

# Crop response to the application of special natural amendments based on zeolite tuff

A. Butorac<sup>1</sup>, T. Filipan<sup>2</sup>, F. Bašić<sup>1</sup>, J. Butorac<sup>1</sup>, M. Mesić<sup>1</sup>, I. Kisić<sup>1</sup>

<sup>1</sup>Faculty of Agriculture, University of Zagreb, Croatia

<sup>2</sup>Institute for Development, Zagreb, Croatia

## ABSTRACT

The conception of these investigations is based on the premise that a way should be found to eliminate, or at least mitigate, the harmful effect of excessive soil acidity without resorting to the massive and costly measures of liming. The main issue addressed in this study is how to increase crop yield by increasing nutrient availability rather than how to neutralize the soil. This as well as our earlier investigations, conducted on pseudogley of mesoelevations, indicate that this can be achieved by the application of special natural amendments (SNA) based on zeolite tuff, under the name Agrarvital (AV), in which clinoptilolite prevails while the remaining part is a mixture of soft lithothamnian limestone and dolomite (SLL+D). These amendments enhance ion exchange in the soil and their activation at a considerably lower pH than it is the case after liming. Fertilizing value of Agrarvital (AV) and lime materials (LM) was evaluated according to the yields achieved and some yield components of the crops grown. The results point to the good fertilizing effect of AV upon yields of winter wheat, maize, soybean and winter barley, equal to or better than the effect of conventional LM applied at several times higher rates.

**Keywords:** fertilizing value; special natural amendments; zeolite tuff; yield and yield components

A number of adverse side effects characterize acid soils. Certain crops simply do not thrive at increased acidity and require neutral reaction. Lime materials (LM) amend these conditions by neutralizing adverse soil acidity. There are, naturally, also other practices that can eliminate or mitigate the adverse effect of excessive soil acidity. Our aim was to do this without resorting to the massive and costly measures of liming, and to eliminate excessive acidity by making use of the well known antitoxic action of LM. Thus, the main issue is how to prevent harmful fixation and retrogradation of soil plant nutrients rather than how to neutralize soil at any cost because, besides its positive effects, neutralization also carries negative side effects. According to some theoretical findings, but also our own experience and laboratory research, we think that this can be achieved by the application of special natural amendments (SNA) based on zeolite tuff, that is, the product available under the commercial name Agrarvital (AV). However, not in terms of eliminating excessive acidity but in terms of intensified exchange of ions, and their activation at a much lower soil pH than it is the case after liming. This supposed to be their advantage over all materials applied for soil neutralization. Zeolites very efficiently retain water and bases, absorb them and exchange them with the same intensity as, for example, montmorillonite. Bases in zeolites are exchanged in equivalent ratios. Ion exchange continues until osmotic pressure is equalized in the crystal and in the solution containing it.

Croatian experience in the application of zeolite tuff based SNA in agriculture and forestry is positive, including research conducted directly under our charge in Aus-

tria (Filipan et al. 1989, 1991a, Butorac et al. 1990, 1992, 1994, 1995a–e, Butorac and Filipan 1996, Mesić 1996).

Zeolite may also be used for other purposes, of which we particularly emphasize their application in water treatment, which has been extensively researched in Croatia (Filipan et al. 1991b, 1997, Ružinski et al. 1993, Cerjan-Stefanović et al. 1994a, 1996 etc.). Attention of researchers in Croatia was attracted by investigations of ion exchange characteristics of modified zeolite (Cerjan-Stefanović et al. 1992) and ion exchange of metal ions by natural zeolites (Cerjan-Stefanović et al. 1994b, Čurković et al. 1997).

Zeolite application in agriculture was studied, naturally, also on a wider global plan (Barbarick and Pirela 1984, Gworek 1992, Allen and Ming 1993, Boettinger and Graham 1993, Eberl 1993, Grube and Herman 1993 etc.). Zeolites are capable of releasing readily soluble nutrients already present in the soil (Eberl 1993) or, for instance, prevent nitrogen loss in urea hydrolysis (Boettinger and Graham 1993). Considerable attention is being paid to natural zeolites as agents immobilizing heavy metals from the groundwater and harmful waste dumps (Grube and Herman 1993). Clinoptilolite and other zeolites possess a cation exchange capacity between 100 and 300 meq/100 g, as well as a high  $K^+$  and  $NH_4^+$  selectivity. Retention of  $NH_4^+$  in structural channels of the mineral may prevent its oxidation into  $NO_3^-$  by bacteria and contribute to reducing the losses of ammonium fertilizers through leaching (Barbarick and Pirela 1984). The primary goal of this research was to test the fertilizing value of SNA based on zeolite tuff, that is, their effect upon the yield and some yield components of certain important field crops as well as on some soil chemical properties.

## MATERIAL AND METHODS

The trial was set up on pseudogley of mesoelevations on locality Lipovljani in central Croatia, in October 1990. In accordance with the research goal, the last basic tillage practice in the trial was preceded by the application of SNA (AV), and LM (quicklime – QL, and mixture of softlithothamnian limestone and dolomite – SLL+D), once for all four trial years. The trial involved a relatively large number of treatments. The fertilizing value of LM and SNA was studied in combination with full and half-mineral fertilizer rates. SNA consist of zeolite tuff, or volcanic ash, containing acid minerals: clinoptilolite with Al/Si ratio 1:5 and phillipsite with Al/Si ratio 1:3, as well as basic minerals: gismondine with Al/Si ratio 1:1 and analcime with Al/Si ratio 1:2. They can be represented by the formula:  $(Me_2)_n \times Al_2O_3 \times SiO_2 \cdot y$ , where  $n$  is the number of cations, and  $x$  and  $y$  depend on zeolite type and are greater than 2. In AV that we studied, clinoptilolite with a very favourable C.E.C. prevailed. AV 01 contains 30% and AV 02 45% zeolite tuff. The remaining part involves SLL+D. Chemical composition of AV, depending on the input components and their mutual ratios, is variable and approximately ranges in the following ratios and percent: water 4.41–9.49, crude ash 82.78–94.78, organic matter 2.69–4.19, CaO 24.50–37.50, SiO<sub>2</sub> 12.50–35.30, F<sub>2</sub>O<sub>3</sub> 0.60–2.90, MgO 5.60–8.50, Al<sub>2</sub>O<sub>3</sub> 2.50–8.90, total K<sub>2</sub>O 0.20–0.61, total Na<sub>2</sub>O 0.43–2.00, carbonic acid 13.37–32.83, total N 0.01–0.08, and total P<sub>2</sub>O<sub>5</sub> 0.02–0.06. Expressed in mg.kg<sup>-1</sup>, copper content amounts to 2.0–20.0, manganese 16.0–136.0, zinc 10.0–26.0, and cobalt 1.4–1.5, while pH ranges from 7.66 to 8.85. SNA (AV) are produced on a silicate carbonate basis and, according to the international classification, they may be classified as amendments that increase soil fertility and ensure undisturbed cycling of plant nutrients in the soil–plant system, influence ion exchange in soil, bind heavy metals and ammonium molecules etc. They are produced in powder form and in granules. Powder particle size ranges from 0.0 mm to 0.36 mm, and that of granules from 3 mm to 5 mm.

Trial treatments can be seen from the table containing results. The trial was set up according to the Latin rectangle method in four replications. Trial plots were 40 m<sup>2</sup>. Sequence of crops involved in the given order: winter wheat, maize, soybean, and winter barley. Standard agrotechnical practices were applied. As regards to fertilization, 160, 66 and 116 kg.ha<sup>-1</sup> N, P and K, respectively, were applied to winter wheat, 180, 66 and 133 kg.ha<sup>-1</sup> to maize, 55, 49 and 131 kg.ha<sup>-1</sup> to soybean (seed was inoculated with *Bradyrhizobium japonicum*), and 135, 44 and 116 kg.ha<sup>-1</sup> to winter barley. The above figures refer to full rates while the trial also involved their half quantities.

Lower QL rate (1) amounted to 3.4 and higher (2) to 6.8 t.ha<sup>-1</sup>, lower AV rate (1) (both types) to 1.5 and higher (2) 3.0 t.ha<sup>-1</sup>, while the lower rate (1) of the mixture of SLL+D was 6.0 and its higher rate (2) 12.0 t.ha<sup>-1</sup>, which in terms of the LM chemical guarantee, i.e. neutralization value, corresponds to the lower and higher rates of QL, respectively.

Yield and some yield components of tested crops, as well as the changes in some soil chemical properties (given in the other paper), served as the main indicators for assessing the efficiency, i.e. fertilizing value, of SNA (AV). This paper, therefore, gives only the basic soil chemical characteristics of pseudogley. They can be briefly summed up as follows: soil pH in Ap, Eg and Bg horizons is, respectively, 3.9, 3.9 and 4.0, hydrolytic (non-exchangeable) acidity  $y_1$  19.0, 19.0 and 15.2, mobile aluminium content 15.8, 15.8 and 14.7 mg.100 g<sup>-1</sup> soil, and base saturation 32.2, 32.2 and 51.5%. Values for the following indicators refer only to the Ap horizon and amount to: humus 1.6%, available phosphorus, potassium and magnesium 18.0, 14.0 and 11.4 mg.100 g<sup>-1</sup> soil, respectively, iron, zinc, copper and manganese 283.6, 2.48, 1.14 and 95.6 mg.100 kg<sup>-1</sup>, respectively. The results were processed by means of the analysis of variance and Duncan's Multiple Range Test (Duncan 1955).

## RESULTS AND DISCUSSION

### Winter wheat

Relatively high yields of winter wheat, cultivar Marija, were achieved in the trial (Table 1). Our interest, however, is directed to the efficiency of particular fertilizers and amendments with regard to yield. The results reflect major typical characteristics of soil (pseudogley), including primarily its actual fertility, and the fertilizing value of SNA (AV) and different types of LM. It was just in the fertilizing effect that certain differences were set out between particular treatments, whereby the applied AV types excelled in efficiency, particularly considering the rates applied. By comparison with the traditional LM, these rates were several times lower while the effects were the same or even better, depending on the type and rates of AV applied.

To be specific, relatively best trial treatments regarding the grain yield of winter wheat were the treatments involving the full mineral fertilization in combination with either higher QL, or higher AV 01 rate. These were followed by the treatments with full mineral fertilization combined with lower AV 01 rate, lower QL rate etc. In terms of statistical significance, equal to them were the treatments involving full mineral fertilization alone or combined with both rates of all amendments, i.e. QL, the mixture of SLL+D, and both AV types, and trial treatments with half mineral fertilization combined with both rates of QL and SLL+D. Pure mineral fertilization was significantly better than the treatments involving half mineral fertilization alone or in combination with the lower rate of mixture of SLL+D, and both rates of AV 01 and AV 02. Consequently, half rate of mineral fertilization in combination with LM and SNA showed a high degree of efficiency as well. AV application on more acid soils should be preceded by a mild form of liming, with possible simultaneous application of both of these materials. Besides its agrotechnical and ecological importance, this is certainly a very

Table 1. Yield and yield components of winter wheat

Treatment	Grain yield (t.ha <sup>-1</sup> )	1000 grains mass (g)	Hectolitre mass	No. of spikes per m <sup>2</sup>
NPK	6.66 abcd	37.5 bcde	76.9 bcd	438 efg
½ NPK	4.95 e	37.0 de	76.4 d	434 efg
NPK + QL – 1	7.45 ab	39.0 a	77.6 abcd	453 bcde
NPK + QL – 2	7.82 a	38.3 abcd	78.2 a	455 bcde
½ NPK + QL – 1	6.41 abcde	38.8 ab	77.4 abcd	431 fg
½ NPK + QL – 2	6.56 abcd	37.8 abcde	77.2 abcd	445 def
NPK + SLL + D – 1	7.14 abc	38.8 ab	77.3 abcd	447 cdef
NPK + SLL + D – 2	7.42 ab	37.8 abcde	77.9 ab	445 def
½ NPK + SLL + D – 1	6.00 bcde	37.3 cde	77.2 abcd	449 bcdef
½ NPK + SLL + D – 2	6.29 abcde	38.8 ab	78.0 ab	452 bcdef
NPK + AVo1 – 1	7.45 ab	38.5 abc	76.9 bcd	463 abcd
NPK + AVo1 – 2	7.76 a	38.8 ab	76.5 cd	483 a
½ NPK + AVo1 – 1	5.20 de	38.3 abcd	77.0 abcd	431 fg
½ NPK + AVo1 – 2	5.81 cde	36.8 e	77.4 abcd	468 abc
NPK + AVo2 – 1	7.19 abc	37.5 bcde	77.2 abcd	421 g
NPK + AVo2 – 2	7.41 ab	38.0 abcde	77.7 abc	469 ab
½ NPK + AVo2 – 1	5.43 de	37.3 cde	77.1 abcd	423 g
½ NPK + AVo2 – 2	5.83 cde	37.3 cde	77.5 abcd	467 abc
LSD 5%	1.32	1.10	1.02	18.81

important economic issue, primarily in terms of prices and optimal rates of both of these amendments. Namely, the applied rate of the mixture of SLL+D is four times higher than the rates of particular types of AV, suggesting that the AV efficiency results from its enhanced ion exchange, that is, owing to tuff AV exerts a complex positive effect on the soil (Filipan et al. 1989, Butorac et al. 1990, 1995d).

As regards the purpose and role of half mineral fertilizer rates, which rendered about one quarter lower yield than full mineral fertilization, one should start from the assumption that nitrogen is the key nutrient in plant nutrition and that within mineral fertilization, it was primarily nitrogen that restricted yields. Biological activation of soil nitrogen was naturally present, however at lower soil temperatures and abundant precipitation it could not have been considerable, which might explain the achieved yields of winter wheat grain in the treatment with half mineral fertilizer rates. Still, the first year results already point to a positive outcome of fertilizing effect of SNA in terms of the expressed conception, especially if the ultimate aim is not the achievement of maximum yield and if the ecological aspect of fertilization is observed, i.e. soil and groundwater protection from contamination. This is in agreement with some of our previous results (Filipan et al. 1991a, Boetlinger and Graham 1993, Grube and Herman 1993, Butorac et al. 1995d). Owing to the mechanisms of its action, the fertilizing effects of AV are obvious.

In the case of the winter wheat yield components, statistically significant differences were obtained for 1000 grains and hectolitre mass and number of spikes per m<sup>2</sup>, though the latter indicator is not a typical yield component, but it naturally largely determines wheat yield (Table 1). In the case of 1000 grains and hectolitre mass,

without going into a more detailed analysis of the results and besides a certain degree of statistical significance, it may be pointed out that the differences between treatments were only slight. As a rule, the best treatments with regard to the number of spikes per m<sup>2</sup> were those involving combined application of mineral fertilizers and SNA, in some treatments even if only half rates of mineral fertilizers were applied.

## Maize

Yields of maize, hybrid Pioneer 3737, achieved in fertilizing treatments range broadly from 5.91 in half mineral fertilization rate to 8.18 t.ha<sup>-1</sup> in the treatment involving combined application of full mineral fertilization and the higher rate of AV 02 (Table 2). This year's results point to increased AV efficiency, naturally taking into the account its type, and applied rate. As a rule, the higher rate has advantages over the lower one, and so does AV with a higher participation of zeolite tuff. This yield is also significantly higher than yields in all the other treatments, except for the combined application of full mineral fertilization with the higher rate of the mixture of SLL+D, and the lower rate of the same AV type. This yield is followed by those obtained in treatments involving combined application of full mineral fertilization and higher rate of QL and lower rate of the mixture of SLL+D, and then in the treatment with combined application of mineral fertilization and the higher AV 01 rate. All the other treatments are significantly worse than the foregoing ones. In terms of statistical significance, treatments with half rates of mineral fertilizers and higher and lower rates of LM and SNA are rather uniform, however with the advantage of

Table 2. Yield and yield components of maize

Treatment	Grain yield (t.ha <sup>-1</sup> )	1000 seeds mass (g)	Hectolitre mass	Length of cob (cm)	No. of rows on cob	No. of kernels in row
NPK	6.04f g	258.7 cde	69.4 bcd	18.8 a	17 a	36 c
½ NPK	5.91 g	249.5 efg	69.2 cd	18.0 bcde	17 a	37 b
NPK + QL – 1	7.00 cde	249.8 efg	70.1 abcd	17.6 de	16 b	35 d
NPK + QL – 2	7.49 bc	268.8 b	70.8 a	17.6 de	17 a	36 c
½ NPK + QL – 1	6.61 def	237.8 h	69.9 abcd	18.0 bcde	17 a	37 b
½ NPK + QL – 2	6.90cde	242.9 fgh	69.1 d	18.8 a	17 a	38 a
NPK + SLL + D – 1	7.46 bc	261.8 bcd	70.2 abc	18.1 bcd	17 a	36 c
NPK + SLL + D – 2	7.70 ab	282.7 a	70.8 a	18.5 ab	16 b	37 b
½ NPK + SLL + D – 1	6.53 def	242.2 fgh	69.1 d	18.3 abc	16 b	35 d
½ NPK + SLL + D – 2	6.83 de	252.0 def	69.8 abcd	18.5 ab	17 a	37 b
NPK + AVo1 – 1	6.63 def	255.8 cde	70.4 ab	18.2 abcd	16 b	37 b
NPK + AVo1 – 2	7.12 bcd	264.1 bc	70.0 abcd	18.6 ab	17 a	37 b
½ NPK + AVo1 – 1	6.48defg	240.5 gh	69.4 bcd	18.0 bcde	16 b	36 c
½ NPK + AVo1 – 2	6.68 de	253.5 de	70.2 abc	18.4 ab	17 a	36 c
NPK + AVo2 – 1	7.71 ab	253.4 cde	69.4 bcd	17.7 cde	16 b	36 c
NPK + AVo2 – 2	8.18 a	271.3 b	70.4 ab	18.3 abc	16 b	36 c
½ NPK + AVo2 – 1	6.37 efg	255.7 cde	68.1 e	17.4 e	16 b	34 e
½ NPK + AVo2 – 2	6.71 de	255.2 cde	69.1 d	18.2 abcd	17 a	37 b
LSD 5%	0.54	9.28	0.86	0.58	0.61	0.80

higher rates over the lower ones, which led to certain significant differences between these treatments. We find it noteworthy that all of these treatments with higher lime and AV rate were significantly better than the full mineral fertilization by itself.

Compensational effect of AV, in the broadest sense, relative to full mineral fertilization deserves special mention, since AV, notably its higher rate, in combination with the half mineral fertilizer rate surpasses in efficiency sole mineral fertilization at its higher rate. This was also one of the major premises governing our choice of fertilizing treatments, i.e. grading of mineral fertilization. In addition to the applied AV rate, AV type played a role as well, that is, the participation of zeolite tuff in it in terms of a more efficient action of the higher rate of AV as well as of AV with a higher zeolite tuff content, similarly to some other results on leached acid soil (Mesić 1996).

The 1000 kernels mass, as the main yield component, was under more pronounced influence of the applied fertilization (Table 2). Not going into a detailed analysis of the achieved results, it can be generally concluded that the effect of the studied factors was very variable, as indicated by the results of the performed DMRT. As regards hectolitre mass, it may be pointed out that the differences between treatments were slight, but with a certain degree of significance among some of them (Table 2). Length of cob was also influenced significantly to a certain degree by trial treatments (Table 2). Number of rows on cob, as the primary and mainly poorly variable yield component, thus negligibly influenced by external factors, reflects just this situation (Table 2). Number of kernels in row differs also negligibly in most treatments,

but still with certain significant differences between treatments involving combined application of half-mineral fertilizer rates with amendments (Table 2).

### Soybean

Yields of soybean seed, cultivar Crusader, vary from 2.93 in half mineral fertilizer rate to 3.58 t.ha<sup>-1</sup> in the treatment involving combined application of half mineral fertilization and higher rate of QL (Table 3). In the same rank with this treatment are also the majority of the remaining treatments involving primarily higher rates of LM and AV in combination with full and half rates of mineral fertilization. High efficiency was consequently recorded in treatments involving half mineral fertilizer rates combined with both rates of the mixture of SLL+D, lower QL rate, both AV types etc. Separate analysis of each treatment would take us too far.

Full mineral fertilization, nonetheless, deserves special mention, which naturally implies a reduced amount of applied nitrogen on account of inoculation. This treatment is among the least efficient trial treatments. Not disregarding potassium, or phosphorus, requirements of soybean, the dominant effect may certainly be ascribed to nitrogen, which soybean had to provide in sufficient quantities through fixation of atmospheric nitrogen by nitrogen fixing bacteria. Therefore, not even the higher nitrogen rate could greatly affect the yield, though it might have led to a reduced activity of nitrogen fixing bacteria, even node atrophy. Though this was not the object of our investigations, it logically fits into their basic conception. In this connection, it could be emphasized that higher rates of both AV types combined with

Table 3. Yield and yield components of soybean

Treatment	Seed yield (t.ha <sup>-1</sup> )	1000 seeds mass (g)	Hectolitre mass	No. of pods per plant	No. of seeds per pod
NPK	3.09 de	186.9 bc	65.9 abcde	44 a	4 b
½ NPK	2.93 e	182.0 c	64.6 bcde	31 efg	4 b
NPK + QL – 1	3.19 cde	193.0 ab	64.4 cde	31 efg	4 b
NPK + QL – 2	3.45 abc	195.9 a	65.1 abcde	42 ab	4 b
½ NPK + QL – 1	3.29 abcd	190.5 ab	63.6 e	33 cdefg	4 b
½ NPK + QL – 2	3.58 a	192.5 ab	66.2 abcde	42 ab	4 b
NPK + SLL + D – 1	3.17 cde	189.0 abc	64.5 cde	29 g	4 b
NPK + SLL + D – 2	3.37 abcd	191.5 ab	67.0 abc	38 abcde	4 b
½ NPK + SLL + D – 1	3.26 abcde	192.7 ab	67.7 a	37 abcdef	4 b
½ NPK + SLL + D – 2	3.33 abcd	192.4 ab	67.4 ab	39 abcd	4 b
NPK + AVo1 – 1	3.10 de	186.4 bc	64.1 de	34 cdefg	4 b
NPK + AVo1 – 2	3.22 bcde	185.5 bc	64.9 abcde	35 bcdefg	4 b
½ NPK + AVo1 – 1	3.18 cde	187.2 bc	65.4 abcde	30 fg	5 a
½ NPK + AVo1 – 2	3.54 ab	193.1 ab	67.4 ab	36 bcdefg	5 a
NPK + AVo2 – 1	3.08 de	191.8 ab	66.0 abcde	34 cdefg	4 b
NPK + AVo2 – 2	3.25 abcde	191.3 ab	66.8 abcd	40 abc	4 b
½ NPK + AVo2 – 1	3.20 cde	185.7 bc	66.4 abcd	32 defg	4 b
½ NPK + AVo2 – 2	3.44 abc	185.7 bc	67.7 a	33 cdefg	4 b
LSD 5%	0.28	6.38	2.35	6.49	0.28

half mineral fertilizer rate are significantly better than full and half rates of mineral fertilizers. Creation of favourable conditions for the action of nitrogen fixing bacteria, by elimination of excessive soil acidity, reduction of mobile aluminium content and increased base saturation by liming, has a direct effect on yield through increased fixation of atmospheric nitrogen. This is in agreement with some previous investigations (Butorac et al. 1992).

We have pointed out only some of the key treatments with which AV may equally compare in order to objectively evaluate its fertilizing value. Irrespective of the type and rate, it may be concluded that AV efficiency is still very high though three years have passed from its application to the soybean growing season. Its efficiency can still compare to that of traditional LM, which were applied at several times higher rates. It is just one of the main advantages of AV that applied at much lower rates it can be equally efficient, even more efficient than conventional LM owing to clinoptilolite as its most active component (Filipan et al. 1989). Some new facts were found for soybean, as a member of *Fabaceae* for which seed inoculation was performed, in which both AV types demonstrated the highest efficiency at the full and half rates of mineral fertilizers.

Significant differences were recorded for the 1000 seeds and hectolitre mass (Table 3). It is noteworthy that the group of treatments with favourable 1000 seeds and hectolitre mass includes a fair number of treatments involving half mineral fertilizer rates combined with LM and both AV types. As regards the number of pod per plants, it must be mentioned that the effects of the studied treatments were relatively heterogeneous although they are very closely related to particular types of amendments

or their rates (Table 3). Still, it is a fact that the number of seeds per pod was very uniform (Table 3).

### Winter barley

Grain yield of winter barley, cultivar Sladoran, varies in a rather wide range, from 2.49 t.ha<sup>-1</sup> in half mineral fertilization to 3.78 t.ha<sup>-1</sup> in full mineral fertilization combined with the higher rate of AV 01 (Table 4). The leading trial treatments being generally those in which higher rates of both AV types were added to full mineral fertilization including combined treatments of higher rates of QL and SLL+D, also with full mineral fertilization.

From the viewpoint of the research goal itself, mention should be made of the exceptionally good response of barley to the application of AV in combination with full mineral fertilization, equal or even better relative to the traditional LM applied at common ameliorative rates, as well as the generally known fact that barley prefers slightly acid to neutral soils. AV application had little effect upon the reduction of soil acidity by comparison to the applied lime materials (Butorac et al. 2002) but, owing to intensive ion exchange (Butorac et al. 1995d), it had a good effect on soil fertility (Butorac et al. 1995b), and thereby also on the barley grain yield. Still, a somewhat better but not significantly better effect than that of AV 02 was recorded for Agrarvital 01. In other words, it is supposed that the positive effects of AV are partly also due to its lime component.

Without going into a detailed analysis of interrelations between particular treatments, it can be said in summary that the applied LM and AV continue showing high effi-

Table 4. Yield and yield components of winter barley

Treatment	Grain yield (t.ha <sup>-1</sup> )	1000 grains mass (g)	Hectolitre mass	No. of spikes per m <sup>2</sup>	Length of spike (cm)	No. of spikelets in spike	No. of grains in spike
NPK	2.90 cde	44.1 ab	63.0 bc	483 d	5.6 a	21 a	21 a
½ NPK	2.49 e	43.2 bcd	61.5 d	404 g	4.8 c	18 c	17 d
NPK + QL – 1	3.14 abcde	42.9 cd	62.6 bc	485 d	5.5 ab	20 ab	20 ab
NPK + QL – 2	3.60 abc	43.2 bcd	62.9 bc	590 a	5.4 ab	21 a	20 ab
½ NPK + QL – 1	3.15abcde	43.2 bcd	62.9 bc	353 h	5.1 bc	20 ab	19 bc
½ NPK + QL – 2	3.06 abcde	44.2 ab	63.2 abc	497 cd	5.6 a	21 a	21 a
NPK + SLL + D – 1	3.48 abcd	43.2 bcd	62.8 bc	450 ef	5.3 ab	20 ab	19 bc
NPK + SLL + D – 2	3.70 ab	43.7 bcd	63.7 ab	485 d	5.5 ab	19 bc	20 ab
½ NPK + SLL + D – 1	3.02 bcde	43.5 bcd	63.2 abc	446 ef	5.1 bc	19 bc	18 de
½ NPK + SLL + D – 2	3.18 abcde	44.8 a	64.3 a	458 ef	5.4 ab	19 bc	19 bc
NPK + AVo1 – 1	3.41 abcd	42.7 d	62.5 c	505 cd	5.4 ab	20 ab	20 ab
NPK + AVo1 – 2	3.78 a	43.1 bcd	63.3 abc	543 b	5.5 ab	21 a	20 ab
½ NPK + AVo1 – 1	3.26 abcd	43.6 bcd	63.5 abc	435 f	5.1 bc	19 bc	18 cd
½ NPK + AVo1 – 2	3.45 abcd	44.0 abc	63.4 abc	460 e	5.2 abc	20 ab	20 ab
NPK + AVo2 – 1	3.58 abc	42.8 d	63.3 abc	401 g	5.4 ab	20 ab	19 bc
NPK + AVo2 – 2	3.73 ab	43.2 bcd	63.6 abc	519 c	5.6 a	21 a	20 ab
½ NPK + AVo2 – 1	2.77 de	43.6 bcd	63.1 bc	405 g	5.2 abc	19 bc	18 cd
½ NPK + AVo2 – 2	2.93 cde	43.6 bcd	63.3 abc	487 d	5.5 ab	19 bc	19 bc
LSD 5%	0.61	0.92	0.97	21.24	0.40	1.55	1.54

ciency in the fourth season, with marked advantage of AV, at the applied rates. However, the reported efficiency was probably largely dependent on the adverse soil moisture caused by occasional severe droughts. For an objective appraisal of the efficiency of the applied rates of both AV types with regard to yield, it might be assumed that the upper limit regarding the duration of the effect has been reached, which also holds for the applied LM, and that the downward trend of their still satisfactory efficiency has started.

Determination of winter barley yield components involved 1000 grains mass and hectolitre mass, the number of spikes, the length of spike, the number of spikelets in spike and the number of grains in spike (Table 4). Not going into a detailed analyses of the obtained results regarding all of the mentioned yield components it could be said, that statistically significant differences, to a certain degree, are recorded among trial treatments. Generally speaking, they are relatively weakly expressed in consideration of 1000 grains and hectolitre mass, and the length of the spike. Of course, in this connection there exists weaker or stronger correlation between yield components and grain yield of winter barley.

Recognizing the rather specific response of each crop to the treatments applied in the trial, the results achieved, primarily yield, point to the excellent fertilizing effect of SNA based on zeolite tuff, as well as to their obvious advantage over traditional LM. Even more so as traditional liming, besides its numerous positive effects, hides in itself also some negative ones, primarily with respect to soil, and its biophase (Person 1988). These may be avoided by the application of SNA based on zeolite tuff and,

at the same time, economic effects may be achieved in addition to the fertilizing effect.

## REFERENCES

- Allen E.R., Ming D.W. (1993): Zeolites in agronomic and horticultural applications – a review. Oklahoma St. Univ., NASA-Johnson Spec. Centar Houston, Ze' 93: 31–32.
- Barbarick K.A., Pirela H.J. (1984): Agronomic and horticultural uses of zeolites: a review. *Zeo-Agriculture*: 95–106.
- Boettinger J.L., Graham R.C. (1993): Zeolite occurrence and stability in soils: an updated review. *Ze' 93*: 49–50.
- Butorac A., Bašić F., Mesić M., Mikolčić S. (1990): Valorizacija različitih vapnenih materijala u kalcifikaciji kiselih tala SP PIK Virovitica. [Studija.] Fak. Poljopriv. Znan.
- Butorac A., Filipan T. (1996): Möglichkeiten der Rekultivierung von Braunkohlekippen im Gebiet von Seftenberg, Deutschland. Präliminarber. Landwirtschaft. Fak. Zagreb, Inst. Entw. Int. Bezieh., Zagreb.
- Butorac A., Filipan T., Bašić F., Mesić M. (1994): Untersuchungen hinsichtlich des Düngungswertes der speziellen natürlichen Substrate (Agrarvital) auf des Basis von Zeolith Tuff. *Mehrjber. Landwirtschaft. Fak. Zagreb, Inst. Entw. Int. Bezieh., Zagreb. Wiss. Ber.*
- Butorac A., Filipan T., Bašić F., Mesić M., Butorac J., Kisić I. (1995a): Response of sugar beet to Agrarvital and waste water fertilizing. I. Root and sugar yield and macronutrient content in root and leaf. *Poljopriv. Znan. Smotr.*, 60: 69–80.
- Butorac A., Filipan T., Bašić F., Mesić M., Butorac J., Kisić I. (1995b): Response of sugar beet to Agrarvital and waste water fertilizing. II. Heavy metals, toxic elements and bo-

- ron content in sugar beet root and leaf. *Poljopriv. Znan. Smotr.*, 60: 81–94.
- Butorac A., Filipan T., Bašić F., Mesić M., Kisić I., Benc S. (1995c): Untersuchungen hinsichtlich des Düngungswertes der speziellen natürlichen Substrate (Agrarvital) auf des Basis von Zeolith-Tuff. *Jber. 1994. Landwirtschaft. Fak. Zagreb, Inst. Entw. Int. Bezieh., Zagreb.*
- Butorac A., Filipan T., Cerjan-Stefanović Š., Butorac J. (1995d): Antitoxische Wirkung spezieller natürlicher Substrate (Agrarvital) auf kontaminierten Boden. *Poljopriv. Znan. Smotr.*, 60: 221–236.
- Butorac A., Filipan T., Mesić M. (1992): Response of soybean to Agrarvital and greeny fertilizing. [Manuscript.]: 1–5.
- Butorac A., Filipan T., Prpić B., Bašić F., Cerjan-Stefanović Š., Killian W., Mutsch F. (1995e): Untersuchungen der Wirksamkeit von natürlichen Bodenhilfsstoffen (Agrarvital-SPS-30, Biosol und Biomag) zur Regeneration degradierter Waldboden in Tirol. *Jber. 1994. Landwirtschaft. Fak. Zagreb, Inst. Entw. Int. Bezieh., Zagreb, Abt. Ackerb. Forstl. Bundesvers.-Anst., Wien, Inst. Forstökol., Zagreb-Wien.*
- Butorac A., Mesić M., Filipan T., Butorac J., Bašić F., Kisić I. (2002): The influence of special natural amendments based on zeolite tuff and different lime materials on some soil chemical properties. *Rostl. Výr.*, 48: 133–138.
- Cerjan-Stefanović Š., Čurković L., Filipan T. (1994b): Ion exchange of metal ions by natural zeolites. [Study.] *Fac. Technol. IRMO, Zagreb.*
- Cerjan-Stefanović Š., Čurković L., Filipan T. (1996): Metal ions exchange by natural zeolites. *Croat. Chem. Acta*, 69: 281–290.
- Cerjan-Stefanović Š., Filipan T., Matijević K. (1994a): Removal of ammonia in waters with natural zeolites. 17<sup>th</sup> BIONN Conf., Budapest, Abstr.
- Cerjan-Stefanović Š., Kaštelan-Macan M., Filipan T. (1992): Ion exchange characterization of modified zeolite. *Wat. Sci. Techn.*, 26: 9–11.
- Čurković L., Cerjan-Stefanović Š., Filipan T. (1997): Metal ions exchange by natural and modified zeolites. *Wat. Res.*, 31: 1379–1382.
- Duncan D.B. (1955): Multiple range and multiple *F*-tests. *Biometrics*, 11: 1–42.
- Eberl D.D. (1993): Controlled-release fertilizers using zeolites. *Ze' 93*: 49–50.
- Filipan T., Butorac A., Bašić F., Blašković H. (1989): The applicability of natural substrata to yield improvement on degraded acid soil. [Study.] *Trilat. Coop. Proj. ICAMAS/ECE/YU, IRMO, Zagreb.*
- Filipan T., Butorac A., Cerjan-Stefanović Š. (1991a): Some biotechnical possibilities of reducing soil and water contamination by nitrates. In: *Proc. 2<sup>nd</sup> Int. Symp. Envir. Geochem., Uppsala, Sweden*: 1–9.
- Filipan T., Ružinski N., Cerjan-Stefanović Š. (1991b): A study of the technological procedure of applying ion exchange in preparation of drinking water with a high content of nitrates. *IRMO Fac. Technol., Zagreb.*
- Filipan T., Ružinski N., Cerjan-Stefanović Š. (1997): Prirodni zeoliti za obradu otpadnih voda s visokim sadržajem dušičnih spojeva. *Sigurnost*, 39: 1–10.
- Grube W.E., Herman J.G. (1993): Heavy metal pollutant fixation by natural zeolites. *Ze' 93*: 112–114.
- Gworek B. (1992): Lead inactivations in soils by zeolites. *Plant and Soil*, 143: 71–74.
- Mesić M. (1996): Korekcija suviše kislosti tla različitim vapnenim materijalima. [Disertacija.] *Agron. Fak., Zagreb, Hrvatska.*
- Person T. (1988): Effects of different liming agents on meth-ods. *Acid. Res.*, 6: 11.
- Ružinski N., Filipan T., Benc S. (1993): Application of natural activated zeolites in the treatment of highly contaminated wastewaters. In: *Zodiac Symp. Biological basis of sustainable animal production, Agric. Univ., Wageningen*: 193–201.

Received on June 22, 2001

## ABSTRAKT

### Reakce plodin na speciální přírodní zlepšovače půdy na bázi zeolitového tufu

Cílem pokusu bylo najít způsob, jak vyloučit nebo alespoň zmírnit škodlivý účinek vysoké půdní kyselosti, aniž bychom prováděli náročná a nákladná opatření související s vápněním. Snahou bylo zvýšení výnosu plodin prostřednictvím lepší dostupnosti živin než neutralizací půdní reakce. Výsledky pokusů realizovaných na pseudogleji ve středních polohách naznačují, že toho lze dosáhnout aplikací speciálních přírodních zlepšovačů půdy (SNA) na bázi zeolitu vyráběných pod názvem Agrarvital (AV), v nichž hlavní složkou je klinoptilolit, zatímco zbývající část tvoří směs měkkého litotamnického vápence a dolomitu (SLL+D). Tyto materiály zvyšují výměnu iontů v půdě a jejich aktivaci při značně nižším pH než v případě vápnění. Výživnou hodnotu Agrarvitalu (AV) a vápencových materiálů (LM) jsme posuzovali podle dosažených výnosů a některých výnosových složek pěstovaných plodin. Výsledky ukazují dobrý hnojivý účinek AV na výnosy ozimé pšenice, kukuřice, sóji a ozimého ječmene, který se rovná nebo je vyšší než účinek tradičních LM aplikovaných v několika-násobně vyšších dávkách.

**Klíčová slova:** hnojivá hodnota; speciální přírodní zlepšovače půdy; zeolitový tuf; výnos a výnosové složky

---

*Corresponding author:*

Prof. dr. sc. Anđelko Butorac, Faculty of Agriculture, University of Zagreb, Svetošimunska 25, 10 000 Zagreb, Croatia, tel.: + 385 1 23 93 957, fax: + 385 1 23 93 981, e-mail: ikisic@agr.hr

---