# The influence of special natural amendments based on zeolite tuff and different lime materials on some soil chemical properties

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**ABSTRACT**

This paper deals with the changes in soil active acidity, mobile aluminium, base saturation, iron and manganese under the influence of quicklime (QL), mixture of soft lithothamnian limestone (SLL) and dolomite (D), and special natural amendments (SNA) based on zeolite tuff. Investigations were carried out on pseudogley of mesoelevations, dystric. The four-year trial was set up according to the Latin rectangle method with 18 trial treatments in four replications. While SNA based on zeolite tuff had little effect on changes of the studied parameters, traditional lime materials (LM), owing also to the fact that they were applied at several times higher rates, had a very positive effect. Soil acidity, iron and manganese were reduced under their influence, mobile aluminium, particularly under their higher rate, was fully blocked or reduced within tolerable limits, and base saturation was raised to a satisfactory level. Effects of SNA depended on the ratio of zeolite tuff and the lime component in them. It could be presupposed that their main efficiency happened in the domain of ion exchange with a positive impact on soil fertility.

**Keywords:** lime material; special natural amendments; zeolite tuff; Agrarvital; soil chemical properties

Fertilizing value of special natural amendments (SNA) based on zeolite tuff was treated in two ways in our research: in terms of their direct effect on the yield and some yield components of trial crops (Butorac et al. 2002), and in terms of their effect on some chemical properties of the soil. Both, naturally, involved comparison with traditional lime materials (LM). Since this paper deals with parameters that characterize soil acidity, for a better understanding of the achieved results it should be noted that adjustment of acid soil pH to a value adequate for crop production is one of the first steps in soil management. For many purposes it is convenient to think of soil pH as the pH of the solution in the pores of a moist soil, since this solution is in contact with the surface of roots, and many chemical reactions in the soil are governed by this solution (Rowell 1988). However, roots are also in contact with exchange surfaces, they affect the pH around them and the weathering of clays is dependent on the presence of pH on the surface of the minerals. We wanted to assess the relations in which soil acidity would change under the influence of materials applied in the trial (SNA based on zeolite tuff and traditional LM – quicklime (QL) and a mixture of soft lithothamnian limestone and dolomite (SLL+D).

Critical pH values differ for different crops. As regards to crops represented in our trial, restricted growth of barley may be expected at pH below 5.9, maize and wheat at pH below 5.5, and soybean below 6.0.

Much attention has been paid to investigating the relation between soil pH and base saturation. Our research also partly follows this trend.

There are multiple ways and methods of controlling adverse soil acidity (liming, application of organic fertilizers, chelate forming compounds, phosphorus fertilizers, molybdenum, quartz, gypsum and neutralization of mineral fertilizers). There are, accordingly, different mechanisms of antitoxic action, from blocking toxic elements through raising $OH^-$ concentration and forming compounds of M(OH) type (M = metal) to blocking toxic elements by raising the concentration of humic acids, fulvic acids and low-molecular organic acids by formation of insoluble organic compounds (metal – humic acid) and soluble complex so-called chelate organic compounds with toxic metals (Palaveev and Totev 1983). Our earlier investigations have indicated the full complexity of these problems, however not a positive outcome of the application of various materials for eliminating excessive soil acidity (Butorac and Tkalec 1974, Butorac et al. 1988, Bašić et al. 1990, Mesić 1996 etc). On the other hand, fertilizing value of SNA and the resulting changes in the soil, partly due to their mineralogical structure and chemical composition, have quite specific character, as confirmed by our own research (Butorac et al. 1994, 1995a, b, c etc.) as well as that done by other authors (Gworek 1992, Cerjan-Stefanović et al. 1992, 1996, Boettinger and Graham 1993, Grube and Herman 1993 etc.) Some major characteristics and mechanisms of zeolite action were described in our preceding paper, dealing with their fertilizing value (Butorac et al. 2002).

## MATERIAL AND METHODS

This chapter gives only a short survey of the materials used in the trial and the methods applied, necessary to understand the results discussed in the paper. Detailed problems relating to this research are presented in the separate paper (Butorac et al. 2002).

The trial (1990–1994) was set up on pseudogley of mesoelevations, medium deep, hydroameliorated, dystric, on locality Lipovljani in central Croatia, according to the Latin rectangle method in four replications and involved 18 fertilizing treatments. In accordance with the research goal, eg. testing the fertilizing value of SNA based on zeolite tuff and different LM with respect to yield and yield components, as well as the changes of some soil chemical properties, the trial, besides full and half rates of mineral fertilizers, included, in combination with them, a lower (1) and a higher (2) rate of SNA marketed under the commercial name Agrarvital (AV), a lower (1) and a higher (2) rate of SLL+D, and a lower (1) and a higher (2) rate of QL. Trial treatments can be seen from the Figures presenting the trial results. Namely, the studied AV types differed in participation of zeolite tuff, in which the mineral clinoptilolite prevails. AV 01 contains 30% zeolite tuff and AV 02 45%. The remaining part is made up of SLL+D, with preponderance of the former.

Test crops in the trial were: winter wheat, maize, soybean, and winter barley, to which the following NPK fertilization (in $kg.ha^{-1}$) was applied: 160, 66 and 116 to winter wheat, 180, 66 and 133 to maize, 55, 49 and 131 to soybean (seed was inoculated with *Bradhyrizobium japonicum*), and 135, 44 and 116 to winter barley. The above figures refer to full rates while the trial also involved their half rates. Lower QL rate (1) amounted to 3.4 and higher (2) to 6.8 $t.ha^{-1}$, lower AV rate (1) (both types) to 1.5 and higher (2) 3.0 $t.ha^{-1}$, while the lower rate of the mixture of SLD+D (1) was 6.0 and its higher rate (2) 12.0 $t.ha^{-1}$, which in terms of the lime material chemical guarantee corresponds to the lower and higher rates of QL, respectively.

The locality where the trial was set up is situated on a Pleistocene terrace formed of redeposited, compacted and through solifluctional processes altered Pleistocene loams. Soil stratigraphy is typical of pseudogley (Ap 0–30 cm, Eg 30–45 cm, and Bg 45–110 cm, typical, mottled, and poorly water-permeable). According to its texture, the soil is silty loam in all three horizons. In Ap and Eg horizons, the soil is porous, of low water capacity and high air capacity. It is less porous in Bg horizon, of moderate water capacity and very low air capacity. Chemical properties are treated separately within the presentation of the achieved results.

Chemical analyses of the soil were made by the common methods.

## RESULTS AND DISCUSSION

Though the research was more broadly conceived and, besides the changes in the actual acidity, mobile aluminium, iron and manganese contents and base saturation, included also some other parameters (non-exchangeable acidity, humus, available phosphorus, potassium and magnesium, contents of zinc, copper, lead and cadmium). This paper addresses only changes related to the five first mentioned parameters. By presenting these results together with the results from previous paper (Butorac et al. 2002), a more complete insight into fertilizing efficiency of SNA based on zeolite tuff would be achieved. Namely, it is known that zeolites are capable of releasing readily soluble nutrients already present in the soil (Eberl 1993).

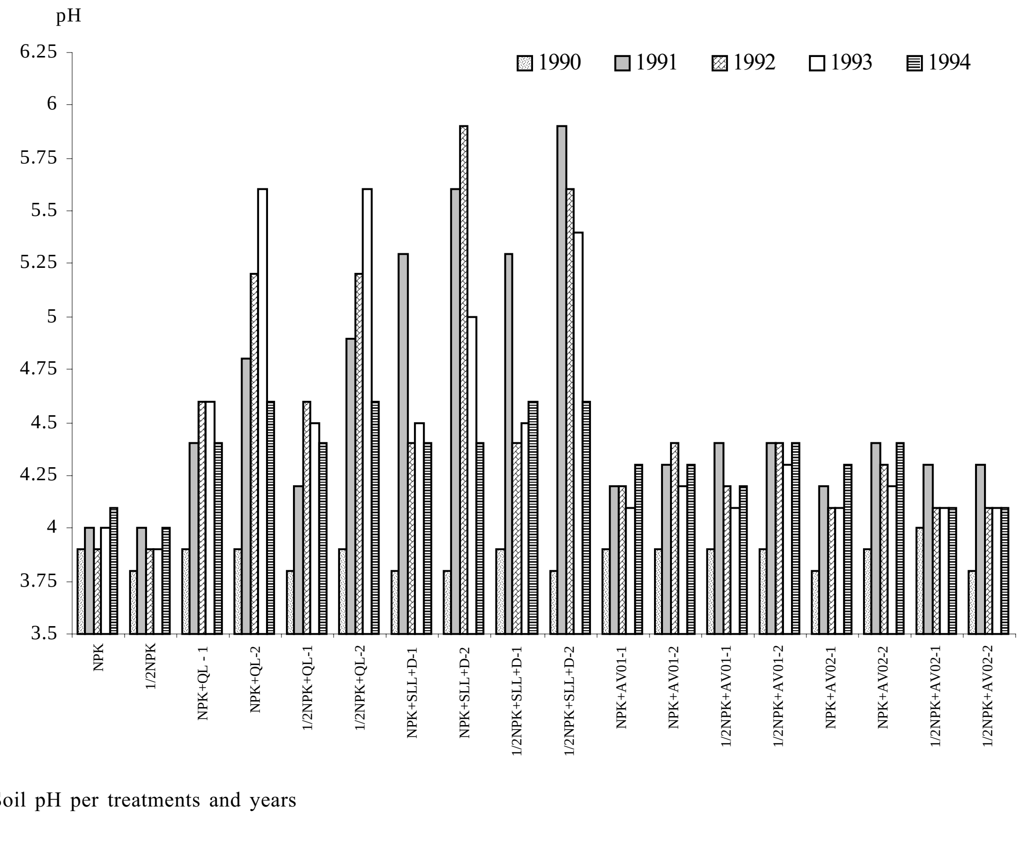


Figure 1. Soil pH per treatments and years

**Actual acidity (soil pH)**

First of all, regarding the actual acidity, it is evident that this is a very strongly acid soil (Figure 1) (Donahue et al. 1990). This is indicated by the initial state of soil pH in all trial treatments. Soil acidity is so high that free mineral acids might certainly be expected in the soil. This is the cause of all negative consequences for the production of most field crops. They equally refer to the toxic action of elements such as aluminium, manganese, iron, copper, zinc, and some other (Palaveev and Totev 1983). The acute need of this soil is elimination, or at least mitigation, of its extreme actual acidity, or application of zeolite based amendments or zeolite itself, which will directly enhance ion exchange and enable unobstructed release and increased availability of plant nutrients (Eberl 1993). The results obtained during the 4-year period illustrate very well how these changes proceeded under the influence of trial treatments.

Actual acidity remained on more or less the same level in the both rates of pure mineral fertilization. Both rates of QL, combined with both mineral fertilizer rates reduced soil acidity, but with a somewhat more pronounced effect of the higher rate. In both cases, the effects were most pronounced at the end of the second and third growing seasons, while they decreased at the end of the fourth growing season. Evaluation of the neutralization value of QL, but also of all LM, should take account of the applied rates and, naturally, also of its physical state, eg. grinding fineness (Butorac et al. 1988, Mesić 1996).

Mixture of SLL+D, at both rates, combined with full and half-mineral fertilizer rates behaves in a slightly different way than analogous treatments with QL. These materials bring about a considerable reduction of soil acidity already in the first year, in the case of the half mineral fertilizer rate and higher rate of the mixture of SLL+D by as much as 2 units of pH value. This might be primarily attributed to the favourable solubility and rapid activation of SLL in the soil, while dolomite is known for its very poor solubility. In the case of the higher rate, the favourable effect continues not only in the second but also in the third growing season while, similarly to QL, its intensive decrease starts in the fourth year.

Both AV types in combination with both rates of mineral fertilizers also caused some reduction in the actual soil acidity, which is in agreement with our previous investigations (Butorac et al. 1995c). There were some small differences between them, depending on the participation of zeolite and lime components as well as the applied rate. The effect of AV actually complies with the nature of this amendment, which arises from its chemical composition. The results obtained with the crops tested in the trial showed that soil reaction, though important to the crops, does not play a decisive role if zeolites are applied along with the lime component (Butorac et al. 2002). Applied at higher rates, AV would surely cause more significant positive changes of the reaction of acid soils. However, in view of the mechanisms of its action, this was not the object of this research. As AV rates were governed by other criteria than the rates of traditional LM, changes of the actual acidity due to AV, though present, are not in the focus of this research either.

Consideration of actual soil acidity would, however, not be complete if the influence of mineral fertilization applied

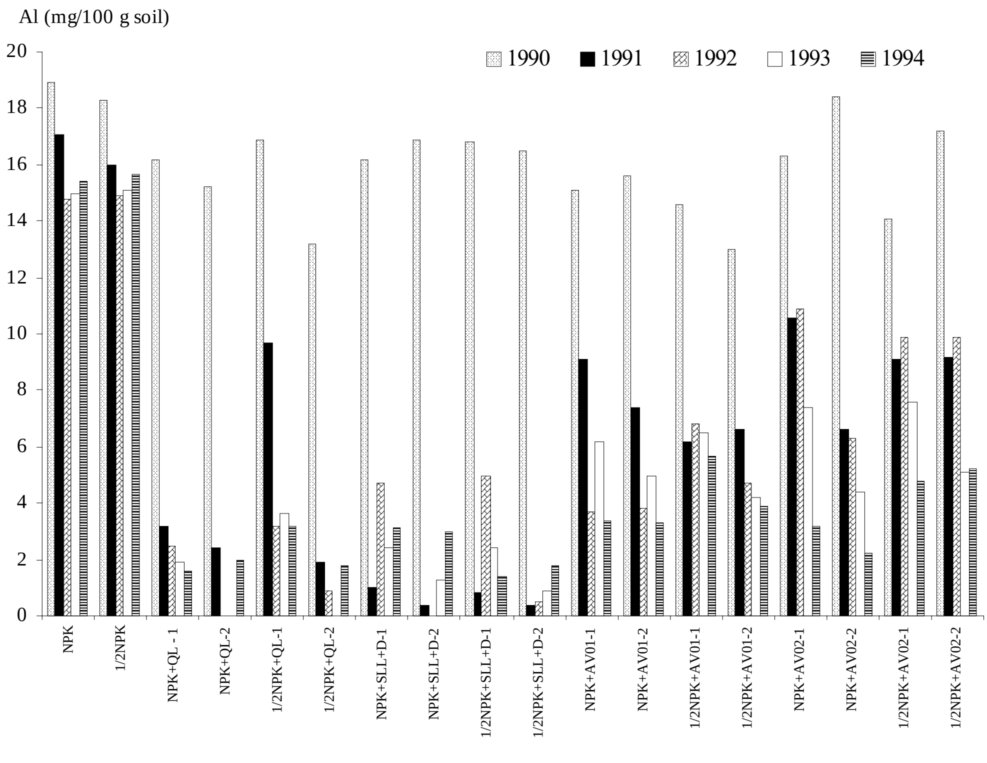


Figure 2. Mobile aluminium content per treatments and years

in the trial was disregarded. It might have been expected that nitrogen fertilization would lead to further acidification of the soil. This obviously did not happen, so it may be assumed that the total complex of agrotechnical practices, along with the crops grown, maintain the achieved balance. This was most probably aided by higher rates of phosphorus and potassium fertilizers with their positive effect in terms of reducing excessive soil acidity and the overall dynamics of the soil liquid phase. It seems likely that, at the higher rate of phosphorus and potassium, phosphorus bound a part of harmful ions, while potassium pushed out part of these ions from the cation exchange complex. Nevertheless, the essential role is that of calcium and magnesium, as well as the applied rates of LM and its physical and chemical guarantee, eg. neutralization index.

### Mobile aluminium

The initial level of mobile aluminium was very high and quite appropriate to the degree of soil actual acidity (Figure 2). The occurrence of mobile aluminium in soil is by itself a sign of its unfavourable chemical properties. The initial values are such as to warn about the extremely low soil fertility. Changes recorded for the mobile aluminium content reflect the changes in active acidity of the soil. This arises from the very nature of aluminium, which may be assigned the leading position in terms of the intensity of soil acidification. Its blocking by various LM at the same time reduces or at least weakens soil acidification processes (Palaveev and Totev 1983), which is directly reflected in the value of soil active acidity.

Mobile aluminium was greatly reduced in all treatments, except for the both rates of pure mineral fertilization, at the end of the first growing season. Moreover, it was almost fully eliminated from the soil or, more precisely, blocked in treatments involving combined application of the mixture of SLL+D with both mineral fertilizer rates. Positive effect was achieved not only with LM, including QL, but it was also present in the application of both AV types. The positive effect of AV, that is, material based on zeolite tuff with a high participation of SLL+D, may be ascribed to its composition, despite the several times lower rates applied than those of traditional LM. The positive trend of all amendments applied continued to the end of the trial period, which might be one of the reasons that can explain the positive effect of AV upon crop yield (Mesić 1996). However, in terms of blocking mobile aluminium, advantage is still on the side of traditional LM, naturally applied at several times higher rates than AV.

### Base saturation

Initial base saturation of the soil was expressly low, considerably below the values that could satisfy the most tolerant criteria (Figure 3) (Butorac et al. 1988). All changes in the soil, and also its base saturation, should be considered in terms of seasonal fluctuations, which often result from a number of factors beyond our control. The season-

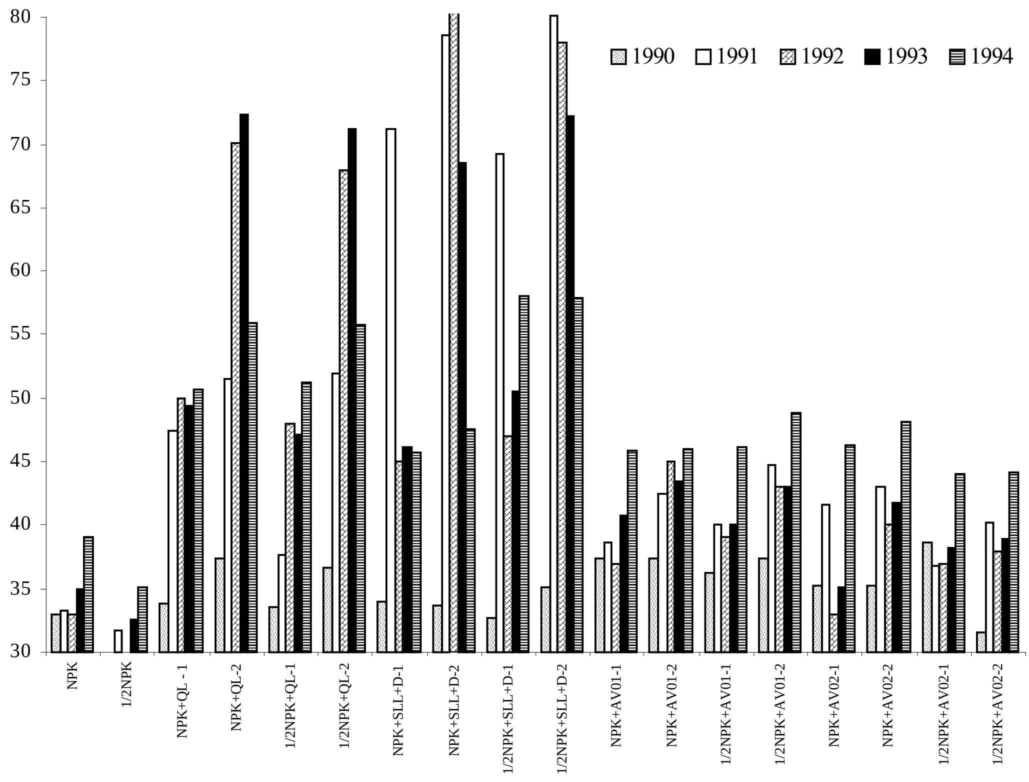


Figure 3. Base saturation per treatments and years

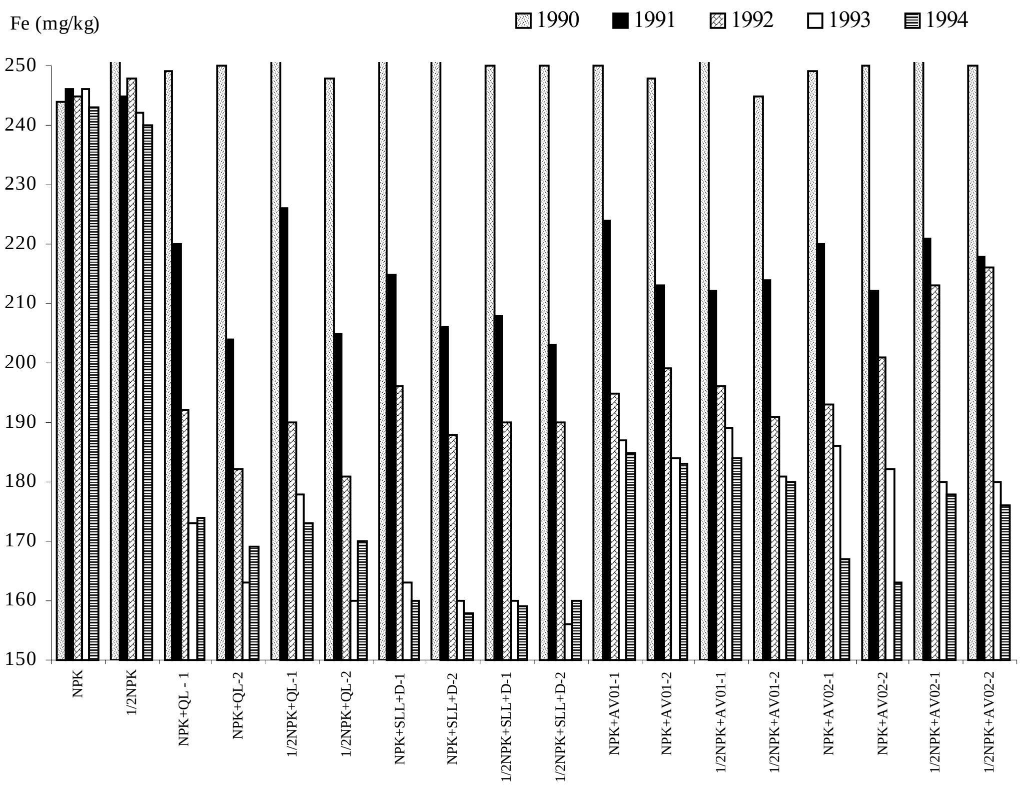


Figure 4. Content of iron per treatments and years

al character of base saturation is especially indicated by the values from the both treatments involving pure mineral fertilization. They, as a rule, increase from the first to the last trial year. Under the influence of QL in its combination with mineral fertilizers they reach satisfactory values. However, basic cation saturation does not provide much information that is not already available from pH values (Donahue et al. 1990), but it does provide numerical val-

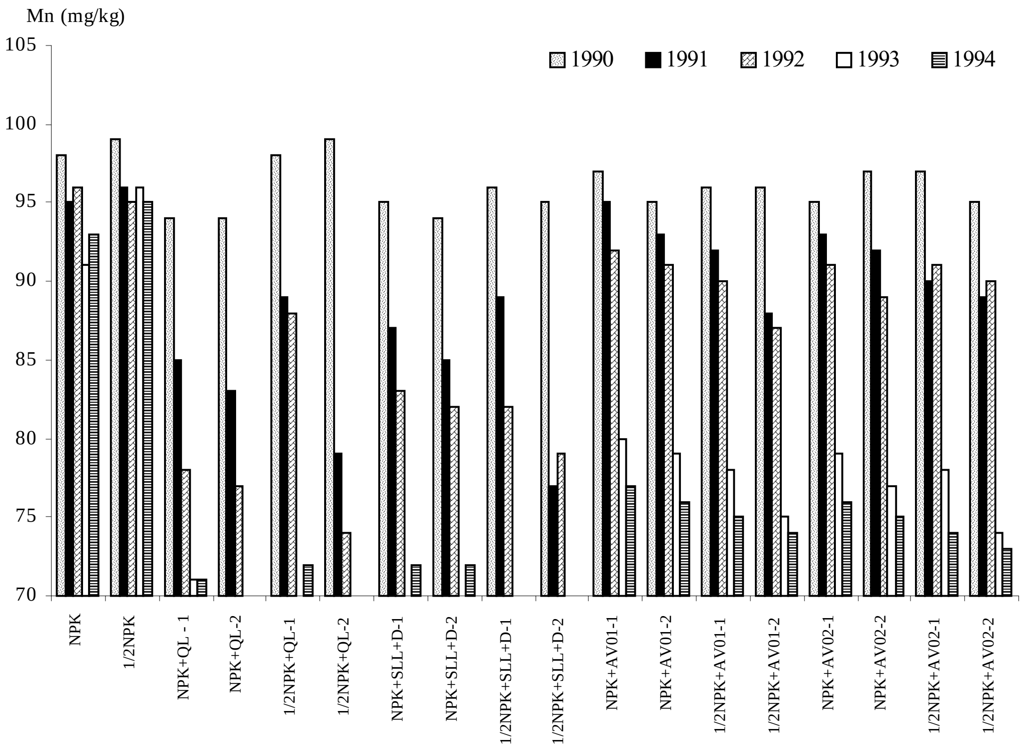


Figure 5. Content of manganese per treatments and years

ues of the amount of exchangeable hydrogen and aluminium ion species on the cation exchange complex.

The best effect on the increase of base saturation was recorded in treatments with pure mineral fertilization combined with the mixture of SLL+D, primarily its higher rate, in which almost optimal saturation was achieved as early as in the second year after application. It was just with the application of the mixture of SLL+D that we wished to achieve rapid and efficient effects, owing to the increased solubility and fast activation of SLL in soil, on the one side, and a longer residual effect due to lower solubility of dolomite, on the other. This is in agreement with our earlier results (Bašić et al. 1990).

A slight increase of base saturation occurred also in treatments involving a combined application of particular AV types and mineral fertilizers. It was more pronounced at the higher AV rate, but was considerably lower than in its combinations with traditional LM. Up to a certain point, account should be also taken of the participation of zeolite tuff in AV, since its increase leads to a decrease of the content of bases (calcium and magnesium) originating from the SLL and dolomite.

**Iron and manganese**

The contents of iron and manganese in soil were relatively high before starting the experiment (Figures 4 and 5). Changes that occurred in their contents are, more or less, in agreement with the changes of active soil acidity. In accordance with this statement, mineral fertilizing practically did not influence iron and manganese content in the soil in the course of the investigation period. On the contrary to this fact, iron and manganese were reduced in all combined treatments of mineral fertilization and QL or mixture of SLL+D in dependence on applied rates and years. Evidently, detoxifying effect of LM is present in this case. This is in agreement with the opinions of many authors, primarily of Palaveev and Totev (1983) including our own results (Butorac and Tkalec 1974, Butorac et al. 1988 etc.).

Considering iron and manganese contents in soil, positive effect was also achieved under the influence of both type of AV. Namely, in the both cases reduction of iron and manganese in soil is obvious, although not so strong in comparison with LM. Grube and Herman (1993) have come to the same conclusions. They consider that natural zeolites can be used as agents imobilizing heavy metals. This is in concordance with our earlier results (Butorac et al. 1995b).

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**ABSTRAKT**

**Vliv speciálních přírodních zlepšovačů půdy na bázi zeolitového tufu a různých vápencových materiálů na vybrané chemické vlastnosti půdy**

Byl sledován vliv nehašeného vápna (QL), směsi měkkého litotamnického vápence (SLL) a dolomitu (D) a speciálních přírodních zlepšovačů půdy (SNA) na bázi zeolitového tufu na aktivní kyselost půdy, obsah mobilního hliníku, nasycení bázemi a na obsah železa a hořčíku. Pokusy proběhly na dystrickém pseudogleji ve středních polohách. Čtyřletý pokus byl založen metodou latinských obdélníků s 18 pokusnými variantami ve čtyřech opakováních. Zatímco SNA na bázi zeolitového tufu měly na změny sledovaných parametrů malý vliv, tradiční vápencové materiály (LM) dosáhly velmi pozitivního účinku také proto, že byly použity v několikanásobně vyšších dávkách. Jejich vlivem došlo ke snížení kyselosti půdy, obsahu železa a hořčíku, a zejména při použití jejich vyšší dávky nastalo úplné zablokování mobilního hliníku nebo jeho snížení v mezích tolerance a nasycení bázemi se zvýšilo na uspokojivou hodnotu. Účinky SNA byly závislé na poměru zeolitového tufu a jejich vápencové složky. Můžeme předpokládat, že k hlavnímu působení došlo v oblasti iontové výměny s kladným dopadem na úrodnost půdy.



**Klíčová slova:** vápencový materiál; speciální přírodní zlepšovače půdy; zeolitový tuf; Agrarvital; chemické vlastnosti půdy



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