

## THE IMPACT OF FERTILISER TYPES ON SOIL'S MACRONUTRIENTS AND MICROELEMENTS CONTENT

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**Abstract.** The main focus of this paper is the study of soil's macronutrients and microelements mobility under the influence of mineral and organic fertilization. Two species of plants were cultivated: winter wheat (*Triticum aestivum L.*) and potato (*Solanum tuberosum L.*). The wheat was cultivated on the same lot during three out of four years of crop rotation, while only one year was devoted to the potato. The evolution of microelements' content such as *Cu*, *Zn*, *B*, *Mo*, *Mn*, respectively, and pH from the fertile soil layer (0-20 cm.) was thoroughly analyzed. The modification of microelements content in the soil resulted on one hand from the application of intensive nitrogen fertilizers on different pre-fertilized plots with phosphorus and potassium, and on the other from the decrease of soil pH. The fertilizers applied to the soil changed the versatile phosphates content due to the changes of the soil's pH value or to the adding of organics or mineral phosphates. Soil pH decreased for both versions: the control version and the variants fertilized only with mineral fertilizers or using both mineral fertilizers and manure. In our research, the values of *Mn*, *Zn*, *Cu* and *B* decrease, between certain limits, together with the increase of the nitrogen fertilizer dose applied, irrespective of the salt type used. Also, we remark that the phosphorous content in the albic luvisol was low, the mineral fertilizers contributing to its increase of 3-12 mg·kg<sup>-1</sup> (depending on the treatments applied to) and the versatile potassium suffers insignificant variations.

**Keywords:** macronutrients, microelements, soils, multiple regression analysis, versatile *Mn*, reducible *Mn*.

### 1. Introduction

Manures and fertilizers have, on a very large scale, similar effects on soils long-term productivity. Therefore the addition of nutrients in either form is essential for the maintenance of soil quality (Douglas and Edmeades 2002).

The mineral long term fertilization had a significant effect on microelements' content, causing even multidirectional changes. During the experience, soil pH decreased for both versions: the control version and the variants fertilized only with mineral fertilizers or using both mineral fertilizers and manure.

After iron (*Fe*) and aluminum (*Al*), manganese (*Mn*) represents the most abundant chemical constituent in rocks making up the earth shell (Davidescu 1981). Soil contains transformed *Mn* under various forms associated with the mineral and organic part.

The variation within the content of microelements was not proportional and resulted from: unilateral fertilization with phosphorus, acidifying effect of fertilizers and liming, which all blocked the solubility of microelements in the soil (Kopeć and Przetaczek-Kaczmarczyk 2006).

As a result of the limestone powder onto acid soils, the *Ca* content in the soil solution and the versatile one

increases leading to the improvement of the plant nutrition with this element. This improvement can be explained also as a result of the precipitation of  $Al^{3+}$  and  $Mn^{2+}$  ions in excess from the soil solution inducing toxicity effects.

Since soil pH seems to be the predominant factor involved in the process of soils trace-metal solubilisation (Butcher *et al.* 1989; Knight *et al.* 1998; Kashem and Singh 2002), the proper evaluation of its effect is critical. The decrease in soil pH is related to the application of nitrogen (in itself or contained in phosphate fertilizer mixtures) (Tuet *et al.* 2000; Kashem and Singh 2002).

Higher concentrations and contents of hydrogen ion ( $H^+$ ), aluminium ( $Al^{3+}$ ) and manganese ( $Mn^+$ ) found in acidic soils are known to be the major causes of poor plant growth due to their toxicity effects to plants and micro organisms such as N-fixing bacteria. Molybdenum is also a component of some bacterial nitrogenase and therefore, is especially important for plants that live in symbiosis with nitrogen-fixing bacteria such as *Rhizobium*. Calcium, magnesium and molybdenum deficient plants exhibit poor growth. The negative effect of acidity on the rootlet absorption of *Mg* can be explained as a result of this competition between  $H^+$  and  $Al^{3+}$  to occupy the same position on the ions transporting molecules

through the cell membrane (Rengel and Robinson 1989). Aluminum is the most important yield-limiting factor in many acid soils (Foy 1988).

The commonly used management practice to ameliorate acid soils is through the surface application of lime (Bolan *et al.* 2003). The major contribution of lime is its ability to supply  $Ca^{2+}$  which is essential for plant growth (White and Broadley 2003) and also to neutralize the toxicity effects of  $H^+$ ,  $Al^{3+}$  and  $Mn^{2+}$  in the soil (Staley and Brauer 2006).

The decrease of pH below 5.5 may be explained by the use of some fertilizers or the soil settlement increases the Mn solubility until toxic levels. The rootlet exudates contribute to the transformation of insoluble  $MnO_2$  in complexes with soluble Mn (Soon and Arshad 2005; Caires *et al.* 2008). The dominant forms of Mn in ferromagnetic concretions composition (balls) are  $Mn_2O_3 \cdot nH_2O$  (Bajescu 1984). In order to become accessible for plants, Mn oxides and hydroxides need to be reduced to  $Mn^{2+}$  ions. Between  $Mn^{2+}$  from soil solution,  $Mn^{2+}$  changeable and superior oxides of Mn there is a dynamic balance controlled by the complexity of reduction conditions (oxidation-reduction). Accessibility of  $Mn^{2+}$  depends on several factors, among which the most important are: pH, microbiological activity, organic matter (OM) and soil humidity regime.

The increase of pH in acid soils by adding limestone decreases evidently the yield of soluble Mn. The cultivated soils have had and currently have modifications of their Mn content. Periodical investigations have shown Mn values between 280 and 3200 ppm total forms and approximately 300 ppm mobile forms (Swaine 1955; Cottenie 1977; Davidescu 1981). A global average figure would be situated between 950 and 1000 ppm manganese (Davies 1980; Bajescu 1984).

The concentration of  $Mn^{2+}$  from soil solution decreases by 100 times for each increasing pH unit (Reichman 2002). The pH-values over 6.5 are favorable for the oxidation of  $Mn^{2+}$  and its change into tri- or tetravalent inorganic forms is almost useless for plants (Karapetyan *et al.* 2005).

Various macro- and microelements are necessary for successful vital activity of plants. They are introduced in balanced proportions and are not subject to selective leaching.

In this paper we focus on studying of soil's macro-nutrients and microelements mobility under the influence of mineral and organic fertilization.

## 2. Materials and methods

The evolution of microelements' content such as Cu, Zn, B, Mo, Mn, respectively, and pH from the fertile soil layer (0-20 cm.) was thoroughly analyzed. The studies presented in this paper result from four years of experiments, which were started in 2005. The main research method was the continuation of the activities in the experimental fields of Agricultural Research and Development Station Suceava - Romania. Two species of plants were cultivated: winter wheat (*Triticum aestivum L.*) and potato (*Solanum tuberosum L.*). The wheat was cultivated

on the same lot during three out of four years of crop rotation, while only one year was devoted to the potato.

We proposed for each sample the following types of fertilizers:

- Super phosphate with 17%  $P_2O_5$ ;
- Ammonium nitrate with 33.5% N;
- Nitro limestone cu 17.6% N and 40%  $CaCO_3$ ;
- Urea with 46.2% N;
- Manure with 0.46% N, 0.32%  $P_2O_5$  and 0.21%  $K_2O$ , to dried substance;
- Slaked lime powder with a neutralization power of 93% as CaO units;
- Potassium salt with 40%  $K_2O$ .

The researches have been carried out for four years, which were started in 2005; only two species of plants were cultivated: winter wheat and potato. The experiment had six variants with the following content:

- Non-fertilized and non-limed witness;
- Mineral nitrogen and phosphorus annually applied fertilizers;
- Manure applied to the potato culture only, non-fertilized for the rest of the years;
- Mineral NP annually applied fertilizers, plus manure to the potato culture only;
- Mineral NP annually applied fertilizers, + applied to soil liming in four stages;
- Mineral NP annually applied fertilizers, + manure to the potato culture, +soil liming applied in four stages.

60 kg of  $K_2O$ /ha, considered as indispensable, were applied to variants 2 and 5 in the year when potato was cultivated (see table 1).

**Table 1.** The experimented treatments on the albic luvisol during four years, for winter wheat and potato

Variant	Winter wheat ( <i>Triticum aestivum L.</i> )	Potato ( <i>Solanum tuberosum L.</i> )
1	unfertilized	unfertilized
2	60-80N+60P <sub>2</sub> O <sub>5</sub>	150N +60P <sub>2</sub> O <sub>5</sub> +60K <sub>2</sub> O
3	mineral fertilizer	mineral fertilizers
4	manure residual effect	40 -50 t/ha manure and mineral fertilizer's residual effect
5	60-80N+60P <sub>2</sub> O <sub>5</sub> , mineral fertilizer and manure's residual effect	150N +60P <sub>2</sub> O <sub>5</sub> +60K <sub>2</sub> O and amendments residual effect
6	60-80N+60P <sub>2</sub> O <sub>5</sub> – mineral fertilizer and amendments	40 -50 t/ha manure and mineral fertilizers and manure residual effect

The dose of amendments was established in order to neutralize the entire hydrolytic acidity, according to the relation: tones CaO/ha = Ah x 0.84 = 5.6 x 0.84 = 4.70 t

The dose has been divided into fractions and applied for four years: in the first year for wheat, in the second year for potato, in the third year for wheat and, finally, in fourth years again for winter wheat.

Winter wheat (*Triticum aestivum L.*) is moderately tolerant to acidity and potato (*Solanum tuberosum L.*) as well.

The data processing has been made by variance analysis, for poly-factorial experiences, the experiences being repeated four times and the harvesting area of the lot being of 12-18 m<sup>2</sup>.

### 3. Chemical determinations

Soil samples have been analyzed from the chemical point of view.

- pH was determined in water extract (soil: water = 1:2.5).
- Easily assimilated phosphorous ( $P \text{ mg}\cdot\text{kg}^{-1}$ ) was determined by the Egner-Riehm Domingo method; phosphorous was extracted from soil by an acid solution of ammonium acetate lactate buffered at pH 3.7;
- Easily assimilated potassium ( $K \text{ mg}\cdot\text{kg}^{-1}$ ), the potassium cations were measured by flame-photometry from the buffered ammonium acetate-lactate extract at pH 3.7 (Egner-Riehm-Domingo method);
- The versatile Mn forms, (soluble in 1 N ammonium acetate solution with pH 7.0), Mn easily reducible (soluble in ammonium acetate + 0.2% hydroquinone);
- The versatile form of Mn (active Mn) was obtained by summation of exchangeable and easily deductible Mn.

Soil samples were mineralized by a  $\text{HNO}_3$  and  $\text{HClO}_4$  solution and afterwards the precipitate was soluble by hydrochloric solution.

In this solution the total content of microelements (*Mo*, *Cu*, *Fe*, *Mn* and *Zn*) was determined by means of atomic absorption spectrometry in air acetylene flames.

Boron was determined by  $\text{HCl}$  method, its content was read by UV – VIS spectrophotometer Cintra 400 at 420 nm wavelength.

The analytical data were statistically calculated. Analysis of variance (one-way ANOVA) was performed on 3 soil properties (pH,  $P_2O_5$  ( $\text{mg}\cdot\text{kg}^{-1}$ ),  $K_2O$  ( $\text{mg}\cdot\text{kg}^{-1}$ )) to test the null hypothesis of any overall treatment effect on individual soil properties.

### 4. Results and discussion

The effect of liming on the concentration of microelements in soil solution was initially by a change of soil reaction.

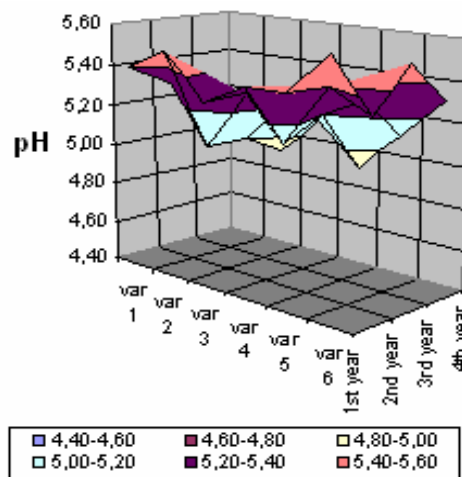
The albic luvisol from Suceava has a small to very small content of versatile phosphorous (because it contains only 14 ( $\text{mg}\cdot\text{kg}^{-1}$  P in the 0-20 cm layer) and an obvious need of phosphorous fertilizers.

In the witness sample without fertilizers and amendments, the pH value decreased from 5.4 in the first years to 5.1 in the sixth years (see figure 1).

The pH decreases in acid soils used as arable were observed in other researches too and explained as a consequence of the decrease of saturation degree with bases under the influence of natural and anthropogenic elements.

Alike elements caused increased consumption of basic cations in order to increase the harvest by the aid of

nitrogen fertilizers, nitrification of ammoniac forms of nitrogenous fertilizers and accentuate leaching of the soluble salts into the processed soils, assortment of mineral fertilizers containing none of the basic cations used by plants, which complete the soil reserves and re-establish the saturation degree with bases.



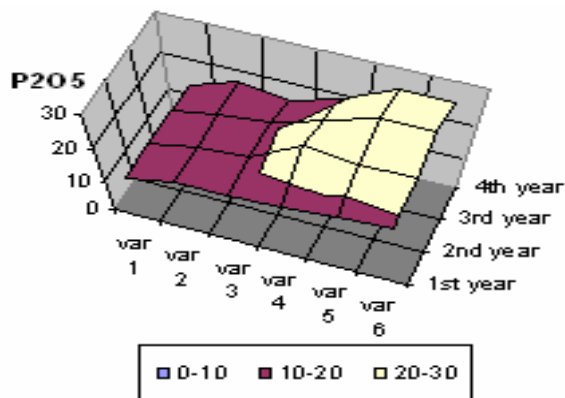
**Fig 1.** Variation of pH depends of variants and year of fertilization

This hypothesis is supported by the work of Raphaël Lambert (Lambert *et al.* 2007). The application of phosphate fertilizers had a clear acidifying effect. As the rate of fertilizer application increases, the reduction of pH is enhanced (Lambert *et al.* 2007).

If the specific consumption of phosphorous for wheat is 12 kg  $P_2O_5$ /tones, for a planned harvest of 2.4 tones, 27.6 kg  $P_2O_5$  was consumed, in the soil 32.4 kg  $P_2O_5$ /ha remained which were added to the existing reserve.

So it can be explained by the fact that in the first year, in the variant 2 fertilized by mineral fertilizers containing 60kg  $P_2O_5$ , the PAL content was 16  $\text{mg}\cdot\text{kg}^{-1}$ , and in the witness 13  $\text{mg}\cdot\text{kg}^{-1}$  P only.

It results an increase of 0.016 mg  $P_2O_5$ /kg or 0,007 mg P/kg in soil. In four years of consecutive application of 60 kg  $P_2O_5$ /ha the increase was approximately of 0.028  $\text{mg}\cdot\text{kg}^{-1}$  P (see figure 2).



**Fig 2.** Variation of  $P_2O_5$  depends of variants and year of fertilization

In fact the increase was of 3 mg·kg<sup>-1</sup> P, showing that an increase of the phosphate solubility in soil also occurred, process amplified by the addition of limestone. However, the values remain at low level so that on these soil types even greater doses of phosphorous fertilizers can be applied.

The association of mineral fertilizers with amendments did not induce significant changes in the amount of soluble K in the soil.

The summary statistics of soil parameters as affected by the 6 variants of fertilization (presented in the table 1) is shown in the table 2.

**Table 2.** Summary statistics of measured the soil pH, P<sub>2</sub>O<sub>5</sub> (mg·kg<sup>-1</sup>), K<sub>2</sub>O (mg·kg<sup>-1</sup>) under the influence of fertilizers and amendments

Parameters	Statistics	Sample variant					
		1	2	3	4	5	6
pH	Mean±	5.275±	5.100±	5.225±	5.150±	5.300±	5.425±
	St. Dev.	0.126	0.271	0.096	0.208	0.141	0.150
	CV(%)	2.389	5.313	1.837	4.0389	2.660	2.765
P <sub>2</sub> O <sub>5</sub> mg·kg <sup>-1</sup>	Mean±	13.500±	16.500±	16.500±	20.750±	23.000±	23.250±
	St. Dev.	0.577	0.577	1.291	3.500	3.559	3.096
	CV(%)	4.274	3.497	7.824	16.867	15.474	13.316
K <sub>2</sub> O mg·kg <sup>-1</sup>	Mean±	52.500±	54.000±	64.250±	55.250±	52.500±	57.250±
	St. Dev.	2.887	3.266	2.062	8.617	2.887	8.180
	CV(%)	5.499	6.048	3.209	15.596	5.499	14.28

St. Dev., standard deviation; CV(%), coefficient of variation in percent.

We remark that the distributions of pH, P<sub>2</sub>O<sub>5</sub>, K<sub>2</sub>O, respectively, can be considered of low-variance, the variant no. 4 has the maximum values for the coefficients of variation CV(%) for P<sub>2</sub>O<sub>5</sub> (mg·kg<sup>-1</sup>) and K<sub>2</sub>O (mg·kg<sup>-1</sup>) and the variant no. 2 has the maximum values for the coefficients of variation for pH.

One-way ANOVA is used to determine if there is statistically significant difference (see table 3) between the means of soil pH, P<sub>2</sub>O<sub>5</sub> (mg·kg<sup>-1</sup>), K<sub>2</sub>O (mg·kg<sup>-1</sup>) and the influence of fertilizers and amendments used in 6 soil treatments respectively. The null hypothesis is that the means are equal: H<sub>0</sub>: Mean 1 = Mean 2 = ... = Mean 6. The alternate hypothesis H<sub>a</sub> is that at least one of the means is different.

**Table 3.** Analysis of variance (ANOVA: Single Factor) summary for soil parameters pH, P<sub>2</sub>O<sub>5</sub> (mg·kg<sup>-1</sup>) and K<sub>2</sub>O (mg·kg<sup>-1</sup>) depending on treatment methods

Soil param.	Source of variation	SS	df	MS	F	P-value	F crit	η <sup>2</sup>
pH	Between Groups	0.267	5	0.053	1.740	0.176	2.773	0.326
	Within Groups	0.553	18	0.031				
P <sub>2</sub> O <sub>5</sub> mg·kg <sup>-1</sup>	Between Groups	319.3	5	63.867	10.403	0.0001	2.772	0.743
	Within Groups	110.5	18	6.139				
K <sub>2</sub> O mg·kg <sup>-1</sup>	Between Groups	394.7	5	78.942	2.742	0.052	2.773	0.432
	Within Groups	518.3	18	28.792				

We found statistically significant differences (P ≤ 0.05) only in P<sub>2</sub>O<sub>5</sub> (mg·kg<sup>-1</sup>) (because F > F crit) and there is not statistically significant differences in pH and K<sub>2</sub>O (mg·kg<sup>-1</sup>) mean values.

The mobility of microelements in the soil suffers changes, on the one hand under the action of the industrial and organic fertilizers and, on the other hand under the action of the amendments (see table 4).

**Table 4.** Summary statistics of measured microelements Cu, Zn, B, Mo and Mn in the soil (mg·kg<sup>-1</sup>)

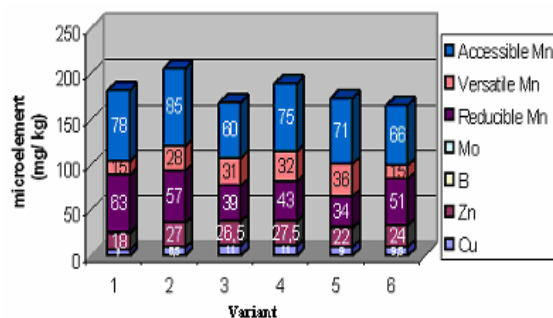
Statistics	Cu	Zn	B	Mo	Reducible Mn	Versatile Mn	Accessible Mn
Mean±	9.333±	24.166±	0.098±	0.110±	47.833±	26.166±	72.500±
St. Dev.	1.538	3.669	0.009	0.015	11.107	9.020	8.871
CV(%)	16.470	15.18	9.18	13.63	23.220	34.470	12.230

St. Dev., standard deviation; CV(%), coefficient of variation in percent.

We remark that the distributions of Cu, Zn, B, Mo and Mn respectively, can be considered of low-variance, Versatile Mn has the maximum values for the coefficients of variation CV (%).

Simard *et al.* 1988, sowed that application of CaCO<sub>3</sub> resulted in a decrease of the concentration of manganese and zinc in soil solution.

The forms of versatile and reducible Mn are typical (see figure 3).



**Fig 3.** Variation of microelements Cu, Zn, B, Mo and Mn in soil (mg·kg<sup>-1</sup>)

The content of versatile Mn in soil without amendments but fertilized is lower than in the variants with amendments, the content of reducible Mn did not suffer any change. The phosphorous acid anions get formed probably with the versatile Mn compounds at lower solubility in the AL reagent. When the amendments are applied, the content of versatile Mn did not suffer any losses of mobility depending on pH. This special variation sense can be explained too as a consequence of the reaction between the phosphorous acid ions with the Ca from amendments. As Ca is more electropositive than Mn, it allows Mn to remain to greater extent as versatile form.

From the agrochemical point of view microelements are important as reserve and also as assimilable forms, from the point of view of the microelements transfer from one compartment to another under the influence of the

natural and anthropogenic physical, chemical and biological conditions as well.

The reaction of soil is very important for the versatility of microelements in soil. In general, the cations solubility decreases with the pH increasing and the solubility of anions (in fact Mo) increases with the pH.

Humus influences mobility because of its fixing power made by carboxylic and phenol groups similar to the chelating capacity of organic matter. The influence of clayey particles is similar whereas soil humidity and temperature stimulate the concentration of microelements in soil solution.

The results of Sanders (Sanders 1983) showed minor and irregular decreases in soil solution of the concentration of copper with an increase of pH. This effect is due to the fact that copper almost always occurs in soil solution in a chelate form and a rate of formation of these complexes only to a small extent depends on soil solution.

The soluble copper in the ammonium acetate – EDTA solution varied between 7-11 mg·kg<sup>-1</sup> Cu, depending on the nitrogenous fertilizer dose applied, the lowest value being registered in unfertilized witness sample whereas the highest one for the maximal dose of nitrogen fertilizer.

Zinc extracted by ammonium acetate - EDTA solution at pH 7 has shown very high values; in the albic luvisol from Suceava it was about 10 times higher than the extracted zinc by HCl 0.1 N solution from similar soils of the Radauti Depression. The lowest values were obtained in unfertilized witnesses and the highest ones in soils fertilized by different nitrogen doses (see table 3). In addition, the fertilizer itself can influence metal solubility in soil. Its phosphate content has a certain effect on Zn solubility (Lambert *et al.* 2007).

Boron extracted from soil by ammonium acetate – EDTA solution offered values of 0.08 mg·kg<sup>-1</sup> in the unfertilized witness and 0.10-0.11 mg·kg<sup>-1</sup> in the fertilized lots. The nitrogen fertilizers increase the extracted amount of boron.

An increase of boron concentration in soil solution under soil liming could be caused by an increase of adsorption of this element on soil particles of the solid layer; which reaches the peak for boron at pH 8-10 (Goldberg and Glaubig 1985).

Molybdenum extracted by ammonium acetate - EDTA solution offered values lower than 0.5 mg·kg<sup>-1</sup> Mo, with the observation that in the unfertilized witness the soil contained 0.09 mg·kg<sup>-1</sup> Mo, and in the nitrogen – fertilized variants the values ranged between 0.10-0.14 mg·kg<sup>-1</sup> Mo. We can observe that, contrary to the theoretical approaches concerning the pH implication in the mobility of microelements, the nitrogen fertilizers increased the mobility of Mo, probably due also to the high level of humus in soil. At higher pH values there is a reduction of the amount of positive charges on soil colloids and an escalation of competition of molybdates and hydroxyl ions for adsorption areas on the particles of solid phase of soil.

## 5. Conclusions

1. The soil reaction decreases lightly during the four years of observations both in the witness and samples fertilized by N and P, but also in the samples with amendments applied periodically.
2. The phosphorous content in the albic luvisol was low, the mineral fertilizers contributing to its increase of 3-12 mg·kg<sup>-1</sup> and depending on the treatments applied to. The versatile potassium suffers insignificant variations.
3. Mineral and natural fertilization was the factor that significantly determined the concentration of microelements in soil.
4. The general rule is that the mobility of microelements Cu, Zn, Mn and B decreases with the increase of pH value, influenced by the amendments applied and conversely, the mobility increases with the pH decrease. In the case of molybdenum, mobility occurs conversely. The mineral fertilizers caused a decrease of the concentration of versatile manganese, zinc and copper while the concentration of boron and molybdenum was increased. It was surprisingly to observe a certain increase of the values in the case of molybdenum, explained by the increased humus content in soil. Excepting the content of active Mn which was generally high, the concentration of the other microelements was in normal limits.
5. Through neutralization of soil reaction (variant 5 and 6), liming caused a decrease of the concentration of manganese, zinc and copper in soil solution, while the concentration of boron and molybdenum was increased.
6. As shown in the results and discussion section, we obtained only one statistically significant difference for P<sub>2</sub>O<sub>5</sub>.
7. The long-term fertilization with organic fertilizers does not result in significant increases in phosphorus and mobile potassium of soil content. There is a good correlation between the content of microelements and nitrogen rates used, irrespective of the type of mineral soil enhancer applied.

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