SOIL TREATMENT EFFECTS OF ZEOLITIC VOLCANIC TUFF ON SOIL FERTILITY

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Abstract: *This paper presents the effect of zeolitic volcanic tuff on soil fertility as a consequence of treating soil with zeolitic tuff supplies (clinoptilolite rich tuff). This high silicon tuff type and the essential features of the clinoptilolite has generated in time changes in soil properties like soil reaction, an effective pH buffering, increase of water absorption and cation exchange properties. The effect of using three different doses of zeolitic volcanic tuff, with and without ammonium nitrate addition as fertilizer, on acid soils was assessed by means of physical and chemical soil parameters, biomass and grain yields. The pH increase of soil treated by volcanic tuff alone or mixed with ammonium nitrate confirmed the buffering effect and suggested the opportunity of using volcanic tuff for conditioning and remedying acid soils. An increase of soil humidity and the enrich of calcium, magnesium and potassium content in soil was also observed. The analysis of extractable mineral content showed the contribution of the zeolitic tuff on increasing soil mineral content and fertility. Global soil fertility enhance, particularly in the neighborhood of the rizosphere, was reflected also by biomass and grain yields increase. The obtained results showed the benefit of using the zeolitic volcanic tuff in conjunction with ammonium nitrate to restore the fertility of low fertile soils. The usefulness of the paper is to inform about the zeolitic volcanic tuff features and its action as soil treatment on soil quality. The importance of this research lies in presenting a technology to restore soils with low fertility using a rather cheap natural resource of our land. In Romania, major deposits of clinoptilolite rich tuff can be found near Mirsid, Salaj County and Barsana, Maramures County. The use of zeolitic volcanic tuff in agriculture might be an alternative for fertilizing and amending low fertile soils as part of practicing an ecological agriculture.*

Key words: *zeolitic volcanic tuff, soil fertility, pH, humidity, cation content, crop yield;*

INTRODUCTION

Most of the soils do not fulfil plant nutrition demands during the entire vegetation period. The soil is often unable to supply adequate water and essential nutrients to the plant because of their characteristics, texture and climate. Heavy soils retain water in excess and sandy ones lose it because of their permeability. Acid and alkaline soils are considered low fertile soils. Frequently, nutrients are leached and as a consequence the soil can no longer supply the whole range of nutrients to the plant. Climate, soil features and texture are extremely important for the plant nutrition by influencing processes concerning the presence and quality of cations within soils on short or long term. A higher cation exchange capacity of the soil ensures complete plant nutrition.

Zeolitic volcanic tuffs show good adsorption and ion exchange properties. For these reasons, they are used both for soil conditioning (ALLEN AND MING, 1995 ; MUMPTON, 1998 ; COLLELA, 1999), removal and control of pollutants from soils (GRUBE ET AL., 1993 ; COLLELA, 1999 ; SOBOLEV ET AL., 2001 ; COPPOLA ET AL., 2002 ; MINATO, 2002). The positive effect of zeolitic volcanic tuff addition has also been reflected by a global increase of soil fertility (LAI AND EBERL, 1986 ; BOWMAN ET AL., 1995; MUMPTON, 1998 ; ANDREWS AND KIMI, 2001 ;

ARMBRUSTER, 2001 ; ALELISHVILI ET AL., 2002). Several studies on application of natural zeolites in agriculture have shown that both soil and plant can benefit from zeolite additions. The zeolitic volcanic tuff cannot be considered just as a fertilizer because it is unable to supply adequate amounts of essential nutrients to soil and then make them available to plants. However, it can be used in conjunction with fertilizers and organic enhancements. NH_4^+ and K^+ modified zeolites behave like slow-release nitrogen or potassium fertilizers as part of the uptake of nutrients by plants and may improve soil fertility and water retention.

In Romania, major deposits of clinoptilolite rich tuff can be found near Mirşid- Sălaj County and Bârsana –Maramureş County. The clinoptilolite content in the original mineral ranges from 60 to 70% (POPOVICI ET AL., 1999; BEDELEANU ET AL., 2002).

The irrational use of mineral fertilizers, massive industrial and animal breeding pollution spoiled the Romanian soils. The use of zeolitic volcanic tuffs in agriculture might be an alternative for treating soils, as part of the trend for practising an ecological agriculture.

This paper deals with the use of Romanian zeolitic volcanic tuff as a conditioning and fertilizing material for low fertile soils.

MATERIALS AND METHODS

Experimental set-up

The experiments were carried out on sites belonging to the Banat's University of Agricultural Sciences and Veterinary Medicine, Timisoara. Each experimental plot measured 6 m^2 of Chernozem-type soil and was sown with oat. The experiments referred to soil treated with tuff: 20t/ha (A_1), 40t/ha (A_2) and 60t/ha (A_3). On other three plots, the same tuff doses as before were mixed with 100kg/ha nitrogen (A_4, A_5, A_6) by using ammonium nitrate as fertilizer. The reference alternative consists of untreated soil (C). The experimental alternatives pursued by this research consist of three different doses of tuff without nitrogen addition (A_1, A_2, A_3) and with nitrogen supplement as ammonium nitrate (A_4, A_5, A_6), also a control alternative (C) consisting of untreated soil (table 1). All the experimental alternatives were carried out in three repetitions.

Table 1.

Description of the experimental alternatives

	A_1	A_2	A_3	A_4	A_5	A_6
Volcanic tuff (t/ha)	20	40	60	20	40	60
Nitrogen (kg/ha)	-	-	-	100	100	100

Soil properties

The physical and chemical properties of the experimental soil are shown in table 2 and table 3.

Table 2.

Physical properties of the soil

Particle size distribution (%) :	
-sand	29,20
-silt	29,70
-clay	39,10
Particle density (g/cm^3)	2,42
Apparent density (g/cm^3)	1,28
Total porosity (%)	47,00
Apparent porosity (%)	13,70

Table 3.

Chemical properties of the soil

pH (H_2O)	6,82
Humus content (%)	2,97
Phosphorus content (ppm)	8,50
Potassium content (ppm)	128,00
Calcium content (ppm)	40,00
Magnesium content (ppm)	40,00

Characterization of the zeolitic volcanic tuff

The material experimented in this research is volcanic tuff from Mirşid- Sălaj County. The clinoptilolite content of the tuff , estimated by X-Ray Diffraction, was about 65 wt%. Besides clinoptilolite, the volcanic tuff contains: illite, micas, feldspar, limonite and quartz (Popovici et al., 2000). The chemical composition of the volcanic tuff (wt%), determined in accordance with Minato (1997), was as follows: SiO_2 -69,00; Al_2O_3 -12,68; Fe_2O_3-1,13; CaO -3,57; MgO -0,75; K_2O -2,64; Na_2O -0,60; TiO_2 -0,13. The cation exchange capacity (CEC), also determined in accordance with Minato procedure (1997), was 80 meq/100g.

Soil samples analysis

Soil samples (0-20 cm depth) were collected at harvest time. To highlight the influence of the tuff characteristics and composition, the following soil properties were analysed: pH, humidity, available nutrients. For pH measurement, the soil/water ratio was 1:2,5. In order to establish the effects of soil treatment with volcanic tuff on soil, the available content of soil nutrients was determined. The analysed soil nutrients were potassium, calcium, magnesium and sodium. Calcium and magnesium soil content were analysed by using the EDTA extraction method along with atomic absorbtion spectrophotometry. After extraction by Egner-Riehm-Domingo method, potassium was determined by atomic absorbtion spectroscopy.

Plant samples analyses

Plant samples (biomass and grain production) were collected at harvest time for each experimental alternative. The improvement of soil fertility, after the treatment with volcanic tuff, was assessed by biomass and grain yields.

RESULTS AND DISCUSSION

Effect of zeolitic volcanic tuff on soil pH and humidity

At harvest time, 4 months after the soil treatment with various doses of zeolitic volcanic tuff, the soil reaction and humidity has changed in comparison with the untreated samples (table 4).

Table 4.

Effect of zeolitic volcanic tuff on soil reaction and humidity

Experimental alternatives	Soil reaction (pH / H_2O)	Humidity (wt.%)
C	6,91±0,10	21,11±0,16
A_1	7,44±0,03	29,11±0,30
A_2	7,35±0,02	25,31±0,20
A_3	7,29±0,02	28,18±0,12
A_4	7,27±0,02	27,52±0,07
A_5	7,30±0,02	27,63±0,37
A_6	7,37±0,02	26,36±0,13

Data are averages of three replicates and are expressed as means ± standard deviation.

The cumulative effect of surface charge and the presence of mobile cations within the zeolite's lattice determined the amphoteric character of the zeolite volcanic tuff, which was manifested as a function of the contact environment (acid or alkaline soil). When applied in various doses on soil, the zeolitic volcanic tuff determined the pH increase, which confirmed COLELLA'S (1999) observation. According to COLELLA (1999), the use of volcanic tuff for acid soil conditioning led to effective pH buffering, neutralizes the hydrolytic and exchangeable acidity of soil.

The acid hydrolyses of ammonium nitrate might explain the slight decrease of pH recorded for A_4 (pH=7,27) and A_5(pH=7,30) experiments. The higher pH value noticed for the soil treated with ammonium nitrate and 60 t/ha tuff (A_6) might be the consequence of higher available zeolitic tuff, which was able to retain ammonium ions of the soil within zeolite's pores. The pH values corresponding to soil treated by mixtures of zeolitic volcanic tuff and ammonium nitrate (A_4-A_6) might suggest the opportunity of using zeolitic volcanic tuff on acid soils for remediation purposes.

As rigid porous media, zeolitic volcanic tuff can absorb and retain large amounts of water, thus acting as a reservoir of available water. The results with report to humidity showed indeed the increase of humidity for the soil treated with zeolitic tuff. Compared to the untreated soil(21%), the treated samples showed values ranging from 25% (A_2) to 29% (A_1). The increase of humidity was also noticed, when soil was treated by mixtures of zeolitic volcanic tuff and ammonium nitrate(table 4).

Effect on soil extractable elements

The chemical composition of the zeolitic volcanic tuff used in experiments showed the presence of calcium, magnesium, potassium and sodium. The cation exchange capacity determined ion exchange processes in the soil solution. For acid soils, protons were preferred in ion exchange reactions.

Table 5.

Variation of extractable elements content in soil

Experimental alternatives	Calcium content(mg/kg)	Magnesium content(mg/kg)	Potassium content(mg/kg)	Sodium content(mg/kg)
C	41,0±2,9	38,6±1,2	134.0±1,6	41,7±1,2
A_1	73,0±2,2	52,0±1,0	150,3±2,1	48,3±1,2
A_2	77,0±1,0	55,0±1,0	153,3±1,2	45,6±2,9
A_3	92,7±2,1	61,7±1,2	162,7±2,1	48,3±1,7
A_4	77,3±1,7	58,0±1,6	136,0±1,6	51,0±2,6
A_5	80,7±1,7	54,0±1,6	130,3±1,2	48,0±0,8
A_6	102,6±2,1	66,7±1,2	132,7±2,1	59,3±1,2

Data are averages of three replicates and are expressed as means ± standard deviation

The biomass production in all experiments was higher than

The results obtained for the extractable content of calcium, magnesium, potassium and sodium in soil after the treatment whit volcanic tuff can also be considered from the perspective of clinoptilolite (a major component of the zeolitic tuff) selectivity as against these cations(table 5). The clinoptilolite selectivity for the analysed cations was as follows: Ca< Mg< Na< K. In addition, the acid medium favoured the process of cation depletion within zeolitic structure (PODE, 1999).The analysis of the obtained results confirmed the expected increase of extractable calcium and magnesium along with the increase of the volcanic tuff dose. The lower values of extractable magnesium could be explained by the chemical composition of the zeolitic volcanic tuff. The addition of ammonium nitrate did not determine significant differences, as for the situation when soil was treated only with volcanic tuff.

The content of extractable potassium increased along with the increase of the volcanic tuff dose. For the soil treated by mixtures of volcanic tuff and ammonium nitrate (A_4-A_6), there were no changes as against the control alternative, probably due to the close selectivity of the volcanic tuff for potassium and ammonium. The extractable sodium content in soil increased slightly during experiments as compared to the control alternative.

Effect of zeolitic volcanic tuff on crop yields

In order to estimate the changes of soil fertility, some crop yields such as biomass and grain production were set up (table 6).

Table 6.

Biomass and grain crop yields of oat

Experimental alternatives	Biomass production (kg/ha)	Grain yield (kg/ha)
C	5021±6	2220±4
A_1	5861±6	2858±9
A_2	5766±12	2858±11
A_3	6500±8	3250±8
A_4	5673±17	2648±6
A_5	6020±16	2731±6
A_6	6428±9	2965±15

Data are averages of three replicates and are expressed as means ± standard deviation

The biomass production in all the experiments was higher than that of the control alternative. The increases ranged from 12,9% (A_1) to 29,4% (A_3) as against the reference. The addition of volcanic tuff determined the increase of grain yields. As compared to the reference, the increases were of 19,3% (A_4) till 33,5% (A_6). The secured crop yields confirmed the useful role of the zeolitic volcanic tuff on soil fertility. From the point of view of biomass production, mixtures of zeolitic volcanic tuff and ammonium nitrate are recommended.

CONCLUSIONS

The effect of adding zeolitic volcanic tuff on Chernozem-type soil was studied by analysing some physical and chemical indicators of soil (pH, humidity, content of extractable elements) and crop yields (biomass and grain).

The pH increase of soil treated by volcanic tuff alone or mixed with ammonium nitrate confirmed the buffering effect of the zeolitic volcanic tuff.

The soil humidity increased by adding the zeolitic volcanic tuff, which was also noticed when soil was treated by mixtures of tuff and ammonium nitrate.

The analyses of extractable elements content showed the contribution of the zeolitic volcanic tuff to the cation content and fertility of the soil. The element content depended not only on the chemical composition of the volcanic tuff, but also on its selectivity towards cations within soil. The selectivity might determine competition among ion exchange processes.

From the point of view of grain yields and biomass production, both tuff adding alone or as a mixture with ammonium nitrate are recommended.

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BIBLIOGRAPHY

1. ALELISHVILI, M., TSITSISHVILI, G., ANDRONIKASHVILI, T., SKHIRTLADZE, N., TSITSISHVILI, V., DOLABERIDZE, N., MIRDZVELI, N., NIJARADZE, M. AND KARDAVA, M. (2002): Agricultural application of analcime. In: 6th International Conference on the Occurrence, Properties and Utilization of Natural Zeolites. Book of Abstracts, Thessaloniki, Greece.
2. ALLEN, E.R. AND D.W. MING (1995): Recent progress in the use of natural zeolites in agronomy and horticulture. In: Natural Zeolites '93, Int.Comm. Natural Zeolites, Brokport, NY
3. ANDREWS, R.D. AND S.B. KIMI (2001): Improvements in yield and quality of crops with NASA zeoponic fertilizer delivery systems : turf, flowers, vegetables and grain. In: Zeolites and Mesoporous Materials at the Dawn of the 21st Century, Stud. Surf. Sci. Catal.135,
4. ARMBRUSTER, TH.(2001): Clinoptilolite-heulandite: applications and basic research. In: Zeolites and mezoporous materials at the Dawn of the 21st Century, Stud. Surf. Sci. Catal. 135,
5. BEDELEANU, H., BEDELEAN, I., POP, D., ARGHIR, G., CALB, I., POPOVICI, E., AND GR. PETRUT (2002)Clinoptilolite-rich pyroclastic deposits from Transilvania, 6th International Conference on the Occurrence, Properties and Utilization of Natural Zeolites, Book of Abstracts, Thessaloniki, Greece.
6. BOWMAN,R.S., HAGGERTY, G.M., HUDDLESTONE, R.G., NEEL, D., AND M.M. FLYNN (1995): Sorption of nonpolar organic compounds, inorganic cations and inorganic oxianions by surfactant-modified zeolite. In: Surfactant-enhanced subsurface remediation, ACS Symposium Series, 594.
7. COLLELA,C. (1999): Natural zeolites in environmentally friendly processes and applications. In: Porous materials in environmentally friendly processes, Stud. Surf. Sci. Catal.125.
8. COPPOLA, E., BATTAGLIA, G., BUCCI, M., CEGLIE, D., COLLELA, A., LANGELLA, A., BUONDONNO, A.(2002): Recovering Cd and Pb-polluted soil by treatment with an organo-zeolite, 6th International conference on the occurrence,properties and utilization of natural zeolites, Book of Abstracts, Thessaloniki, Greece.
9. GRUBE, JR., W.E., AND J.G. HERRMANN (1993): Heavy metal pollutant fixation by natural zeolites. Proceedings of the 4th International Conference on the Occurrence, Properties and Utilization of Natural Zeolites, Idaho, USA.
10. LAI, T.M. AND D.D. EBERL (1986): Controlled and renewable release of phosphorous in soils from mixture of phosphate rock and NH_4-exchanged clinoptilolite. Zeolites 6.
11. MINATO, H. (1997): Standardization of methods for zeolite speciality determination and techniques for zeolite resources utilization, Natural Zeolites, Sophia'95, Pensoft Publishers,
12. MINATO,H. (2002): New techniques with applications for zeolites associated to clays for the remediation of polluted soils and clay barriers, 6th International Conference on the Occurrence, Properties and Utilization of Natural Zeolites, Book of Abstracts, Thessaloniki, Greece.
13. MUMPTON, F.A. (1998): The role of natural zeolites in agriculture and aquaculture, Zeo-Agriculture, Westview Press, Boulder, Colorado.
14. PODE, R., BURTICA, G., PODE, V. AND POPOVICI, E. (1999): Sorption of transient metal ions into clinoptilolite from waste water and recycling the used zeolite into a composite fertilizer. In: Porous Materials in Environmentally Friendly Processes, Stud. Surf. Sci. Catal. 125.
15. POPOVICI, E., BURTICA, G., PODE, R., BEDELEANU, I. AND CALB, I. (1999): Romanian volcanic tuffs exploitation in environmental protection. In: Natural microporous materials in environmental technology. Kluwer Academic Publishers, Netherland.

16. POPOVICI, E., BURTICA, G., PODE, R., MARCU, C., IVAN, M. AND CURUCIUC SUCEVEANU, A. (2000): The physicochemical study on obtainment and ecological application on manganese-modified clinoptilolite. Balkan Physics Letters.
17. SOBOLEV, W., ILYIN, V., BOBONICH, F. AND BARANY, S. (2001): Application of sorbing composites on natural zeolite basis for heavy metals contaminated territories rehabilitation. In: Zeolites and mesoporous materials at the Dawn of the 21st Century, Stud. Surf. Sci. Catal. 135, CD.