Comparison of methods for soil acidity measurement in Nyírlugos (Hungary) long-term field expriment

Imre Vágó[A], László Tolner[B], Imre Czinkota[B], Márk Rékási[C] and Imre Kádár[C]

[A]Faculty of Agricultural Science, University of Debrecen, Böszörményi Street 138, H-4032, Hungary, Email: vago@agr.unideb.hu
[B]Faculty of Agriculture and Environmental Sciences, Szent István University, Gödöllő, Páter K. Street 1, Hungary, E-mail: Tolner.Laszlo@gmail.com, Imre.Czinkota@gmail.com
[C]Research Institute for Soil Science and Agricultural Chemistry of the Hungarian Academy of Sciences, Budapest, Herman Ottó Street 15. E-mail: Rekasi@rissac.hu, kadar@rissac.hu

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 the 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 (y1). In the measurement suggested by Kappen (1929) 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.

Key Words

Soil acidity, slow titration, brown forest soil, long-term field experiment

Introduction

The soil's basic functions may suffer a loss by natural or anthropogenic acidification. 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. 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 (Uexküll - Mutert 1995; Várallyay *et al.* 1980).

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 „kovárvány" by Láng István (1973). 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 (Kádár 2007). 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 (y1). In the measurement suggested by Kappen (1929) 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. 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. 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.* 2000).

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	pH	pH	Hydrolytic acidity,	CEC	Sum of bases
code	(H_2O)	(KCl)	y_1	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

The hydrolytic acidity values were determined according to Kappen (1929). 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 suspensions were shaken at room temperature for one hour then filtrated. The filtrates were titrated with 0.1 M/dm^3 NaOH solution in presence of phenolphthalein indicator 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 titration equipment designed for this purpose (Czinkota *et al.* 2002). The titrations themselves 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.

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.

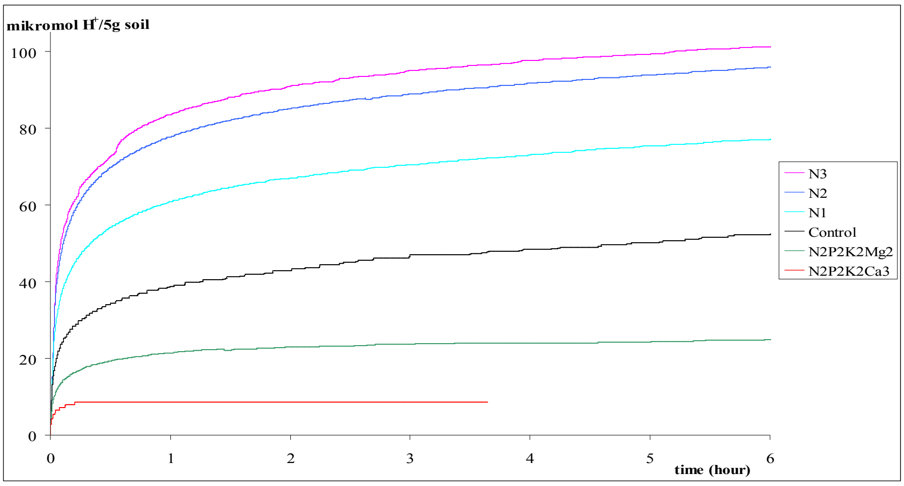

Figure 1. Titration curves of the soils of different treatments in the average of 4 replications.

The reliability of the extrapolated values is based on applied mathematical model. In our previous research works the proton exchange reactions were described as the sum of two first order kinetic equations (Filep and Csubák 1997):

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

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 small as possible and the complete exponential model must be transformed into a linear model (Tolner, L. and Füleky, Gy. 1995).

To solve these problems the following function were used:

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

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 values (k)

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**
$\mathbf{A_0}$	208.2	199.8	205.6	131.8
$\mathbf{A_1}$	199.5	235.7	199.9	330.1
$\mathbf{A_2}$	90.2	121.4	111.4	0.0
$\mathbf{A_3}$	155.7	165.7	113.4	388.1
$\mathbf{A_4}$	247.6	337.6	295.8	166.7
$\mathbf{A_0 + A_1 + A_2 + A_3 + A_4}$	**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**

* consumed cm^3 of 0.1 M/dm^3 NaOH to titrate back 50 g soil after 1 hour shaking with 0.5 M/dm^3 Ca-acetate solution (pH 8.2)

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:

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

where: $\mathbf{z_1 = 1-e^{-k1t}}$ $\mathbf{z_2 = 1-e^{-k2t}}$ $\mathbf{z_3 = 1-e^{-k3t}}$ $\mathbf{z_4 = 1-e^{-k4t}}$
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

* consumed cm^3 of 0.1 M/dm^3 NaOH to titrate back 50 g soil after 1 hour shaking with 0.5 M/dm^3 Ca-acetate solution (pH 8.2)

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: according to Kappen (1929) – 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 (Kappen, 1929) 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.

References

Czinkota I, Filep Gy, Rékási M, Czanik P (2002) An equipment and software for improved estimations of soil acidity. *Agrokémia és Talajtan* **51**, 63-73.

Filep Gy, Csubák M (1997) A protonátmenettel járó felületi reakciók kinetikája talaj/vizesoldat rendszerekben. *Agrokémia és Talajtan* **46**, 159-170.

Kádár I (2007) Some lessons learned from the Nyírlugosi long-term field experiment. COLAR07, Debrecen (Ed J Lazányi) pp. 37-43.

Kappen H (1929) Die Bodenazidität. Springer Verlag. Berlin. 363. p.

Láng I (1973) Műtrágyázási tartamkísérletek homoktalajokon. Akad. Doktori Disszertáció. Kézirat. MTA. Budapest.

Tolner L, Füleky Gy (1995) Determination of the Originally Adsorbed Soil Phosphorus by Modified Freundlich Isotherm. *Commun. Soil Sci. Plant Anal.* **26,** 1213-1231.

Uexküll HRvon, Mutert E (1995) Global extent, development and economic impact of acid soils. In: Plant soil interactions at low pH. Eds. Date R. A. - Grundon N. J. - Rayment G. E. - Probert M. E. Kluwer Academic. 749-752. p.

Várallyay Gy, Szűcs L, Murányi A, Rajkai K, Zilahy P. (1980) Map of soil factors determining the agro-ecological potential of Hungary (1:100,000) II. *Agrokémia és Talajtan*. **29,** 35-76.