic fertiliser—mature cattle manure, the average composition thereof, according to a number of authors (DeLuca and DeLuca, 1997; Bary *et al*., 2000; Larney *et al*., 2006), being as follows: the content of N—0·5%, P_20_5—0·3%, K_20—0·6%, electrical conductivity—6·32, organic matter—25%, the C:N ratio—18:1), included the following:

a) Treatment 1 (T_1) = NPK (50 g m^{-2}) + Manure (1 kg m^{-2}), and
b) Treatment 2 (T_2) = Agrozel (1 kg m^{-2}) + Manure (1 kg m^{-2}).

Treatment 1 is the most commonly applied basic treatment in a number of crops, fruit ones in particular, in Serbia. The treatments were performed in the spring of 2002 and 2003. The Agrozel type of zeolite and manure as well as the compound NPK mineral fertiliser were distributed on the elementary plot in a 1 m wide band along the rows in autumn and then rotary tilled into the soil to a depth of 25–30 cm.

Each treatment included four replications. Each replication comprised 20 m of vertical blackberry trellis and 20 m of strawberry rows.

Changes in soil chemical and basic fruit chemical characteristics as well as in the yield of strawberry and blackberry (t ha^{-1}) were monitored during the two-year research period.

As regards basic chemical characteristics of the fruit, the contents of soluble solids (° Brix) and total acids as expressed through malic acid (%) were measured. A Zeiss laboratory refractometer was used to determine the soluble solids content. The total acid content was determined by titration with 0·1N NaOH with two or three drops of combined phenolphthalein indicator being added previously to the filtrate.

The experimental data were subjected to the analysis of variance. The LSD test at $p < 0{\cdot}05$ and $p < 0{\cdot}01$ was used for mean separation. The data were analysed by the ANOVA statistical programme (SPS Statistica 5·0 Software).

Origin and Characteristics of the Agrozel Type of Natural Zeolite

Natural zeolite commercially named as Agrozel originates from deposits in Eastern Serbia. Its final processing (grinding and packaging) is performed at the Belgrade Institute of Technology of Nuclear and Other Raw Materials. It is being marketed as Agrozel for use in plant production.

Its structure is predominated by mineral clinoptilolite (>60%). As regards its chemical composition, Agrozel is a hydrated alumosilicate of alkaline and alkaline earth metals (Na, K, Ca, Mg); therefore its ideal chemical formula may be written as:

$$M_{x/n}\left[Al_xSi_yO_2(x+y)pH_2O\right]$$

where M is the monovalent (Na^+, K^+) or divalent (Ca^{2+}, Mg^{2+}, Ba^{2+}) cation and n is the ion valence.

Agrozel has a particle size of 0–1·0 mm, cavity volume of about 34%, high thermal stability and the cation exchange capacity (CEC) of 216 mmol M^+100 g^{-1} (Daković *et al*., 2007).

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It possesses infinite three-dimensional polyedric crystal structure, with a great open cavity allowing cation exchange (Baerlocher *et al*., 2001). As such, it has ion-exchange and adsorption traits, water binding and release strengths as well as heavy-metal binding capacity (Treacy and Higgins, 2001). It can, hence, indirectly increase the availability of certain biogenic elements and provide more favourable ambient conditions for plant root and nutrient uptake from the soil. There are different applications of zeolite in agriculture (Markovic *et al.*, 1995; Polat *et al*., 2004).

There are increasing zeolite applications in fruit production, as reported in several papers (Polat *et al*., 2004).

RESULTS

The study results were examined through changes in the chemical characteristics of the soil after the two-year applications of Agrozel and cattle manure to the soil, and, subsequently, through changes in fruit yield and basic fruit chemical properties of strawberry and blackberry grown on the soil.

Soil Chemical Properties

Table III presents the research results on changes in the soil chemical properties occurring during the two-year applications of both NPK fertilizer and manure as well as on those induced by Agrozel and manure treatments.

The T_1 treatment with NPK + manure did not result in *any significant changes* in the above characteristics at the 0–20 cm soil depth after 2 years. The humus content mildly increased (from 2·92 to 3·25%), as opposed to other parameters examined showing no significant changes. Similar results were obtained at depths of 20–40 and 40–60 cm.

The T_2 treatment with Agrozel + manure induced certain changes in the soil chemical characteristics after two years of investigation.

Soil acidity (pH) at the 0–20 cm depth decreased considerably (from 5·07 units before the trial to 6·01 following two years of investigation). It was also reduced at greater soil depth, the decrease being, however, lower than that reported for the 0–20 cm depth, namely, it increased from 4·88 to 5·58 units at the 20–40 cm soil depth and from 4·86 to 5·58 units at the 40–60 cm depth.

Table III. Soil chemical properties at different treatments

Soil depth (cm)	Soil properties	NPK + Manure		Agrozel + Manure		LSD	
		Prior to trial	Two years after	Prior to trial	Two years after	$p < 0.05$	$p < 0.01$
00–20	pH	5.07	5.10	5.07	6.01*	0.74	1.17
	Humus (%)	2.92	3.25	2.92	3.50	0.31	0.52
	Total N (%)	0.14	0.15	0.14	0.18	0.04	0.07
	P_2O_5 (mg kg^{-1})	68.0	70.5	68.0	148.5**	23.0	44.0
	K_2O (mg kg^{-1})	263.0	300.0	263.0	>400.0**	51.0	84.0
20–40	pH	4.88	5.12	4.88	5.58	0.74	1.17
	Humus (%)	1.12	1.12	1.12	1.23	0.31	0.52
	Total N (%)	0.06	0.06	0.06	0.06	0.04	0.07
	P_2O_5 (mg kg^{-1})	24.0	68.0	24.0	90.0	23.0	44.0
	K_2O (mg kg^{-1})	321.5	320.0	321.5	>400.0*	51.0	84.0
40–60	pH	4.86	5.15	4.86	5.58	0.74	1.17
	Humus (%)	0.98	0.70	0.98	0.59	0.31	0.52
	Total N (%)	0.05	0.06	0.05	0.03	0.04	0.07
	P_2O_5 (mg kg^{-1})	29.5	28.5	29.5	30.0	23.0	44.0
	K_2O (mg kg^{-1})	160.0	200.0	160.0	200.0	51.0	84.0

*$p < 0.05$; **$p < 0.01$.
The asterisks indicate a significant difference between means at the value of p mentioned above.

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The humus content at the 0–20 cm soil depth increased from 2·92 to 3·50%. The increase was also registered at the 20–40 cm soil depth, but it was found to be smaller—from 1·12 to 1·23%. The humus content within the 40–60 soil depth was found to decrease from 0·98 to 0·59% after two years of investigation.

As regards the content of total nitrogen, no changes across soil depth were recorded after the two-year Agrozel and cattle manure applications.

An increase in available phosphorus (P_2O_5)—from 68·0 to 148·5 mg kg^{-1}—was registered at the 0–20 cm soil depth. It was also detected at the 20–40 cm soil depth, and was found to be 24·0 to 90·0 mg kg^{-1}, whereas the nutrient content at greater soil depth did not change after two years of treatment. (Jakovljević and Pantović, 1991).

There was a high increase in the content of available potassium (K_2O) at all soil depths. The content increased from 263·0 to more than 400·0 mg kg^{-1} at the 0–20 cm soil depth and from 321·5 to more than 400·0 mg kg^{-1} at the 20–40 cm soil depth, whereas the increase was found to be least pronounced at the greatest soil depth (40–60 cm), the content being raised from 160·0 to 200·0 mg kg^{-1}.

Strawberry and Blackberry Yields and Basic Fruit Chemical Characteristics

The results on both strawberry and blackberry yields and basic fruit chemical characteristics in different treatments are presented in Table IV.

In the NPK + manure and Agrozel + manure treatments, the average strawberry yield in the two-year investigations was 8·69 and 9·41 t ha^{-1}, respectively.

The average blackberry yield in the two-year research was found to be 13·86 t ha^{-1} in the combined NPK fertiliser and manure treatment (T_1) and 14·34 t ha^{-1} in the Agrozel-manure treatment (T_2).

The soluble solids content in the strawberry fruit was 10·20° and 10·35° Brix in the T_1 and T_2, respectively. In blackberries, the content ranged from 9·65° Brix in T_1 to 9·74° Brix in T_2.

The content of total acids expressed as malic acid in strawberry fruit was 0·82% in the T_1 and that in the T_2 did not differ any significantly, being 0·81%. In blackberries, the content was recorded to be 1·04% and 0·98% in the T_1 and T_2, respectively.

DISCUSSION

Analysis of Changes in Soil Chemical Properties

The two-year manure and compound NPK mineral fertiliser (15:15:15) treatments of the soil the characteristics thereof being presented in Table II did not induce significant changes in its basic chemical characteristics. Acidity

Table IV. Yield and basic chemical properties of strawberry and blackberry fruits

Trait examined	Fruit species	Treatments (A)						LSD	
		NPK + Manure			Agrozel + Manure				
		Year (B)		Mean	Year (B)		Mean		
		2002	2003		2002	2003		$p < 0.05$	$p < 0.01$
Yield (t ha^{-1})	Strawberry	8.33	9.05	8.69	8.57	10.24	9.41**	0.29	0.68
	Blackberry	13.70	14.02	13.86	13.77	14.90	14.34*	0.42	0.95
Soluble solids (%)	Strawberry	10.12	10.28	10.20	10.29	10.40	10.35	0.21	0.38
	Blackberry	9.70	9.61	9.65	9.75	9.73	9.74	0.18	0.41
Total acids (%)	Strawberry	0.83	0.80	0.82	0.88	0.74	0.81	0.09	0.16
	Blackberry	0.95	1.13*	1.04	0.89	1.07*	0.98	0.09	0.19

*$p < 0.05$.; **$p < 0.01$.
The asterisks indicate a significant difference between means at the value of p mentioned above.

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decreased, but to a small degree. The uncontrolled, unplanned, and in this case excessive addition of compound NPK fertiliser to the soil already containing an optimum available potassium content ($263{\cdot}0\,mg\,kg^{-1}$) and being supplied with available phosphorus ($68{\cdot}0\,mg\,kg^{-1}$) resulted not only in a slight change in acidity, but also in an additional increase in available potassium and phosphorus contents, particularly at the 0–20 cm soil depth. These results are in accordance with those by Stevanovic *et al.* (1999) who reported that high compound NPK fertiliser rates applied annually (in bands) in a blackberry orchard brought about specific disturbances in mineral nutrition, primarily due to the accumulation of higher potassium amounts in the soil. The two-year cattle manure treatment resulted in a humus content increase, particularly at the 0–20 cm soil depth, its content having increased from 2·92 to 3·25%. Considering the average organic matter content of 25·0% in well-matured cattle manure (Džamić and Stevanović, 2000), the reaction was as expected and in line with the results of the stated author.

As opposed to that, the two-year applications of the Agrozel-manure combination resulted in significant changes in soil chemical characteristics. pH was significantly decreased, namely by 0·94 units at the 0–20 cm depth, 0·70 units at the 20–40 cm depth and 0·72 units at the 40–60 cm soil depth. Similar results on acidity decrease were obtained by Jelic *et al.* (2007). Apart from increasing the soil humus content, manure has a favourable effect by decreasing acidity due to the significant proportion of H_2CO_3 (Jakovljević and Pantović, 1991) reacting with the soil adsorptive complex. This results in the formation of $NaHCO_3$ which in the aqueous solution dissolves into weak non-dissociating H_2CO_3 and strong dissociating NaOH, with several OH^- ions occurring in the soil, thus resulting in an acidity decrease (Augstburger, 1983). The exchangeable cation sites of agrozel are occupied by exchangeable divalent metal Ca^{2+} ions (Baerlocher *et al.*, 2001) being substituted in the soil solution with other ions. Once in the soil solution, they indirectly induce decrease in acidity.

It is for similar reasons that the potassium content increased ($>400{\cdot}0\,mg\,kg^{-1}$) at the 0–20 and 20–40 cm soil depths. Agrozel is dominated by the K^+ ion containing mineral clinoptilolite. The ion-exchange property is one of the important characteristics of zeolite, which has the CEC of $216\,mmol\,M^+100\,g^{-1}$ (Baerlocher *et al.*, 2001; Daković *et al.*, 2007). As one of the elements with the highest ion-exchange capacity (Treacy and Higgins, 2001), potassium as an exchangeable ion is easily released from the zeolite lattice into the soil solution, its soil content thus increasing.

Analysis of Strawberry and Blackberry Yields and Basic Fruit Chemical Properties

Fruit species thrive best in neutral to mildly acid soils, with the exception of some species which can be most successfully cultivated also in acid or even alkaline soils with pH_{nKCl} exceeding 10·0, the yields, however, generally decreasing (Singh *et al.*, 1997). Our results on the yield of strawberry and blackberry grown in acid soils conform to the reports by the said authors. The yield increased following different two-year soil treatments.

The average two-year research results for both trial years suggest that a higher strawberry yield was attained in the T_2 soil treatment than in the T_1, the difference being statistically highly significant. This was due to considerable improvements in soil conditions (acidity decrease and humus content increase) in T_2 as opposed to T_1 (Table III).

As a fruit species with a shallow root system, the strawberry responded very rapidly to the improvements in soil conditions induced by the combined use of Agrozel and manure in the soil, resulting in a higher strawberry yield in T_2 than in T_1 as early as in the first research year. This was most likely due to the improvements in soil chemical properties, acidity decrease and humus content increase. Humus has very significant positive effects on the cultivation of all crops (Lal, 2006).

The average study results for both trial years suggest that the T_2 soil treatment gave a higher blackberry yield as opposed to T_1, the difference being statistically significant. This was due to significant improvements in soil conditions (acidity decrease, humus content increase) in T_2 as compared to the T_1 (Table III).

The lower yield increase in the blackberry as compared to that in the strawberry resulted from a deeper root system of the blackberry, with cattle manure and Agrozel being incorporated primarily into the 0–20 cm soil depth.

The T_2 treatment of the blackberry orchard in the second research year induced either highly significant or significant yield differences as compared to other combinations. This was in conformity with the results by Jelic *et al.* (2007), according to which the most pronounced effect of manure application to vertisol was recorded 3 years after treatment.

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The different treatments employed did not significantly affect the content of soluble solids in strawberry and blackberry fruits.

Similar patterns were observed in the total acid contents in strawberry and blackberry fruits. There was a statistically significant difference only in the total acid content between the 2003 and 2002 blackberries in both treatments. Fruit sampling for the analysis was performed at the beginning of August. The results suggest that the high precipitations of 86·7 mm m^{-2} characterising the second half of July and the August of 2003 (Table I) were the main reason for the increased contents of total acids in blackberry fruits as compared to the former year.

CONCLUSION

The results presented in this study may suggest the following: the two-year applications of the Agrozel natural zeolite and manure to the soil resulted in changes in the soil chemical properties. The pH at the depth of 0–20 cm considerably decreased (from 5·07 units prior to trial establishment to 6·01 following the two-year study period). A decrease in pH was also recorded at greater soil depths although it was lower than at the 0–20 cm depth. The humus content at the 0–20 cm soil depth increased from 2·92 to 3·50%. The increase, although lower than the former one, was also registered at the 20–40 cm depth. The content of total nitrogen did not show any significant changes across the soil depth following the two-year treatment with Agrozel and cattle manure. There were, however, increases in phosphorus and particularly potassium contents.

This resulted in higher yields of the crops (strawberries and blackberries) grown in this soil and fertilised with Agrozel and manure over the two-year period than of those treated by standard applications of the NPK fertiliser and manure. The average strawberry and blackberry yields increased from 8·69 to 9·41 t ha^{-1}, and from 13·86 to 14·34 t ha^{-1}, respectively.

Basic chemical properties of the strawberry and blackberry fruits (soluble solids and total acid contents) were not significantly affected by zeolite and organic fertiliser applications to the soil.

The Agrozel type of natural zeolite, when combined with organic fertiliser (manure), can be successfully used to remediate soils having unfavourable chemical properties as well as to enhance the cultivation of certain fruit crops on them.

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