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EVALUATION OF SOILS ACID-BASE SUSCEPTIBILITY

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1. INTRODUCTION

The soil is a component of the natural environment, part of the biosphere together with air and water. On the other hand it is the agriculture's most important mean of production, conditionally renewable natural source that constitutes 1/5 of our national wealth. The survival and development of modern society is directly connected to the soil and its functions:

- The supply of the population with food in adequate amount and quality;
- Provide clean water and air;
- Provide pleasant environment, living conditions (KÁDÁR, 1998; VÁRALLYAY, 2005).

These functions may damage if the soil becomes acidic because of natural or anthropogenic causes. The soil acidification and the amelioration of acidic soils is a worldwide problem. Acidic soils cover 30% of the world's ice free land area. The handling of this issue is important in both environmental and agricultural point of view: one part is the protection of natural ecosystems and the other is sustainability of the production of agricultural areas.

In Hungary this problem has great importance because 42% of the agricultural area is susceptible for acidification and on 13% of the area the liming is absolutely necessary. Thus more than the half of our agricultural area is concerned (VÁRALLYAY et al., 1980).

The better knowledge of soils acid-base buffering capacity and susceptibility is important because of their amelioration and protection. The buffering capacity has great importance in both – acidic and alkali – pH range. The acid buffering capacity plays role in the neutralization of acidic precipitation, acidic fertilizers, etc. The base neutralization capacity has great significance in the determination of lime dose for acidic soils amelioration. There are numerous methods for the measurement of soils acid-base buffering capacity. But their relations to the soil characteristics and to each other are not elucidated in details.

The aim of this work was to investigate the background of parameters describing soil acid-base buffering capacity and its relation to each other and to the soil properties.

The relationship between soil properties and the kinetics of buffer reactions was also studied with pH-stat titrations.

2. LITERATURE REVIEW

The soil is able to buffer the impacts of the environment. One part of this attribute is the acid-base buffer capacity (FILEP - FÜLEKY, 1999).

The amount of strong acid required to reduce the pH of a system to a reference pH value is termed acid buffering or neutralizing capacity (VAN BREEMEN et al., 1983). The susceptibility is the reciprocal of buffering capacity.

The fate of the acid load in soil can be the following:

- neutralization by free bases (CaCO_3 , Na_2CO_3)
- the acidic soil solution can leak to the groundwater in soils that have low cation exchange capacity
- acid ions enter into cation exchange reactions with cations already present on the soil cation exchange complex (MC FEE et al., 1977).

The most important buffer reactions are (FILEP - RÉDLYNÉ, 1988):

1. protonation and deprotonation of organic and inorganic colloids
2. development and decomposition of easily weathering minerals and organo-mineral complexes
3. transformations of Al-hydroxide polymers and / or Al-hydroxocomplexes
4. $\text{CaCO}_3 - \text{Ca}(\text{HCO}_3)_2 - \text{CO}_2$ system.

The dominating acid-base buffer systems of soils are functioning at different pH values because of the behaviour of permanent and variable (pH-dependent) charges (FILEP - RÉDLYNÉ, 1988; ULRICH, 1981).

The easiest way to characterize acid-base buffering capacity of soils is the potentiometric titration (FILEP, 1991). From the titration curves different parameters can be calculated that gives information about the buffering capacity.

The area under the titration curve or the difference between the area under the titration curve and the reference curve (titration without soil) is suitable for

characterization of soil buffering capacity. However these parameters are only qualitative (MURÁNYI, 1987; FILEP, 1991).

For quantitative estimation the equation suggested by FILEP (1991) can be appropriate:

$$\text{pH}_x = \text{pH}_0 - K (m_b)^Q \text{ and } \text{pH}_x = \text{pH}_0 + K (m_s)^Q \quad /1$$

Where: pH_x is the equilibrium pH after the addition of given amount alkali (m_b) or acid (m_s). pH_0 is the pH of the suspension at the beginning of the titration, K is the initial pH change after the addition of one unit alkali or acid and Q is a constant showing the tendency of pH change.

According to VAN SLYKE (1922) buffering capacity can be calculated by differentiation of titration curves:

$$\beta = d m_b/d \text{pH}, \text{ or } -d m_s/d \text{pH} \quad /2$$

Where: β is buffering capacity, m_b is the amount of added alkali, m_s is the amount of added acid. This means that β is the pH change caused by the added acid or alkali. Its measure: meq OH^- or H^+ /100g soil/1 unit pH change.

The buffer capacity can be also described by the amount of acid or alkali requirement of soil to reach a given pH value (YUAN – LAVKULICH, 1995).

The rate of chemical reactions in soil – including buffer reactions – may differ in order of magnitude. Chemical processes can last for seconds, minutes, hours and even thousand years (FILEP - FÜLEKY, 1999). The rate of reaction is the amount of transformed material during a given time period. The reaction rate may depend only on one reactant concentration. This is called first order reaction. In second order reaction the rate is dependent on either concentration of the reactants or the square of one reactants concentration (BREUER, 1995). The researches concerning the kinetics of buffer reactions proved that the proton transfer reactions on soil surfaces can be considered as a pseudo first order reactions (ARINGHIERI - PARDINI, 1983, 1985; FILEP - CSUBÁK 1997). If the amount of reactants (H^+ or OH^- entering to the soil) is

small compared to the other components of buffer reaction (active groups on soil surface: its amount is constant) the reaction can be described by a first order reaction equation.

Many measurements proved that the reactions have two steps: one faster and a slower process (ARINGHIERI - PARDINI, 1983, 1985; FILEP - CSUBÁK 1997; ROSSEL - MC BRATNEY, 2003; ONODA - DE BRUYN, 1966). The faster process takes place on readily accessible soil surfaces while the slower process occurs mostly on the inner surface of soil particles.

3. MATERIALS AND METHODS

For the investigations 25 soil samples from Hungary were used. The upper limit of plasticity index according to Arany (K_A) and the clay + silt % were determined. The pH of samples were measured in 1:2.5 soil : water and 1:2.5 soil : 1 M KCl solution suspensions after 24 hours equilibration. Organic matter content (OM%) was measured by the method of Tyurin. Hydrolytic acidity (HAC_1) values were determined by the alkali titration of 1:2.5 soil : Ca-acetate (pH = 8.2) suspension after one hour shaking (KAPPEN, 1929).

The actual cation exchange capacity (CEC_{act}) and exchangeable cation content measurement was performed by the modified method of GILLMAN (1979), the potential cation exchange capacity (CEC_{pot}) and exchangeable cation content measurement by the modified method of BASCOMB (1964) (TEMMINGHOFF, 2000).

The acid-base titrations were performed in 1:20 soil : water or 1 M KCl suspensions. For 5g part of each soil samples (<2 mm) 0.1 M NaOH or HCl was added in increasing amounts: 0; 1; 2; 4; 6; 8; 10; 12; 14; 16; 20; 24; 28 meq H^+ /100g soil or OH^- /100g soil. After acid and alkali addition the suspensions were completed to 100 cm^3 with water or 1 M KCl solution. The titration curves were obtained by plotting the equilibrium pH values against the added base or alkali.

The pH-stat titrations were carried out with equipment designed for this purpose (CZINKOTA et al., 2000). For the measurement 1:40 soil : 1 M KCl solution was used. The pH of continuously stirred soil suspension was measured with a pH-selective electrode. Signals from the pH electrode were first amplified then digitised to provide

input for the computer, where they were transformed to pH values using preliminary calibration. The pH measurement was made in every second. The measurement system was built using Radelkis OP-0808P pH electrode, Schott Titronic 96 automatic burette, ALTAIR BT AAD2816S amplifier and analogue digital converter and an I486 pc.

The time of measurements was at least 8 hours. The limit value was pH = 8.2 and pH = 3. For the titration 0.1 M NaOH and HCl was used. In case of 16 samples the titration to pH = 8.2 was also performed in N₂ atmosphere.

4. RESULTS AND DISCUSSION

Based on correlations between different soil properties one can state that the examined parameters were not independent. The soils with greater clay + silt fraction had greater organic matter content. Thus these two parameters theoretically can be considered as “colloid content” of the soil. The difference between potential and actual cation exchange capacity shows the amount of H⁺ bounded by variable charge and also the amount of variable charge. Since variable charges were protonated (because of the acidic pH of the samples) exchangeable basic cations were adsorbed only by permanent charges. Thus actual CEC and partly the sum of exchangeable basic cations (mostly Ca²⁺) showed the amount of permanent charges of the investigated soils. The organic matter content and clay + silt % correlated better with potential CEC than with actual. This means that both clay and organic matter had significant amount of variable charge. The hydrolytic acidity and exchangeable Al³⁺ was in reverse order with soil pH but its value increased in function of colloid content.

4. 1. Buffer capacity parameters

The soil acid-base buffering capacity was investigated with titration curves (Figure 1). From titration curves five buffer capacity parameters were calculated.

The first evaluation method was the fitting of a power function (suggested by FILEP, 1991) on titration curve:

$$\text{pH}_x = \text{pH}_0 - K (m_b)^Q \text{ and } \text{pH}_x = \text{pH}_0 + K (m_s)^Q$$

Where: pH_x is the equilibrium pH after the addition of given amount alkali (m_b) or acid (m_s). pH₀ is the pH of the suspension at the beginning of the titration. K is the

initial pH change after the addition of one unit alkali or acid ($\Delta\text{pH} / 1 \text{ meq H}^+ / 100\text{g}$ or $\text{OH}^- / 100\text{g}$) and Q is a constant showing the tendency of pH change that is the percentage of pH change caused by 1 % acid or alkali load increment ($\Delta\% \text{pH} / \Delta\% \text{ meq H}^+ \text{ or OH}^- / 100\text{g soil}$).

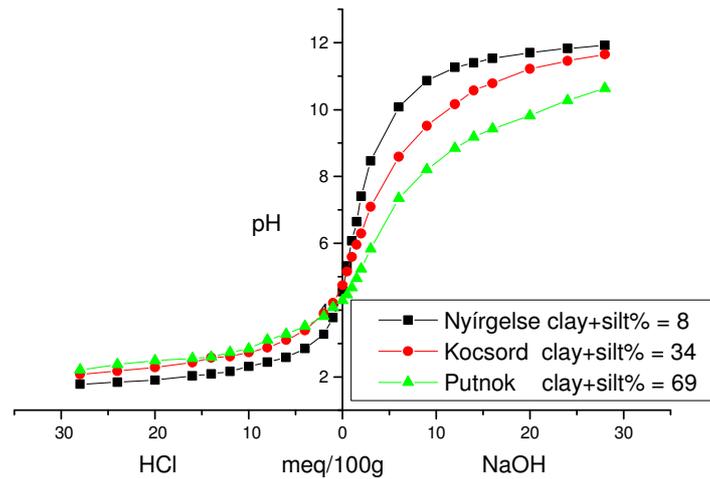


Figure 1. Titration curves of soils with different texture (background: 1 M KCl)

The function was fitted to the first and the second part of the curve separately (Figure 2). Based on the parameters obtained at the first part one can state that the acid buffering capacity of the investigated soils was two times greater than base buffering capacity. If the titration was carried out in 1 M KCl the difference was threefold. According to the results of the stepwise linear regressions in the first part of the titration curve the initial pH change (K) was determined by the clay + silt content of the soil at either acidic or alkali loads. The Q value showed connection with CEC in case of acid load and with clay + silt content at alkali load.

In case of the second part of titration curves the Q and K parameters did not show any relation with the investigated soil properties.

The Q and K parameters describing the first part of the titration curve correlated. The regression between them could be described by a power function.

The second examined buffer capacity parameter was the amount of acid or alkali requirement of soil to reach a given pH value ($\text{pH} = 3$ and $\text{pH} = 8.2$). According to this parameter the base buffering capacity was determined by the clay + silt and organic

matter content and exchangeable Al^{3+} . In case of acid buffering the amount of exchangeable basic cations and exchangeable Ca^{2+} were the most important soil parameters.

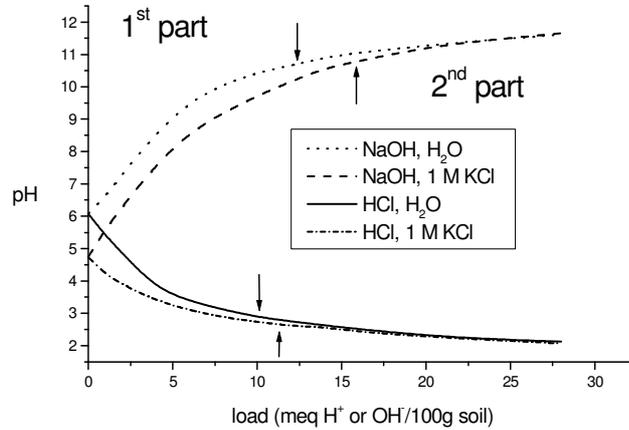


Figure 2. The two parts of the titration curve. Arrows show the end between the two parts. Downward arrows belong to the titrations in deionised water.

The soil components that play role in acid-base buffer reactions are active at different pH values. Therefore the relationships between buffer capacity and soil properties were analysed at different acid and alkali loads as well as pH values. For these investigations the buffer capacity characterized by the difference between the area under the titration curve and the reference curve (A), by the area under the curve of pH-change (A2) and by the derivative of titration curve (β) were used. The relations between these parameters and soil properties were analysed by stepwise linear regressions.

In case of alkali loads the A value was mostly related to clay + silt, organic matter and exchangeable Al^{3+} content (Table 1). If the soil was treated with acid the A value correlated better with exchangeable basic cations and CEC. This means that the acid buffering capacity is mostly connected to the permanent charges while base buffer capacity is determined by variable charges and cations causing acidity.

The area under the curve of pH-change (the initial pH value of the titration was subtracted from each pH value at the different loads) related to the clay + silt content in case of alkali loads. Against acid treatments the clay + silt content was also the most important buffer component between the loads of 0-6 meq H^+ /100g. Over 6 meq

$H^+/100g$ load HAC_1 , pH and potential CEC showed the closest correlation with A2. The A2 value was in reverse order with every soil property but soil pH. The A2 values were in inverse proportion with buffering capacity (A), thus they can be called susceptibility parameters.

The buffering capacity characterized by the derivative of titration curves (β) is suitable to investigate the buffer capacity in function of pH (Table 2). At strongly acidic and acidic pH the buffering capacity was predicted by CEC. The slope of regression curve decreases in function of pH. Therefore at higher pH the difference between soil's buffering capacities become smaller in function of CEC.

Table 1. Equations describing the connection between soil properties and buffer capacity (A) at different load levels. (Background: 1 M KCl)

Load (meq H^+ or OH^- /100g)	Equation	R^2
Titration with HCl		
0-1	$A = 0.39pH - 1.31$	0.56***
1-2	$A = -0.72Al_{act} + 0.03Ca_{act} + 0.56$	0.76***
2-4	$A = 0.09Ca_{act} + 0.49$	0.58***
4-6	$A = 0.09Ca_{act} + 0.27$	0.72***
6-8	$A = 0.08Ca_{act} + 0.16$	0.71***
8-10	$A = 0.07Ca_{act} + 0.09$	0.69***
10-12	$A = 0.06Ca_{act} + 0.06$	0.66***
12-14	$A = 0.04CEC_{act} + 0.02$	0.61***
14-16	$A = 0.04CEC_{act} - 0.02$	0.62***
16-20	$A = 0.07CEC_{act} - 0.04$	0.63***
20-24	$A = 0.06CEC_{act} - 0.08$	0.53***
24-28	$A = 0.06CEC_{act} - 0.16$	0.48***
Titration with NaOH		
0-1	$A = -0.9pH + 0.008clay + silt\% + 7.2$	0.90***
1-2	$A = -0.9pH + 0.02clay + silt\% + 8.1$	0.87***
2-4	$A = 0.07clay + silt\% + 1.1Al_{act} + 5.5$	0.88***
4-6	$A = 0.08clay + silt\% + 1.4Al_{act} + 3.4$	0.89***
6-8	$A = 0.08clay + silt\% + 1.4Al_{act} + 2$	0.90***
8-10	$A = 0.08clay + silt\% + 1.2Al_{act} + 1.1$	0.92***
10-12	$A = 0.08clay + silt\% + 0.9Al_{act} + 0.6$	0.94***
12-14	$A = 0.07clay + silt\% + 0.7Al_{act} + 0.3$	0.95***
14-16	$A = 0.06clay + silt\% + 0.6Al_{act} + 0.1$	0.95***
16-20	$A = 0.11clay + silt\% + 1Al_{act} - 0.14$	0.95***
20-24	$A = 0.09clay + silt\% + 0.75Al_{act} - 0.4$	0.94***
24-28	$A = 0.08clay + silt\% + 0.6Al_{act} - 0.38$	0.91***

From pH = 6 to 8-8.5 mostly soil's clay+silt content, from pH = 8.5 to 9.5 organic matter and CEC showed the strongest correlation with buffer capacity. At higher pH (10<pH<11) clay+silt content determined buffer capacity the most.

These results show that the soil properties were in different relations with buffer capacity and susceptibility at different acid or alkali loads and pH values.

The investigations showed that the connection between a given soil property and buffer capacity parameter was not always linear. In some cases, a power function result in better correlation coefficients between them (Table 3). In function of organic matter and - in most cases - clay+silt content the buffering capacity changed by a power function because by the growth of colloid content the surfaces that are involved in buffer reactions may increase by higher rate.

Table 2. Equations describing the connection between soil properties and buffer capacity (β) at different pH values. (Background: 1 M KCl)

pH	Equation	R ²
2	$\beta = 1.4\text{CEC}_{\text{act}} + 31$	0.82***
2.5	$\beta = 0.61\text{CEC}_{\text{pot}} + 12.7$	0.37*
3	$\beta = 0.17\text{CEC}_{\text{pot}} + 5.6$	0.65***
3.5	$\beta = 0.16\text{CEC}_{\text{pot}} + 2.6$	0.80***
4	$\beta = 0.12\text{CEC}_{\text{pot}} + 1.4$	0.86***
4.5	$\beta = 0.08\text{CEC}_{\text{pot}} + 0.08\text{HAC}_1 + 0.82$	0.97***
5	$\beta = 0.55\text{OM}\% + 0.64$	0.71***
5.5	$\beta = 0.01\text{clay+silt}\% - 0.17\text{Al}_{\text{act}} + 0.87$	0.78***
6	$\beta = 0.02\text{clay+silt}\% + 0.89$	0.76***
6.2	$\beta = 0.02\text{clay+silt}\% + 0.83$	0.80***
6.5	$\beta = 0.02\text{clay+silt}\% + 0.93$	0.73***
7	$\beta = 0.02\text{clay+silt}\% + 0.90$	0.78***
7.5	$\beta = 0.03\text{clay+silt}\% + 0.92$	0.84***
8	$\beta = 0.03\text{clay+silt}\% + 0.94$	0.90***
8.5	$\beta = 0.05\text{clay+silt}\% + 0.94$	0.92***
9	$\beta = 0.2\text{CEC}_{\text{pot}} - 0.98$	0.86***
9.5	$\beta = 0.05\text{clay+silt}\% + 0.1\text{CEC}_{\text{pot}} + 1.15$	0.89***
10	$\beta = 0.09\text{clay+silt}\% + 1.77$	0.91***
10.5	$\beta = 2.4\text{OM}\% + 0.15\text{CEC}_{\text{pot}} + 1.4$	0.84***

The relation between buffer capacity (A) and each soil parameter was investigated at different acid and alkali loads. The method of this assay was the following: the R² values of the regressions between soil properties and buffer capacity parameters at different load levels were plotted against loads. This investigation indicated that soil properties could be divided into two groups according to their relation with buffer capacity (Figure 3). The two groups were the same for both acid and alkali titrations. Organic matter, clay+silt %, CEC, the sum of bases belonged to the same group. The connection between buffer capacity and these properties became stronger in function of

loads. The second group was the pH and exchangeable Al^{3+} . These parameters were in stronger correlation with buffer capacity at smaller loads. This division shows that if acid or alkali loads were small, the original soil pH determined the area under the titration curve, while at larger loads the soil's buffer reactions became more important in the determination of suspension pH.

Table 3. Type of the relation between soil properties and buffer capacity

parameter	Type of titration	pH (H2O)	pH (KCl)	OM%	clay +silt%	HAC ₁	CEC _{pot}	CEC _{act}	S _{act}	Ca _{act}	Al _{act}
A	bw	lin -	lin -	pow +	pow +	lin +	pow +	pow +			lin +
	bkcl	lin -	lin -	pow +	pow +	lin +	pow +	pow +			lin +
	aw	lin +	lin +	pow +	pow +	lin +	lin +	lin +	lin +	lin +	lin -
	akcl	lin +	lin +			lin -	lin +	lin +	lin +	lin +	lin -
A2	bw	pow +	pow +	pow -	lin -	pow -	pow -	pow -	lin -	lin -	pow -
	bkcl	pow +	pow +	pow -	lin -	pow -	pow -	pow -			pow -
	aw	lin +	lin +	pow -	lin -	pow -	pow -	pow -	lin -	lin -	lin -
	akcl	pow +	lin +	pow -	lin -	pow -	pow -	pow -			pow -
Q	bw	lin -	lin -	pow +	pow +	pow +	lin +	pow +	lin +	lin +	
	bkcl	lin -	lin -	pow +	pow +	pow +	pow +				lin +
	aw			pow +	pow +	pow +	pow +	pow +	pow +	lin +	
	akcl	lin -	lin -	pow +	pow +	pow +	pow +	pow +			lin +
K	bw			pow -	pow -	pow -	pow -	pow -	lin -	lin -	
	bkcl	lin +	lin +	pow -	pow -	pow -	lin -	lin -			lin -
	aw			pow -	pow -	pow -	pow -	pow -	lin -	lin -	lin -
	akcl	lin +	lin +	pow -	lin -	pow -	lin -	lin -			lin -
OH _{pH8,2}	bw	lin -	lin -	pow +	pow +	lin +	pow +	pow +			lin +
	bkcl	lin -	lin -	pow +	pow +	lin +	pow +	pow +			lin +
H _{pH3}	aw			pow +	pow +		lin +	lin +	lin +	lin +	
	akcl				lin +		lin +	lin +	lin +	lin +	
β	bw	lin -	lin -	pow +	pow +	pow +	pow +	pow +			lin +
	bkcl	lin -	lin -	pow +	pow +	pow +	pow +	pow +	lin +	lin +	lin +
	aw			pow +	pow +	pow +	pow +	lin +	lin +	lin +	
	akcl	lin -	lin -	pow +	pow +	pow +	pow +	lin +	lin +	lin +	lin +

(lin: linear, pow: power, +: direct ratio, -: inverse ratio; bw: alkali titration in water, bkcl: alkali titration in 1 M KCl, aw: acid titration in water, akcl: acid titration in 1 M KCl)

The only exception of this grouping was hydrolytic acidity: in case of alkali loads its correlation with buffering capacity did not show any change in function of loads while at acid treatment it correlated only at small loads with acid buffer capacity.

Summarizing the investigations of the relationship among buffer capacity parameters and soil properties the following statements can be made:

At acidic pH or acid loads in case of each buffer capacity parameter the cation exchange reactions on permanent charges were responsible for buffering. The soil samples were acidic therefore the variable charges were protonated. Thus the basic cations were all adsorbed by permanent charges. That is why the amount of permanent charges in the investigated soils can be represented by the actual CEC and

approximately by the sum of bases and exchangeable Ca^{2+} . That explains the correlation between these parameters and acid buffering capacity. Against alkali loads or at alkali pH the acidic cations (exchangeable Al^{3+} , hydrolytic acidity) were in direct proportionality with base buffering capacity. This means that OH^- ions of the alkali loads reacted with the H^+ , deriving from the Al^{3+} hydrolysis or from variable charges. The results showed that besides organic matter the investigated soils clay fraction possessed significant amount of variable charges too. In most cases the buffering capacity was in significant correlation with CEC, hydrolytic acidity, caly+silt % and organic matter. Thus eventually the colloid content of the soil was the most important in acid-base buffering capacity irrespectively of soil pH or acid and alkali loads.

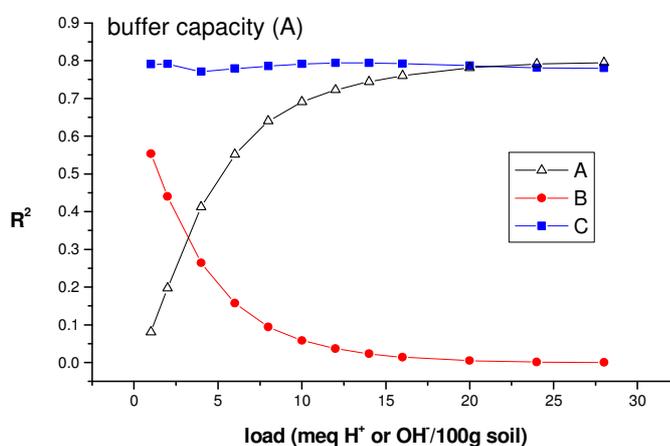


Figure 3. The changes of the connection between soil properties and buffer capacity (A) in function of acid and alkali loads. (A: OM%, caly+silt%, CEC, sum of bases, exch. Ca^{2+} , Mg^{2+} , Mn^{2+} , HAC_1 at HCl titration; B: pH, exch. Al^{3+} ; C: HAC_1 at NaOH titration)

The relation between acid and base buffering capacity was also investigated. These properties were in correlation only at three buffer capacity calculation methods. According to our results acid buffer capacity (Q) and susceptibility (K) values were in direct proportion with base buffer capacity values. The acid neutralization capacity was three times higher than base buffer capacity, which was the result of the acidic pH of soil samples. The acid and base buffer capacity given as the difference between the areas under the titration curve and the reference curve (A) correlated only at the smallest (1 meq H^+ or OH^- /100g) load, because in this case the deviation of suspension pH from

the original pH was not significant. The acid and base susceptibility (A2) were in direct proportionality up to 16 meq/100g loads. The A2 value depended mostly on the buffer reactions and not on the original pH of the soil. At the average pH of the soil samples each buffer system take part in acid-base buffering. Thus either alkali or acid loads were applied the degree of pH change was similar. To sum up the above, in case of these buffer capacity calculation methods the base and acid neutralization capacity are concluded from each other.

About the utilization of the buffer capacity parameters the following statements can be made:

The equation parameters (K, Q) suggested by FILEP (1991) are related with each other, therefore only one of them could be sufficient to describe buffering capacity and susceptibility of soils. The initial pH change caused by one unit of acid or alkali ($K \{ \Delta pH / 1 \text{ meq } H^+ / 100g \text{ or } OH^- / 100g \}$) has more simple measure unit, thus it can be the better one for the description of buffer capacity or susceptibility.

The areas under titration and pH-change curves (A, A2) show the buffering capacity and susceptibility without measure that is why these parameters provide only qualitative information. But these area values are appropriate for investigation of buffer capacity in function of acid or alkali loads. The advantage of β value (the derivate of titration curve) compared to the area parameters is its well-defined measure: $\text{meq } OH^- \text{ or } H^+ / 100g \text{ soil} / \Delta 1pH$.

All of five measurement methods are readily executable with the appropriate software. For detailed analysis the method of VAN SLYKE (1922) might be the most suitable one. The easiest way to characterise buffering capacity and susceptibility with one number is the determination of K and Q function parameters (FILEP, 1991). But in case of more detailed titration curves this method would be also appropriate for detailed buffer capacity analysis.

The background (1 M KCl solution or deionised water) solution influenced the suspension pH thus buffer capacity parameters. In 1 M KCl the exchangeable Al^{3+} correlated more times with buffer capacity parameters than in water. The organic matter content, clay+silt %, hydrolytic acidity and CEC did not show such trend. The cause of this phenomenon is that in the suspension made of KCl solution the K^+ exchanged Al^{3+} and decreased the pH. The values of K and Q parameters were lower in KCl solution

than in deionised water. In case of the buffer capacity defined as the amount of acid or alkali requirement of soil to reach a given pH value, the base buffering capacity increased, the acid neutralization capacity decreased in KCl solution.

4. 2. pH-stat titration

The pH-stat titrations were carried out with equipment that is able to keep the soil suspension pH at a predefined value (pH = 3 and 8.2) by addition of acid or alkali. The proton exchange reactions were described as the sum of two first order kinetic equations on the basis of data pairs indicating the volume of added alkali or acidic solution and the time. By extrapolating this function, to infinite time the maximum acid or alkali consumption at a given pH value could be calculated. The applied formula according to FILEP and CSUBÁK (1997) was the following:

$$y = C + a_1 \cdot (1 - e^{-k_1 t}) + a_2 \cdot (1 - e^{-k_2 t}) \quad /3$$

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 measurement settings influenced the result of the titration:

The longer the measurement time was the greater the base and acid consumption became in both slower and faster processes. Beside this the rate constant showed gradual decrease.

Investigating the conditions of the measurement, the effect of CO₂ content of the air proved to be an important factor. The comparison of the results of alkali titrations in N₂ atmosphere and in air showed that the CO₂ diffusing into the suspension during the measurement could increase the base consumption 1.5 times at present measurement settings.

Investigations of the relationships among kinetic parameters showed that base and acid consumption of fast and slow processes and rate constants are independent. The sum of base and acid consumption values ($C+a_1+a_2$) were also independent from each other.

The relationship among soil properties and kinetic parameters are shown in Table 4 and 5.

The C value (the fastest buffer reactions) at pH = 8.2 titration correlated mostly with exchangeable Al^{3+} and hydrolytic acidity and colloid content of the soil, proving the important role of ions causing acidity in the base buffer capacity. At pH = 3 titration the C value was determined mostly by the sum of exchangeable basic cations and exchangeable Ca^{2+} . These results proved the important role of permanent charges in acid buffer reactions.

The C value at pH = 3 correlated also with CEC but not with colloid content of soils. However in case of alkali titrations the colloid content was in relation with buffer reactions but CEC was not. The background of this difference is that in case of acid loads the cation exchange on permanent charges is the main buffer reaction. That is why the CEC is the most important parameter in buffering. But in case of alkali titration the fastest base buffer reactions were connected to the H^+ desorbed from variable charges. Further important circumstance is that the CEC value was in permanent change during the alkali titration and thus it did not correlate with base consumption of the fastest buffer reactions.

Table 4. Correlation among soil properties and kinetic parameters at titration pH = 3 (Pearson correlation) Abbreviations see: equation 3.

parameters	C	a_1	k_1	a_2	k_2	$C+a_1+a_2$
pH (H ₂ O)	0.419*	-0.289	0.011	-0.054	0.011	0.138
OM%	0.123	0.453*	-0.049	0.437*	-0.229	0.424*
clay+silt%	0.203	0.632**	-0.062	0.595**	-0.381	0.612**
HAC ₁	-0.003	0.476*	-0.151	0.225	-0.252	0.228
CEC _{act}	0.460*	0.620**	-0.277	0.773**	-0.448*	0.867**
exch. Ca _{act}	0.527*	0.454*	-0.153	0.658**	-0.307	0.797**
exch. Al _{act}	-0.158	0.181	-0.276	0.081	-0.208	0.000
Sum of exch bases _{act}	0.506*	0.495*	-0.177	0.695**	-0.330	0.818**
CEC _{pot}	0.399	0.710**	-0.295	0.805**	-0.509*	0.871**

The acid and base consumption of faster process showed correlations with the same soil parameters: organic matter, clay+silt content, hydrolytic acidity, CEC and the sum of exchangeable basic cations. In faster buffer reactions all of the buffer systems present in the investigated soils were involved.

The a_2 and a_1 values of acid titrations correlated with the same soil properties. The base consumption of slower process did not show any relation with the soil properties. The CO_2 diffusion into the suspension might cause this phenomenon.

Table 5. Correlation among soil properties and kinetic parameters at titration pH = 8.2 (Pearson correlation) Abbreviations see: equation 3.

parameters	C	a_1	k_1	a_2	k_2	$C+a_1+a_2$
pH (H_2O)	-0.803**	-0.315	-0.047	-0.086	-0.301	-0.708**
OM%	0.725**	0.664**	-0.303	-0.052	0.364	0.581**
clay+silt%	0.656**	0.749**	-0.126	-0.061	0.596**	0.589**
HAC ₁	0.932**	0.730**	-0.164	-0.092	0.468*	0.778**
CEC _{act}	0.142	0.636**	-0.037	-0.006	0.581**	0.227
exch. Ca _{act}	-0.218	0.473*	-0.080	-0.165	0.427*	-0.141
exch. Al _{act}	0.918**	0.307	-0.025	0.173	0.223	0.853**
Sum of exch bases _{act}	-0.169	0.504*	-0.090	-0.137	0.461*	-0.088
CEC _{pot}	0.352	0.755**	-0.111	0.031	0.623**	0.430*

The sum of acid consumption (asymptotic value) correlated the best with CEC ($r = 0.87$ ill. 0.81) and sum of exchangeable bases ($r = 0.82$). This means that acid buffering capacity was mainly dependent on the permanent charges. The asymptotic value of alkali titration was in the closest relation with exchangeable Al^{3+} ($r = 0.86$). Beside this soil parameter the colloid content and hydrolytic acidity and soil pH was in correlation with base consumption. From these results one can state that against alkali loads the main buffer processes were those that released H^+ to the soil solution.

The rate constant of faster process (k_1) was one order of magnitude higher than this of slower process. According to present results the soil properties did not influence the rate of the faster process. At titration pH = 3 the rate constant of slower process (k_2) was in inverse ratio with CEC. This means that the higher is the CEC the buffer reactions are the slower. The rate constant of slower process at alkali titration was influenced by the CO_2 diffusion into the suspension. That is why it did not correlate with any soil property.

The results of titration to $\text{pH} = 8.2$ were compared to the hydrolytic acidity values measured by the method of KAPPEN (1929). The hydrolytic acidity is an important parameter in the lime requirement estimation of acidic soils. For this comparison the equation 3. was modified: the C constant was eliminated from the equation. By comparing the data from this function with those obtained using the Kappen method it was found that the acidity released in a single extraction was determined by the faster desorption process but the equilibrium values of the process might be twice as high as the acidity measured using the Kappen method. Investigating the cause of this difference it was found that an increase in acidity caused longer reaction half times, in other words a slower reaction. This means that at higher acidity values the acidifying ions are adsorbed even on the less accessible parts of soil components. The increase in soil humus content and to lesser extent the clay + silt content were responsible for the slower desorption. The results of this research confirmed that the longer diffusion paths caused by the macromolecules of humus and the inner binding sites of the clay fraction are mainly responsible for the decrease in the desorption rate.

Values calculated from the modified function for one-hour extraction were also compared with the acidity values obtained after single extraction with Ca-acetate. It was found that in soils having HAC_1 values higher than $2.5 \text{ meq} / 100\text{g}$ the acidity titrated in 1 hour at constant pH was 1.5 times greater than that desorbed by calcium acetate over the same length of time. The difference increased with a rise in acidity.

5. NEW RESULTS

1. The initial pH change after the addition of one unit alkali or acid (K parameter of the function suggested by FILEP, 1991) is suitable for describing susceptibility and the tendency of pH change (Q) can be considered as buffer capacity. The K and Q values were in inverse proportion. This relation can be described by power function. Because of this relation only one of these parameters is sufficient to describe soil acid-base buffer capacity.
2. The slope of a regression curve between a given soil property and buffer capacity parameter changes in function of acid and alkali loads and pH values.

3. The connection between a given soil property and buffer capacity parameter was not always linear. In some cases, a power function described the relation better.
4. In case of each buffer capacity parameter at acidic pH or acid loads the cation exchange reactions on permanent charges were responsible for buffering. Contrary to alkali loads or at alkali pH the acidic cations (exchangeable Al^{3+} , hydrolytic acidity) were in direct proportionality with base buffering capacity. In most cases the buffering capacity was in significant correlation with CEC, hydrolytic acidity, clay+silt % and organic matter. Thus eventually the colloid content of the soil was the most important in acid-base buffering capacity irrespectively of soil pH or acid, alkali loads.
5. The use of 1 M KCl solution as a background of the titrations influenced both buffer capacity parameter values and the relation between buffering capacity and soil properties.
6. The kinetic study of buffer reactions showed that the increase in soil humus content and to lesser extent the clay + silt content decreased the rate of the reactions. The results of this research confirmed that the longer diffusion paths caused by the macromolecules of humus and the inner binding sites of the clay fraction are mainly responsible for the decrease in the desorption rate.
7. The acidity values (HAC_1) obtained in a single Ca-acetate extraction (KAPPEN, 1929) were determined by the faster desorption process of pH-stat titration but the equilibrium values measured by this latter method may be twice as high as the acidity measured using the Kappen method.

6. PRACTICAL RELATIONS

1. The equipment used for pH-stat titrations is suitable for more accurate determination of potential acidity of soils than present measurement methods. Thus based on this equilibrium method lime requirement estimation can be more exact.
2. Based on the results of the linear regressions between buffering capacity parameters and soil properties the buffering capacity can be estimated without direct measurement.

3. After the improvement of my results this work can be partly the basis of the designation of sites for waste deposition.

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