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DEVELOPMENT OF A NEW, MORE ADEQUATE METHOD FOR THE DETERMINATION OF SOIL ACIDITY

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ABSTRACT. Soil acidification is a relevant problem in Hungary – just as in other parts of the world. Liming and remediation of acidic soils are essential regarding both environmental and agricultural concerns. The nowadays most applied liming material determination method is not exact enough and does not reflect enough the quality and quantity of different soil acidity forms. The main reason for that is, that with the used hydrolytic acidity measurement method only the amount of protons that are set in rapid reactions till the equation point can be titrated. With the new elaborated „pH-stat" method we measure the amount of KOH and time needed to reach the standard pH-value 6.5 with a longer titration. The enlarged reaction time enables protons, bound on fine inner pores of soils, to dissociate. By the analysis of titration curves the actual and the potential soil acidity can be differentiated. Our measurement results make a more exact calculation of the need amount of liming material possible. The experiments carried out in three sites of acidic soils with maize plants showed that the present Hungarian liming recommendation system results lime overdose that is unnecessary and partly harmful.

Keywords: soil acidity, slow titration, "pH-stat"

INTRODUCTION

The soil's basic functions may suffer a loss by natural or anthropogenic acidification. In Hungary this problem has a great importance because the area susceptible for acidification covers more than the half of the country's land. The knowledge of the exact value of soil acidity is important because of lime requirement estimation, thus their amelioration and protection of soils (Várallyay et al., 1980; Várallyay, 2006; Husti, 2006).

In Hungary and in some other countries the CaCO3 amount needed to ameliorate acid soils is calculated by considering their hydrolytic acidity (HAC1). In the measurement suggested by Kappen (1929) the acidity of the equilibrium solution of the soil's Ca-acetate extract is quantified. This acidity value shows only the equilibrium value of H+ amount corresponding to the given soil/extractant ratio. To determine the total releasable surface acidity the soil must be continuously percolated or the soil/extractant ratio must be changed (Filep, 1999).

For the elimination of this principle error of Kappen's method the soil acidity can be determined by the pH-stat titration of the soil suspension (Czinkota et al., 2002).

Based on the new soil acidity determination method a new technology has been developed for the amelioration of acid soils. According to this technology the amount of liming material is equal to the amount of H+ in the liquid and solid phase and the H+ deriving from protolytic reactions. The hungarian liming recommendation system that is based on the hydrolytic acidity gives about twice as high lime doses than the new method.

Csatho (2001) found that lime doses according to the recommendation system are adequate to loamy clay and clay soils but on sand and sandy loam 50 % of the full lime dose was the most efficient. As a result of the treatments the soil properties (CEC, pH, hydrolytic acidity) has changed in long-term experiment (Kátai, 2006).

In this work the yield and element composition of plants grown on traditionally limed, limed after the new method and unlimed soils will be compared.

MATERIALS AND METHODS

For the experiment 3 sites with low soil pH were chosen from the farms of the partners of KITE Ltd, Nádudvar. The soil properties of these sites can be seen in Table 1. The experiments had 3 treatments in 4 replications in randomised plot design. The area of each plots were 0.1 ha. The treatments were the calculated full lime dose according to traditional and new method.

The hydrolytic acidity values were determined according to Kappen (1929). The air-dried and grinded soil samples were treated with 0.5 M/dm3 calcium acetate solution adjusted to pH 8.2 in the ratio 1:2.5). The suspensions were shaken for one hour then filtrated. The filtrates were titrated with 0.1 M/dm3 sodium hydroxide solution in presence of phenolphthalein indicator and the hydrolytic acidity

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values were calculated from the amount of alkali consumed (0.1 M/dm3 NaOH cm3 for 50 g air dried soil).

Table 1

Some properties of soil samples

Site	Álmosd 1.	Álmosd 2.	Vasmegyer
K_A^*	29.9	30.7	38.7
HAC_1	14.77	16.43	28.59
pH-KCl	4.52	4.46	3.63
pH-$CaCl_2$	4.56	4.49	3.71
Bulk density kg/dm^3	1.38	1.39	0.87
Lime dose t/ha	7.68	8.78	19.25

** upper limit of soil plasticity*

The lime dose of the traditional method was calculated by the following formula: lime dose =17.4*KA*HAC1/1000 (tons per hectare). Where KA is the upper limit of plasticity and HAC1 is the hydrolytic acidity.

The pH-stat titrations were carried out in 0.01 M/dm3 CaCl2 solution with the multi-channel titration equipment (Figure 1) which was designed for this purpose (Czinkota et al., 2002). The titrations were performed in 1:25 ratio 0.01 M/dm3 calcium chloride solution suspensions (Filep et al., 2008). The fixed limit value of the titration was adjusted to pH = 6.5.

Fig. 1 The multi-channel slow titration equipment

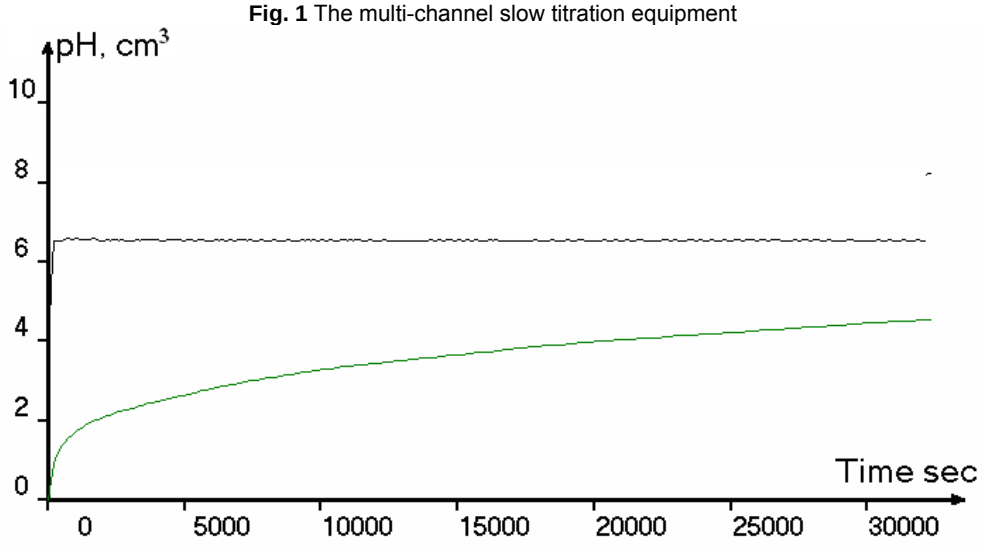

Fig. 2 Typical titration curves

The typical titration curves are to be seen in the Picture 2. The upper line shows the relation between pH value of the soil suspension and the time, the lower one the titration solution volume and the time relationship.

According to the equation used for evaluation of titration curves the lime doses requirement can be calculated as follows:

$CaCO_3$ g/kg soil = $(C + a_1 + a_2) \cdot c / 2m$

Whereas:

$C + a_1 + a_2$ are the consumed titration KOH solution (cm^3),

c is the concentration of titrating solution (M/dm^3),

m is the analysed soil mass (g).

The result was trans-calculated to CaCO3 tons per hectare value (Table 1).

The liming material was centrifuged sugar industry sludge with 80 % calcium carbonate content. The applied plant was maize (Zea mays L.) in both experimental years (2006, 2007). The plant samples were taken on 27th June 2006. Determination of plant element concentrations was carried out with ICP-AES method after cc. HNO3 + H2O2 digestion in the laboratory of RISSAC, Budapest. At harvest time the grain yield of maize and the moisture content were measured. The yield mass values were converted to the value of May (14 % moisture content). For the statistical evaluation of the data 2 and 3 factorial ANOVA was used.

RESULTS AND DISCUSSIONS

Foremost the element concentrations of plant samples in the first year of the experiment were compared in function of production site and liming treatments. The Ca content of the plants were influenced by both site and liming technology. In every treatment the maize in Vasmegyer contained less Ca than the plant samples of the two Álmosd site. The average values showed the same trends (Table 2).

Table 2

Ca content in maize (above ground parts together) in function of liming treatments and site (mg/kg)

Site	Control	New dose	Old dose	Average
Vasmegyer	3980	4694	4692	4455
Álmosd 1	5662	6150	6693	6168
Álmosd 2	5502	6510	5977	5997
Average	5048	5785	5787	
$LSD_{5\%}$		550		952

Table 2 shows that new dose liming heightened the Ca content of maize compared to that of the control but the old dose did not increased it further.

Only the site significantly influenced the K content of the maize. In the average of the treatments the K content in Vasmegyer was 3.1 % while on Álmosd 1 site 1.8 % and on Álmosd 2 1.5 %. The LSD5% value was 0.5 % thus K content on the Álmosd sites are the same but on the Vasmegyer site it was twofold higher. The average value of the treatments for the control treatment was 2.4 % for old dose 2.1% and for new dose 2.0 %. The LSD5% value for these data was also 0.5 % thus the decrease in K content of the plants caused by liming was not significant.

The P and S content of the plant samples were equalized. Nor the site neither the liming treatment had any significant influence on maize P and S content (Table 3 and 4).

Table 3

P content in maize (above ground parts together) in function of liming treatments and site (mg/kg)

Site	Control	New dose	Old dose	Average
Vasmegyer	3281	3293	3177	3250
Álmosd 1	3113	3305	3139	3186
Álmosd 2	3281	3293	3177	3250
Average	3225	3297	3165	
$LSD_{5\%}$		241		241

Table 4

S content in maize (above ground parts together) in function of liming treatments and site (mg/kg)

Site	Control	New dose	Old dose	Average
Vasmegyer	3281	3293	3177	3250
Álmosd 1	3113	3305	3139	3186
Álmosd 2	3281	3293	3177	3250
Average	3225	3297	3165	
$LSD_{5\%}$		241		241

The Cu content of the maize was significantly different on the different sites. In the average of the treatments the Cu content in Vasmegyer was 6.4 in Álmosd 1 7.9 and in Álmosd 2 8.1 mg/kg. The LSD5% is 0.7 thus there was no difference between the two Álmosd sites but on Vasmegyer the Cu content of maize was significantly smaller. This phenomenon can be the consequence of the high organic matter content of the Vasmegyer soil. The average values of the treatments were 7.0 mg/kg for control, 7.8 mg/kg for new dose and 7.5 mg/kg for old dose. The LSD5% value (0.7) showed that the Cu content of the plants increased significantly even in the new dose lime treatment. The Cu content decrease in the old dose treatment was not significant.

The Fe content of the plants did not change in function of sites (Table 5). The Fe content increased significantly only in the new dose treatments according to the average of the sites. The application of old dose didn't cause further Fe increment is the maize. On the Vasmegyer soil the old dose liming decreased the Fe content of the maize compared to the new dose treatment (LSD5% = 19 mg/kg).

Table 5

Fe content in maize (above ground parts together) in function of liming treatments and site (mg/kg)

Site	Control	New dose	Old dose	Average
Vasmegyer	133	175	156	155
Álmosd 1	160	150	156	156
Álmosd 2	144	160	176	160
Average	146	162	162	
$LSD_{5\%}$		11		11

The maize grain yield mass of the two years of the experiment (counted in the value of May: 14% moisture content) was evaluated in function of the site, lime dose and year with 3 factor ANOVA (Table 6).

Table 6

Maize grain yield mass calculated to the value of May in function of year, site and liming treatment (t/ha)

Year	2006			2007		
Site	Control	New dose	Old dose	Control	New dose	Old dose
Vasmegyer	8.92	9.16	7.84	7.12	7.67	7.23
Álmosd 1	9.01	8.70	8.11	7.96	7.98	8.01
Álmosd 2	8.21	8.01	7.59	8.57	8.66	8.59
Average	8.71	8.62	7.85	7.88	8.10	7.94
LSD_5 %			0.54			

The average of new dose treatment in the year 2006 showed not significant change compared to the control but the traditional calculated dose caused yield depression. In the second year (2007) one year after liming the effects are not that significant. The yield increment in the new dose and old dose treatment was not significant compared to the control. The old dose treatment caused yield decrease compared to control and new dose treatment in the average of years and sites too.

The average values for the different treatments were the following: control 8.3, new dose 8.36 and traditional dose 7.9 t/ha. The LSD5% for these values was 0.38. The average of the yield on the three sites was not different significantly. The yield in 2007 was significantly smaller than in 2006. This decrease was in accordance with the changes of nationwide yield thus it is caused by the dry weather.

CONCLUSIONS

These experiments confirm the results of former experiments that the lime amount calculated from the hydrolytic acidity is excessive. This investigation proved that this lime amount decreases the maize yield and element content compared to the approximatelly half dose (after the new method) of the calculated lime amount. These experiments showed that the present Hungarian liming recommendation system results lime overdose that is unnecessary and partly harmful.

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