Comparison of methods for soil acidity measurement in Nyírlugos (Hungary) long-term expriment
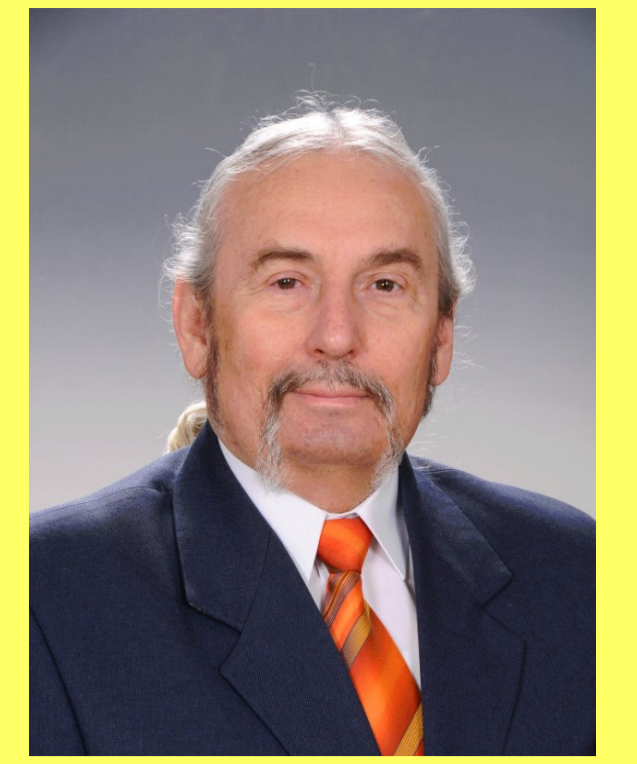
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Abstract
Soil acidification and the amelioration of acidic soils is a world wide problem. Acid soils occupy approximately 30% of the world's ice free land area. The knowledge of the exact value of soil acidity is important because of lime requirement estimation, thus their amelioration and protection of soils. In Hungary and in some other countries the $CaCO_3$ amount needed to ameliorate acid soils is calculated by considering their hydrolytic acidity (y_1). In the measurement suggested by Kappen the acidity of the equilibrium solution of the soil's Ca-acetate extract is quantified. The amount of acidity titrated in the equilibrium solution depends on the acidity of the soil and on the suspension pH. To determine the total releasable surface acidity the soil must be continuously percolated or the soil/extractant ratio must be changed. 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. Our results show that the new method can characterise quantitatively soil acidity thus it can give the basis for the lime requirement calculation.

Introduction
The knowledge of the exact value of soil acidity is important because of lime requirement estimation, thus their amelioration and protection of soils.
For the investigation of mineral fertilization and liming a field experiment was set up in Nyírlugos on acidic sandy brown forest soil with alternating thin layers of clay substance.. By now this experiment is one of the oldest in Hungary. The treatments of the experiment can be seen in Table 1.

Table 1. Fertilization and liming treatments in the experiment, kg/ha/yr (Brown forest soil, acid sand, Nyírlugos, Nyírség region, Hungary) (Kádár, 2007)

Nutrient levels	Applied nutrients				
	N	P_2O_5	K_2O	$CaCO_3$	$MgCO_3$
0	0	0	0	0	0
1	50	60	60	250	140
2	100	120	120	500	280
3	150	180	180	1000	-

As a result of the treatments the soil properties (CEC, pH, hydrolytic acidity) has changed. Thus the soils of different treatments can serve as a basis of the comparison of different acidity measurement methods.
In Hungary and in some other countries the $CaCO_3$ amount needed to ameliorate acid soils is calculated by considering their hydrolytic acidity (y_1). In the measurement the acidity of the equilibrium solution of the soil's Ca-acetate extract is quantified. The amount of acidity titrated in the equilibrium solution depends on the soility and on the suspension pH. But this acidity value does not equal to the total amount of releasable H^+. It shows only the equilibrium value corresponding to the given soil/extractant ratio. For the elimination of this principle error of this method the soil acidity can be determined by the pH-stat titration of the soil suspension.

Methods
For the experiment 6 treatments of the field experiments soil was investigated: control, N_1, N_2, N_3, $N_2P_2K_2Ca_3$, $N_2P_2K_2Mg_2$. The properties of samples are shown in Table 2.

Table 2. Properties of the investigated soils (Kádár, 2007)

Treatment code	pH(H_2O)	pH(KCl)	Hydrolytic acidity, y_1	CEC	Sum of bases
					meq/100g
Control	5.4	4.3	7.6	3.4	1.2
N_1	5.0	4.2	9.6	3.4	0.7
N_2	4.7	3.6	12.6	3.4	0.5
N_3	4.6	3.5	13.6	3.3	0.4
$N_2P_2K_2Ca_3$	6.8	6.4	3.6	3.6	2.5
$N_2P_2K_2Mg_2$	6.3	6.0	4.8	3.8	2.2

Determination of hydrolytic acidity: the samples were treated with 0.5 M/dm^3 Ca-acetate solution adjusted to pH 8.2 in the ratio of 1:2.5. The filtrates were titrated with 0.1 M/dm^3 NaOH solution and the hydrolytic acidity values were calculated from the amount of alkali consumed (0.1 M/dm^3 NaOH cm^3 for 50 g soil).
The pH-stat titrations were carried out in 0.01 M/dm^3 $CaCl_2$ solution with the multichanel titrator designed by Czinkota (Picture 1).
The titrations were performed in a 1:25 ratio 0.01 M/dm^3 $CaCl_2$ solution suspensions. The fixed limit value of the titration was pH = 6.5.

Picture 1. Multichanel titrator

Results
The titration curves of the soils of different treatments are shown in the Figure 1. The endpoint of the titration could be determined by extrapolation. The reliability of the extrapolated values is based on applied mathematical model.

$$y = A_0 + A_1*(1-e^{-k1t}) + A_2*(1-e^{-k2t}) \qquad (1)$$

where:
C amount of base or acid to reach the given pH, meq/100g
y amount of fed base or acid, meq/100g
t time, sec
a_1 base or acid consumption of faster process, meq/100g
a_2 base or acid consumption of slower process, meq/100g
k_1 rate constant of faster process, s^{-1}
k_2 rate constant of slower process, s^{-1}

The 5 parameters of the model (A_0, A_1, A_2, k_1, k_2) were calculated by non-linear regression. The estimations of the parameter values are not independent from each other. Especially the different combinations of A_1 - k_1 and A_2 - k_2 parameter pairs may give models that describe the measured values with the same reliability.

This phenomenon can cause problems if the task the comparison of different soil samples is. That is why the model should be modified: the parameters must be independent, the number of parameters should be as smaall as possible and the complete exponential model must be transformed into a linear model.
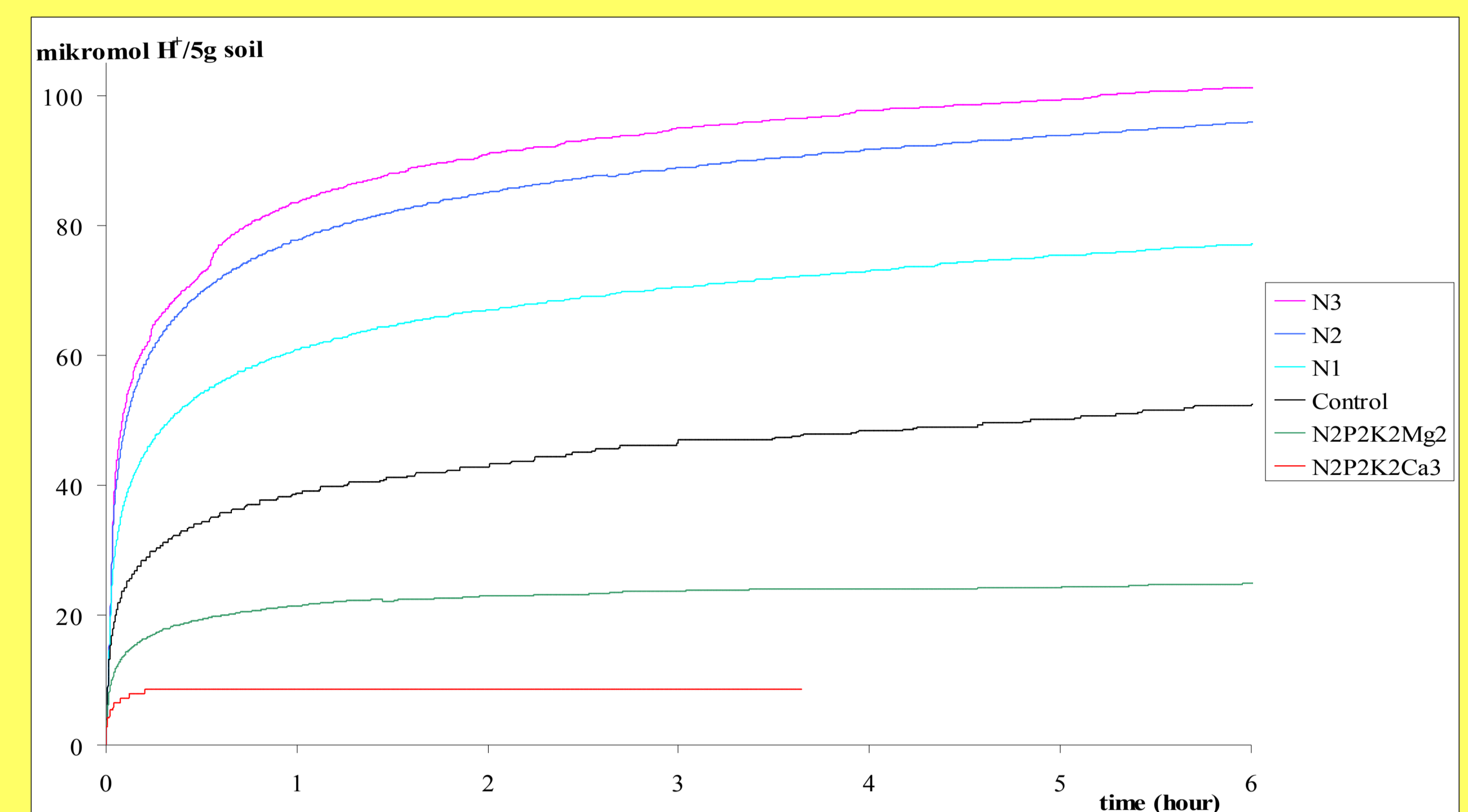

Figure 1. Titration curves of the soils of different treatments in the average of 4 replications.

To solve these problems the following function were used:

$$y = A_0 + A_1*(1-e^{-k1t}) + A_2*(1-e^{-k2t}) + A_3*(1-e^{-k3t}) + A_4*(1-e^{-k4t}) \qquad (2)$$

For the model fitting the k parameters were constant (k_1=12,0; k_2=3,0; k_3=1.0; k_4=0,08) so as the A – k pairs with the same index were independent. The model with these parameters reach the 99% of alkali consumption as presented in Table 3.

Table 3. The time required to reach the 99% of base consumption of the reactions with different rate constant values (k)

rate constant, k	12.0	3.0	1.0	0.08
required time (hours)	0.38	1.53	4.60	57.56

With the combination of reactions with different rate constant gave a well fitted model (Table 4).

Table 4. Parameter values of the titration N_3 treatment soil (I - IV replications)

Parameters / replications	I.	II.	III.	IV
A_0	208.2	199.8	205.6	131.8
A_1	199.5	235.7	199.9	330.1
A_2	90.2	121.4	111.4	0.0
A_3	155.7	165.7	113.4	388.1
A_4	247.6	337.6	295.8	166.7
$A_0 + A_1 + A_2 + A_3 + A_4$	901.2	1060.2	926.1	1016.7
g soil	4.8556	4.9322	5.0264	5.0155
In the measure of y_1	11.79	13.66	11.71	12.88

In the column of replication IV (Table 4) can be seen that not all titrations can divide into 4 different rated reactions. In this case the A_2 value of the reaction with k_2=3.0 was 0.0.
The calculation was carried ot with a 4 parameter linear regression according to the following model:

$$y = A_0 + A_1*z_1 + A_2*z_2 + A_3*z_3 + A_4*z_4 \qquad (3)$$

where: $z_1 = 1-e^{-k1t}$ $z_2 = 1-e^{-k2t}$ $z_3 = 1-e^{-k3t}$ $z_4 = 1-e^{-k4t}$
The sum of base consumption ($A_0 + A_1 + A_2 + A_3 + A_4$) was calculated in case of each replications from the A values resulted from the regression. These values represent the alkali consumption extrapolated for infinite time. These values are determined by the acidity releasable from the surfaces of soil colloids. The titrated acidity values were given in the measure of y_1. The averages of different treatments can be seen in Table 5.

Table 5. The titrated acidity values in case of different treatment soils

Measured and calculated characteristics	Treatments code						LSD$_{5\%}$
	N_3	N_2	N_1	Control	NPKMg	NPKCa	
titration µmol/5g soil	125.1	116.1	93.8	70.8	30.9	8.6	
In the measure of y_1	12.51	11.61	9.38	7.08	3.09	0.86	2.00

For the validation of titrated acidity values the results were correlated with the difference between CEC and sum of exchangeable basic cations (CEC-BC). The CEC-BC values can conclude to the amount of ions causing acidity ($Al^{3+} + H^+$) (Table 6).

Table 6. Acidity of the investigated soil samples detemined with different methods: y1 and the the difference between CEC and sum of exchangeable basic cations (CEC-BC)

Measured and calculated characteristics	Treatments code						LSD$_{5\%}$
	N_3	N_2	N_1	Control	NPKMg	NPKCa	
CEC-BC (meq/100 g)	2,9	2,9	2,7	2,2	1,6	1,1	0,4
Hidrolytic acidity (y1)	13,6	12,6	9,6	7,6	4,8	3,6	2,1

Both of the acidity values measured by traditional and new titration method resulted the same LSD$_{5\%}$ values (Table 5 and 6).

Conclusion
It can conclude from the above that the new method can characterise quantitatively soil acidity thus it can give the basis for the lime requirement calculation.