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THE FACTORS INFLUENCING THE BUFFERING CAPACITY OF SOILS AND THEIR IMPORTANCE IN HORTICULTURAL CULTIVATION

THESES OF THE DOCTORAL DISSERTATION

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1. PRECEDENTS AND THE SET AIMS

In horticulture there are numerous requirements to the soil and growing matter due to the different needs of plants. The complexity and peculiarity of growing preconditions the increased interest towards regulating the balance between the processes in the soil and the plant vegetation phases. To control this one has to know the peculiarities of the soil, the root-treating matter that characterize the fundamental changes caused by various influences – sensitivity and (lack of sensitivity =) buffering capacity.

To determine and estimate the buffering capacity of the used matters horticulture applies various, sometimes contrary criteria. Soils and growing matter with high buffering capacity have no sensitivity to a certain degree towards acidifying and alkalinizing influence, which is beneficial for maintaining the optimal reaction for the plant. However, the root treating matter must not have a buffering effect, moreover, it must not modify the composition of the allocated fostering solution.

To create artificial soils and mixtures various organic and mineral materials are used to treat roots and cover the soil. The acid-base buffering capacity of organic materials is usually high. It can be assumed that it is caused by a substantial reducing ability (*why investigate if we know it is high?*), for we have little numerical data on the widely used organic matter like peat or compost. The researchers pay little attention to investigating the acid and alkaline load of organic leftovers on the surface of the soil that are either left or specially placed there. Previous scientific results and the newest researches enable the researchers to interpret and estimate the acid-base buffering ability of organic matters in horticulture and to present more precise theses.

The primary aim of investigating the minerals' acid-base buffering capacity is to solve the problems connected with acidification of the environmental elements. In the researches of such kind besides the regularities of applying organic materials in horticulture one has to take into account other points of view to evaluate the acid-base reduction; however, the latter needs further analyses.

The procedure applied in the analysis of acid-base titration curves was elaborated for mineral soils. To investigate the buffering capacity of organic and some mineral materials the method should be further developed. Researchers of horticulture need further indices to numerically characterize the buffering capacity of organic and mineral materials.

In creating artificial soils and growing matter one of the most important tasks is to set the proper pH value for the plant. In horticultural practice the need to increase and decrease the pH value may emerge. Due to various reasons the low and high acid-base buffering capacity can hinder the accurate regulation of reaction. A further problem is the lack of an appropriate, easily achievable, accurate method to determine the necessary amount of acidifying and alkalinizing materials, the producer often works with an estimated amount. Specialized literature suggests exclusively estimation on the basis of acid-base titration curves, however, the proper method and the principles of evaluation and application are lacking.

The main aim of my research is to get acquainted with and evaluate the natural organic and mineral materials' acid-base buffering capacity, to reveal the possibilities of regulating their reaction, to analyze their importance from the point of view of horticulture. To achieve the main aim I have put forward the following research tasks:

- to adapt the potentiometric titration method used in soil researches to organic and mineral materials, to analyze the acid-base titration curve of the growing matter and artificial soil taking into account the peculiarities of their elements and conditions of their application;
- to determine the exact parameters appropriate for the quantitative estimation of the organic and mineral materials' acid-base buffering capacity and to set their measurement unit;

- to study the titration curve of organic materials used in horticulture, to determine and estimate their buffering capacity, and to conduct their comparative analysis;
- to investigate the titration curve of minerals and products from them used in horticulture, to determine and estimate their buffering capacity, and to conduct their comparative analysis;
- to analyze the possibilities of applying the parameters characterizing titration curves and buffering capacity in research and practical tasks dealing with changes caused by the reaction of organic and mineral materials;
- to reveal and analyze the importance of acid-base buffering capacity in horticultural practice.

2. MATERIALS AND METHODS

2.1 The organic and mineral materials under investigation

For my research I have chosen 20 organic and 12 mineral materials used in horticulture (as well). I have determined the parameters characterizing the acid-base buffering capacity of high moor peat and low moor peat, coir, organic manure, composts of various ripening, their constituent elements, undecomposed plant litter, crushed straw periodically coming to the surface or specifically placed there to cover the soil. Among the minerals I used for the research were river sand, rock wool, burnt clay stone, perlite, bulbous perlite, Cornish stone, bentonite, natrium bentonite, humus bentonite, vermiculite, powder (0,1 – 0,25 mm) and bigger grain (2 – 3 mm) zeolite and alunite.

2.2 The procedure applied in the analysis of acid-base titration curve

I determined the concentration of acid and alkaline solutions per unit of the material under investigation on the basis of proton or hydroxide-ion.

I prepared a series of suspensions by adding an increasing concentration of HCl or NaOH to the 20 g mineral samples and the 10 g organic matter samples. To determine the initial pH value of the sample I made one distilled water suspension as well. In researching minerals in the proportion 1:2,5 sample : solution the maximum proton or hydroxide-ion load was 12,5 $\mathrm{cmol \cdot kg^{-1}}$. The analysis of the titration curve of organic materials and minerals capable of taking in and retaining great amounts of water was conducted in the proportion 1:10 sample:solution. With organic materials I applied the maximum proton or hydroxide load of 25 $\mathrm{cmol \cdot kg^{-1}}$. With minerals in the proportion 1:10 sample:solution the maximum proton or hydroxide load was 12,5 $\mathrm{cmol \cdot kg^{-1}}$ as well. After an hour of mixing in a concentric mixing machine I left the sample series for 24 hours. Before measuring I determined the balance pH value of the mixed and subsided suspension in the series.

The samples were examined in such a form and grain size that are usually applied while cultivating plants. The carbon dioxide in the air increases the consumption of alkali, therefore, the analysis of titration curves was conducted in vacuum. To perform the measurements I used WTW InoLab pH/Ion Level 2 measuring machine and SenTix 61 combined electrodes.

2.3 Estimating the acid-base buffering capacity

I showed the $[H^+] - pH$ and $[OH^-] - pH$ correlations revealed during the measurements in diagrams and in this way I got the titration curve of the analyzed material. The latter helped to determine the parameters characterizing the buffering capacity (Table 1).

Table 1. The indices applied in estimating the acid-basis buffering capacity

Name	Mark	Measurement unit
acid buffering capacity	${}^{a}BC$	proportional measurement unit
alkali buffering capacity	${}^{b}BC$	proportional measurement unit
acid sensitivity index	${}^{a}Sen$	pH $cmol^{-1}$ kg
alkali sensitivity index	${}^{b}Sen$	pH $cmol^{-1}$ kg
1 cmol kg^{-1} pH reduction caused by acid in comparison to the initial (pH_0) value	${}^{a}Sen_0^1$	pH $cmol^{-1}$ kg
1 cmol kg^{-1} pH increase caused by alkali in comparison to the initial (pH_0) value	${}^{b}Sen_0^1$	pH $cmol^{-1}$ kg
acid buffering index	${}^{a}\beta$	cmol pH^{-1} kg^{-1}
alkali buffering index	${}^{b}\beta$	cmol pH^{-1} kg^{-1}
the amount of acid causing pH value decrease in comparison to the initial (pH_0) value	${}^{a}\beta_0^1$	cmol pH^{-1} kg^{-1}
the amount of alkali causing pH value increase in comparison to the initial (pH_0) value	${}^{b}\beta_0^1$	cmol pH^{-1} kg^{-1}

Acid buffering capacity and alkali buffering capacity. I determined the buffering capacity value on the basis of the area limited by the titration curve. To perform the calculations on the diagram besides the titration curve of the analyzed sample I made two more that formed the basis for the comparison. One was the titration curve of quartz sand which corresponds to the titration curve of a zero buffering capacity material. The line crossing pH=7 and the abscissa parallel line form the titration curve, or to be exact a line, of such an „absolute buffering material" that is capable of neutralizing any acid or alkaline that is added. The „absolute buffering material" line and the quartz sand titration curve form the area of the „absolute buffering material's" buffering capacity, its value both in acid and in alkali is maximum. To avoid the deviations caused by the differences in the initial pH values I moved the titration curve of the analyzed sample in parallel with the ordinate axis till the initial pH value coincided with the starting point of the „absolute buffering's" titration curve (pH=7).

The buffering capacity of organic and mineral materials can be defined as the proportion of the area limited by their titration curve and the titration curve of quartz sand as well as the line of the „absolute buffering" and the quartz sand titration curve. As a result we get fractions smaller than one, and to make calculations of the buffering capacity easier I multiply it by 100. I calculated the buffering capacity value in acids and alkali separately. I marked the acid load buffering capacity ${}^{a}BC$ and the alkali load ${}^{b}BC$. In the experiment the lower index ${}^{a}BC_{12,5}$ and ${}^{b}BC_{12,5}$ shows the maximum acid or alkali load applied for the agent per 1 kg expressed in cmol.

Acid sensitivity index and alkali sensitivity index. Sensitivity can be determined on the basis of the acid-basis titration curve. Its numerical value is equal to the pH change caused by one cmol acid or basis applied to one kilogram of material. Its measurement unit is: pH cmol^{-1} kg. The marks are: ${}^{a}Sen$ – acid sensitivity index, ${}^{b}Sen$ – alkali sensitivity index.

Sensitivity index comprises the pH change caused by 1 cmol kg^{-1} acid or basis in comparison to the initial value (pH$_0$) of the material under investigation. To mark them I used the following phrases ${}^{a}Sen_{0}^{1}$ or ${}^{b}Sen_{0}^{1}$ where the 0 index is the zero point of titration, the upper index refers to the amount of load evoking the change. The *Sen* value can change within the 1 cmol kg^{-1} load, while Sen_{0}^{1} does not take these changes into account. The values of the two sensitivity indices coincide in case when the function between the pH changes caused by acid or alkali loads within 1 cmol kg^{-1} load remains linear. I used Sen_{0}^{1} to estimate the buffering capacity of minerals.

Acid buffering index and alkali buffering index. Thus, the buffering index and the sensitivity index values of the examined materials can be determined on the basis of ${}^{a}Sen$ and ${}^{b}Sen$. The acid buffering index is marked ${}^{a}\beta$, while the alkali buffering index is marked ${}^{b}\beta$.

The numerical value of the buffering index is equal to the amount of acid or alkali that is capable of reducing or increasing the material's pH by one unit. Its measurement unit is cmol pH^{-1} kg^{-1}.

For the buffering index similarly to the sensitivity index I used indices for the acid or alkali necessary for the pH to change in comparison with the starting value (pH$_0$). I marked them ${}^{a}\beta_{0}^{1}$ and ${}^{b}\beta_{0}^{1}$. It is possible to determine their numerical values on the basis of the titration curves. ${}^{a}\beta_{0}^{1}$ and ${}^{b}\beta_{0}^{1}$ are reciprocal to the ${}^{a}Sen_{0}^{1}$ and ${}^{b}Sen_{0}^{1}$ parameters only in case the titration curve is linear in the given section.

3. RESULTS

3.1 The adapted method for analyzing the acid-basis buffering capacity of organic and mineral materials

The procedure used for analyzing mineral soils did not prove adequate in many cases to research the acid-basis buffering capacity of materials used in horticulture. Therefore, I improved the method to make it appropriate for the analysis of the acid-basis titration curves of organic and mineral materials, growing media and artificial soils. The organic and mineral materials are analyzed in such a grain size and form that are used in growing plants. The method takes into account the samples' substantial or changing moisture content, thus, I refer the amount of the sample to dry substance to analyze the titration curves; the amount of water in the sample is extracted from the amount of solution used to model the load. The above-mentioned method enables us to measure the real buffering capacity of the materials containing large amounts of water as well as to compare the parameter values of samples containing various amounts of water.

On the basis of the acid and alkali buffering index values calculated from the titration curves of the high moor peat from Ivano-Frankivsk and the low moor peat from Pötréte I compared the method for mineral soils and the further developed version. In case of samples with huge water content the amount of acid buffering index values calculated for dry substance or damp substance differs by 1,5 – 1,8, in case of alkali buffering index the differences range between 1,2 – 2,9. The two-sample match t-test proved for both the high moor peat and the low moor peat that the average values for the buffering indices calculated with the correction for moisture content are the highest with at least *p=0,001* significance level.

3.2 The acid-basis buffering capacity of organic materials

It can be determined for each of the organic materials under investigation that their titration curve is almost linear, the points analyzed during titration form a line (Figure 1 and 2). The relations between concentrations of acid or alkali added as load and the balance pH values of suspensions can be treated as functions.

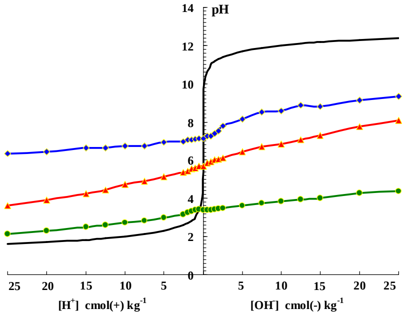

Figure 1. The titration curves of peats and coirs:

◆ – the Hahót low moor peat;
▲ – coir;
● – Voloscsa light brown high moor peat;
— quartz sand

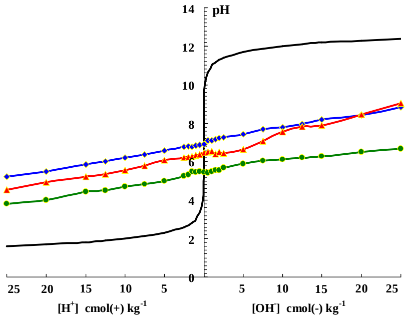

Figure 2. The titration curves of compost and ground coverings:

◆ – composted recrement;
▲ – crushed straw;
● – pine leaf-litter;
— quartz sand

The line allocated on the titration points crosses the ordinate axis at the pH value of the organic material in water solution. Its steepness shows the degree of changes that the acid or alkali concentration increase by a unit causes in the pH value of balance solutions. The pH reduction during acid titration shows acid sensitivity. According to the definition, pH increase during alkaline titration testifies to alkaline sensitivity. I used the acid sensitivity and the alkaline sensitivity indices to present the pH changes in numerical form. I introduced the phrase ^{a}Sen to mark acid sensitivity, and ^{b}Sen to mark alkaline sensitivity.

The titration curves of organic materials can be written down with the help of the following functions:

for acid titration:

$$\mathrm{pH_a} = \mathrm{pH_{H_2O}} - {}^{a}\mathrm{Sen}\left[\mathrm{H^+}\right] \qquad (1)$$

for alkaline titration:

$$\mathrm{pH_b} = p\mathrm{H_{H_2O}} - {}^{b}Sen\left[OH^-\right] \qquad (2)$$

where: $\mathrm{pH_a}$ and $\mathrm{pH_b}$ – are the suspension balance pH values after adding a certain concentration of acid or alkali;

$\mathrm{pH_{H_2O}}$ – is the pH value of the organic material’s water suspension;

$[H^+]$ and $[OH^-]$ – show the concentration of acid or alkali added as a load to the organic material, expressed in cmol kg^{-1};

On the basis of equations (1) and (2) we can calculate sensitivity
for the acid media:

$${}^{a}\mathrm{Sen} = \frac{\mathrm{pH_{H_2O}} - \mathrm{pH_a}}{\left[\mathrm{H^+}\right]} \qquad (3)$$

for the alkaline media:

$${}^{b}\mathrm{Sen} = \frac{\mathrm{pH_a} - \mathrm{pH_{H_2O}}}{\left[\mathrm{OH^-}\right]} \qquad (4)$$

The numerical value of the sensitivity index is equal to the pH decrease or the pH increase that one cmol acid or alkali causes when added to one kilogram of material.

On the basis of formulae (3) and (4) the sensitivity measurement unit is – pH cmol^{-1} kg.

The smaller the ^{a}Sen or ^{b}Sen values the less sensitive is the material under investigation under acid and alkaline load. Theoretically, the minimal acid and alkaline sensitivity indices can be equal to zero which testifies to the lack of sensitivity to influences. In reality such sensitivity can be assumed for materials with large buffering capacity, e.g. organic materials and exclusively with small acid or alkaline load. The maximum value of the sensitivity index, judging from its definition, should be within the pH range. Distilled water which has neutral reaction and quartz sand are characterized by maximum sensitivity to acid and alkaline influence.

The reverse of the acid sensitivity index is the acid buffering index, marked as – $^{a}\beta$, the reverse of the alkali sensitivity index is the alkali buffering index – $^{b}\beta$. The acid buffering index value is equal to the amount of acid that lowers the pH value of one kilogram of organic material by one unit, the alkali buffering index value is equal to the amount of alkali that increases the pH value of one kilogram of organic material by one unit. Its unit of measure is cmol pH^{-1} kg^{-1}.

I conducted a linear equation matching (Figure 3 and 4) of the titration points of peats, composts and ground coverings under investigation according to the smallest squares method. The value of determination coefficient is 0,96 – 1,00, the matching standard error varies in the range 0,03 – 0,26 pH depending on the organic material. The F-test verified the rightfulness of the model in each case.

The cause of the linear character of the organic materials' titration curves can be accounted for by the following. The differences between the pH values of proton's functional groups capable of binding and submission are small, the dissociation stages overlap, therefore there are no clear maximums on the titration curves, during titration the pH value changes in a monotonous and steady way. The titration points form a line, which is different depending on the characteristics of the organic material, but it usually goes moderately up under a small directional angle from the acid area to the alkaline one.

The linear model describing the titration process of the organic material is valid only within the examined acid or alkali concentration. To analyze the titration points I used maximum 25 cmol kg^{-1} acid and alkaline load. To expand the validity of the linear character more researches with a greater concentration range are needed. Under a greater load the titration curve may become flat significantly changing the straight steepness, thus the function will describe the process with significant error.

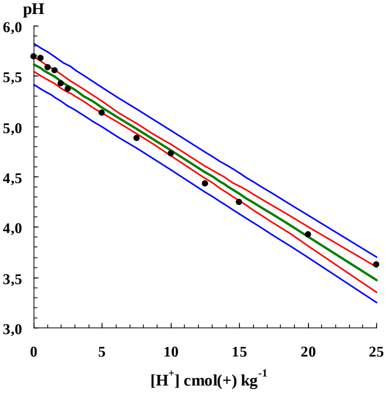

Figure 3. The influence of the acid treatment aimed at reducing the balance pH value of coir

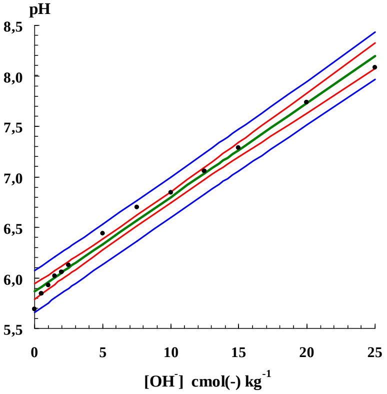

Figure 4. The influence of the alkaline treatment aimed at increasing the balance pH value of coir

● the value measured; — regressive straight line;
— 95% confidence band; — 95% prediction limit

Judging from the pH change during regression the band is small and large, during alkaline load we overestimate its pH value, while during medium concentration we underestimate it. The confidence bands show the limits within which the regressive straight line moves within the pH range (Figure 3 and 4).

3.3 The sensitivity index and the buffering index values of organic materials

The parameters of linear functions allocated at the organic materials' titration points show the numerical values of acid and alkaline sensitivity indices. I calculated the buffering indices on the basis of the sensitivity indices. The numerical values of sensitivity and buffering indices characterizing the organic materials' acid-basis buffering capacity are summarized in Table 2.

Table 2. The sensitivity and buffering index values calculated from the acid-basis titration equation of organic materials

The name of the organic material	sensitivity index		buffering index	
	^{a}Sen	^{b}Sen	$^{a}\beta$	$^{b}\beta$
	pH cmol^{-1} kg		cmol pH^{-1} kg^{-1}	
Peats				
Lithuanian white high moor peat	0,08	0,08	12,5	12,5
Voloscsa light brown high moor peat	0,05	0,04	20,0	25,0
Ivano-Frankivszk dark brown high moor peat	0,06	0,06	16,7	16,7
Voloscsa dark brown mixed peat	0,06	0,10	16,7	10,0
the fibrous low moor peat from Király-tó	0,04	0,04	25,0	25,0
the fibrous low moor peat from Hanság	0,05	0,07	20,0	14,3
Pötréte low moor peat	0,06	0,11	16,7	9,1
Szélmező low moor peat	0,13	0,21	7,7	4,8
Hahót low moor peat	0,03	0,09	33,3	11,1
Coir				
coir	0,09	0,09	11,1	11,1
Composts, raw materials				
manure	0,11	0,17	9,1	5,9
composted cattle manure	0,03	0,06	33,3	16,7
raw recrement	0,11	0,18	9,1	5,6
composted recrement	0,07	0,07	14,3	14,3
composted recrement +poultry manure	0,04	0,10	25,0	10,0
Ground coverings				
undecomposed leaf-litter (indigenous beech forest)	0,09	0,06	11,1	16,7
undecomposed leaf-litter (oak park)	0,05	0,08	20,0	12,5
undecomposed leaf-litter (pine forest)	0,07	0,05	14,3	20,0
undecomposed leaf-litter (fruit)	0,11	0,06	9,1	16,7
crushed straw	0,08	0,11	12,50	9,1

The average acid sensitivity index of organic materials is 0,07 pH cmol^{-1} kg, the minimum value is 0,03 pH cmol^{-1} kg, while the maximum is 0,13 pH cmol^{-1} kg. The average alkaline sensitivity index of investigated organic materials is 0,09 pH cmol^{-1} kg, its values vary between 0,04 – 0,21 pH cmol^{-1} kg. The average value of the acid buffering index is 17,0 cmol pH^{-1} kg^{-1} (minimum – maximum: 7,70 – 33,3 cmol pH^{-1} kg^{-1}), while the average value of the alkaline buffering index is 13,5 cmol pH^{-1} kg^{-1} (minimum – maximum: 4,8 – 25,0 cmol pH^{-1} kg^{-1}).

3.4 Estimating the acid-basis buffering capacity of minerals

The minerals' acid-basis buffering capacity varies greatly, their buffering capacity ranges from zero to very high values. I classified the minerals with similar buffering capacity (Table 3). I singled out five categories on the basis of the acid and alkaline buffering capacity ${}^{a}BC_{12,5}$, ${}^{b}BC_{12,5}$, and the pH change caused by 1 cmol kg^{-1} acid or alkali in comparison with the initial value (pH_0) – ${}^{a}Sen_{0}^{1}$, ${}^{b}Sen_{0}^{1}$. Due to various relations and buffering mechanisms classification is performed separately on the basis of acid and alkaline parameters.

The first category of the investigated materials includes: river sand, perlite, rock wool, burnt clay stone and Cornish stone. These minerals from mining and those produced by heat treatment have no buffering capacity, they are very sensitive even to the smallest amounts of acid and / or alkali. Their titration curve follows the titration curve of quartz sand. Their acid and alkali buffering capacity is below 20 units. Their balance pH value per cmol kg^{-1} changes by more than two units after adding acid or alkali.

Among the minerals in the first category rock wool's titration curve shows greater deviation. It differs from all the other inert non-organic media by the fact that its buffering capacity increases with the increase of acid loads. In acid media below pH <5 rock wool dissolves, the compounds of basic cations in its content get to the solution and neutralize a substantial part of the acid added for the treatment. Due to proton absorption accompanying dissolving the pH value of rock wool after adding the maximum 12,5 cmol kg^{-1} acid load does not decrease lower than pH 4.

Table 3. Classification of minerals according to their acid-basis buffering capacity

Category	Considered buffering capacity	$BC_{12,5}$	Sen_0^1	Minerals		
			pH cmol^{-1} kg	**under acid and alkaline loads**	**under acid loads**	**under alkaline loads**
I.	very low	0 – 20	> 2,00	river sand perlite (rock) rock wool burnt clay stone Cornish stone		
II.	low	21 – 40	1,01 – 2,00	extended perlite	zeolite	
III.	medium	41 – 60	0,31 – 1,00	bentonite	sodium bentonite	zeolite
IV.	high	61 – 80	0,15 – 0,30	vermikulite	alunite	sodium bentonite
V.	very high	> 80	< 0,15	humus bentonite		alunite

The two analyzed fractions (0,1 – 0,25 mm and 2 – 3 mm) of zeolite (klinoptilolite) buffer the alkaline loads on a medium level and belong to the third category considering the alkali buffering capacity. The titration curves of zeolite fractions of significantly differing sizes show closely similar results, the difference between their buffering capacity values is not significant (Figure 5). In other words, the increase of surface size does not cause substantially higher neutralization of alkali. During the alkaline titration of zeolite I determined the amount of the remainder sodium-ions at some titration points besides the pH values. I experienced great sodium-ion absorption in both fractions of zeolite when I presented the concentration of Na^+ solutions (NaOH load) in the form of a function (Figure 6). Klinoptilolite exchanges its own cations during titration for the added sodium hydroxide Na^+ ions. Taking into account klinoptilolite’s cation preference, only weaker basis-forming cations (compared to sodium hydroxide) can get to the balance solution. Thus, in the process of zeolite alkaline titration not hydroxide ions are neutralized, but the alkaline metal is exchanged for a weaker basis-forming metal.

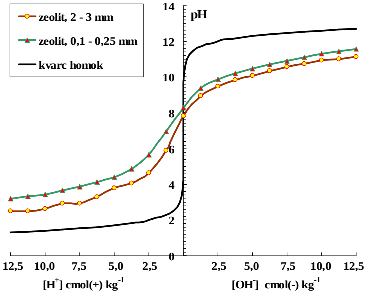

Figure 5. The titration curves of zeolite's two fractions

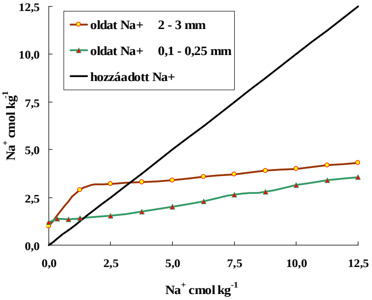

Figure 6. The change of Na^+ balance solutions' concentration during the alkaline titration of zeolite's two fractions

The straight line formed during the alkaline titration of bentonite can be matched, its pH value increases by 0,31 after adding one cmol kg^{-1} NaOH. Na-bentonite's titration curve is linear in the whole pH interval. Having a strong alkaline reaction Na-bentonite is more sensitive to acid than to alkali. The acid's sensitivity index is 2,5 times higher than the alkali's buffering index value.

Vermikulite can be classified into the fourth category, its buffering capacity is high both in acid and alkaline media. Vermikulite's titration curve is not steady, its buffering capacity significantly increases with greater acid and alkaline loads.

Alunite has significant buffering capacity in both acid and alkaline media. Its titration curves are linear. Alunite is more sensitive to acid than to alkaline loads, its alkaline buffering index value ($^{b}\beta$ = 6,7 cmol pH^{-1} kg^{-1}) is twice as large as the acid buffering index ($^{a}\beta$ = 3,5 cmol pH^{-1} kg^{-1}).

Humus bentonite belongs to the fifth category. Its buffering capacity is very high, one cmol kg^{-1} acid treatment causes only pH=0,11 decrease, while the same amount of alkali causes pH=0,10 increase. The character of the titration curve and the buffering capacity indices testify to the fact that one third of humus bentonite's organic components play a determining role in neutralizing acids and alkalis.

3.5 Calculating the changes of organic materials' reaction on the basis of the buffering index

Regulating organic materials' reaction on the basis of the buffering index. The buffering index is the index-number of the amount of acid or alkali necessary to change pH by one unit. Judging from its definition it can be used to calculate the necessary amount of acidifying or alkalinizing materials with the aim of setting the optimal reaction for the plant.

The necessary amount of calcium-carbonate necessary to increase the pH value – proportionally to the volume of the organic material – can be calculated on the basis of the alkali buffering index by means of the following formula:

$$L_{CaCO_3} = (pH_X - pH_{H_2O}) \cdot {}^{b}\beta \cdot T_S \cdot l \tag{5}$$

where: L_{CaCO_3} – is the necessary amount of $CaCO_3$, g m^{-3};

pH_X – is the pH value to be achieved;

pH_{H_2O} – is the pH initial value determined in a water solution;

${}^{b}\beta$ – is the alkaline buffering index, cmol pH^{-1} kg^{-1};

T_S – is the volume of the organic material, kg m^{-3};

l – is the necessary amount of alkaline material necessary to neutralize one cmol hydrogen-ion, g $cmol^{-1}$, (in case of $CaCO_3$ $l = 0.5$ g $cmol^{-1}$)

The necessary amount of acidifying materials to decrease the pH value can be calculated on the basis of the acid buffering index by means of the following formula:

$$A = (pH_X - pH_{H_2O}) \cdot {}^a\beta \cdot T_S \cdot f \qquad (6)$$

where: A – is the amount of agent necessary to reduce the pH value, g m^{-3};

${}^a\beta$ – is the acid buffering index, cmol pH^{-1} kg^{-1};

f – is the necessary amount of acidifying material necessary to neutralize one cmol hydrogen-ion, g $cmol^{-1}$, (for sulphur f = 0,16 g $cmol^{-1}$, aluminium-sulphate f = 1,11 g $cmol^{-1}$, iron-sulphate f= 0,72 g $cmol^{-1}$)

Interpretation and measurement units of the other parameters coincide with formula (5).

Calculating the acid and alkaline reducing capacity of the ground-covering organic materials. Knowing the buffering indices one can calculate the acid or alkaline neutralizing capacity of the organic materials regularly coming to the surface or specifically placed there. To do this one has to know the amount of the organic materials on the territory.

I used the following formulae for calculations:

$$|H^+| = {}^a\beta \cdot \Delta pH \cdot m \cdot 0{,}01 \qquad (7)$$

$$|OH^-| = {}^b\beta \cdot \Delta pH \cdot m \cdot 0{,}01 \qquad (8)$$

where: $|H^+|$ and $|OH^-|$ – show the amount of acid and alkali causing the ΔpH change, kmol ha^{-1};

${}^a\beta$ and ${}^b\beta$ – are the acid buffering index and the alkaline buffering index, cmol pH^{-1} kg^{-1};

ΔpH – is the pH change taken into account during estimation;

m – is the amount of organic material found per unit of a territory, t ha^{-1};

0,01 – is the conversion coefficient between cmol kg^{-1} and kmol t^{-1}.

3.6 New scientific results

1. I have determined that the acid-basis titration curves of peats, composts, organic materials covering the ground are linear. The relation between the balance pH values of acid or alkaline concentrations and suspensions can formally be dealt with as a linear function.

2. During the analysis of linear functions I have come to the conclusion that the straight line's steepness forms the value of the organic material's sensitivity index, while the ordinate axis crossing point forms the pH value measured in water solution. The acid or alkaline buffering indices can be defined as the reverse of the corresponding sensitivity indices.

3. I have proved beyond doubt that the sensitivity index and the buffering index are exact parameters properly characterizing the organic materials' buffering capacity. The sensitivity index of organic materials is 0,03 – 0,15 pH cmol^{-1} kg, the buffering index is 5,0 – 30,0 cmol pH^{-1} kg^{-1}.

4. I have found out that the acid and alkaline titration curves of humus bentonite, Na-bentonite, alunite are linear. Their sensitivity indices range between 0.10 – 0.41 pH cmol^{-1} kg, their buffering indices are between 2,4 – 10,0 cmol pH^{-1} kg^{-1}.

5. Zeolite (klinoptilolite) neutralizes acid weakly and alkali moderately. I have proved that zeolite's buffering capacity can be accounted for by the fact that during sodium-hydroxide titration the alkaline metal is exchanged for the mineral's weaker basis-forming metal ions.

6. Rock wool as an inert media is very sensitive to acid treatment. I have shown that with increased load its buffering capacity increases greatly during its dissolving due to the free basic compounds and its pH value does not decrease below pH 4 even after adding large amounts of acid.

7. I have improved the acid-basis buffering capacity research method and made it applicable to analyze the titration curves of organic and mineral materials,

artificial soils, and growing media. The procedure takes into account the sample’s moisture content and emphasizes its structural peculiarities.

8. I have elaborated a category system to determine the acid-basis buffering capacity of organic and mineral materials. I have singled out five buffering capacity categories, the criteria for differentiation are the acid-basis buffering capacity value and the pH change caused by one cmol kg^{-1} acid or alkali in comparison with the initial value.
9. I have defined the indices characterizing the acid-basis buffering capacity of organic and mineral materials. I have elaborated a marking system that includes the amount of acid and alkaline loads characterizing to a great degree the numerical value of the buffering capacity, and reflects the correlations between various parameters. I have assigned a measurement unit to each of the buffering capacity indices.
10. I have revealed that in many branches of horticulture the regulation of processes in the soil, the control of the soil-plant connection is based on the growing media’s large buffering capacity or its lack.

CONCLUSIONS, RECOMMENDATIONS

Effective regulation of the soil's acid-basis balance presupposes being well aware of the regularities, mechanisms, and characteristic parameter values of acid and alkaline neutralization. In many branches of horticultural cultivation regulation of the processes in soil is performed by applying or combining materials possessing large buffering capacity; less prominent changes, less sensitive materials (mainly organic), or those lacking buffering capacity attract less attention of the scientists, though their application (mainly minerals) would give the necessary total control. The expectations from the buffering capacity of artificial soil and root-treating media are aimed at regulating the processes in the soil, at controlling the needs and possibilities of the soil-plant relation system.

The organic and mineral materials used in horticulture (as well) were classified into five categories on the basis of their acid-basis buffering capacity. The criterion for differentiation was the acid or alkaline buffering capacity value and the pH change caused by one cmol kg^{-1} acid or alkaline treatment in comparison with the initial (pH_0) value.

Peats, composts, the compost's raw materials, plant leftovers regularly coming to the surface or specifically placed there possess the greatest acid-basis buffering capacity per unit of volume. The titration curves of the above-mentioned organic materials are linear. The relations between the balance pH values of acid or alkaline concentration and suspension loads can be written down by means of linear equations.

For the quantitative representation of the organic materials' buffering capacity I suggest using the numerical values of the acid or alkaline sensitivity indices and their reverse – the acid or alkaline buffering indices calculated from the linear equations of the titration curves.

The investigated organic materials' acid sensitivity index ranges between 0,03 – 0,13, alkaline sensitivity index varies between 0,04 – 0,21 pH $cmol^{-1}$ kg. The acid buffering index values are 7,7 – 33,3, while the alkaline buffering indices constitute 4,8 – 25,0 cmol pH^{-1} kg^{-1}.

The acid-basis buffering capacity of the analysed minerals varies greatly and characterizes each of the suggested categories. I consider appropriate two parameters to characterize the acid-basis buffering capacity of minerals: the acid or alkaline buffering capacity value, and the amount of pH change caused by one cmol kg^{-1} acid or alkaline load. The latter parameter relates to the most important changes of minerals from the point of view of cultivation.

It would be plausible to single out zeolite containing 70% klinoptilolite from the other minerals with buffering capacity due to both its mechanism of neutralizing alkali, and horticultural applicability. During the alkaline titration of klinoptilolite sodium-ion is exchanged for a weaker basis-forming metal ion. Thus, as the building element of growing media klinoptilolite is both capable of preventing sodium accumulation, and the increase of pH.

The organic materials' great or changing moisture content significantly changes the titration curves. The averages of acid and alkaline buffering indices calculated for dry and damp sample volume differ at least by $p=0,001$ significance level. My suggestion makes it possible to take into account the correction for moisture content during measurements.

The numerical values of buffering indices are appropriate to determine the amount of acidifying and alkalinizing agents necessary to regulate reaction. The same parameters can be used to estimate the buffering capacity of organic materials covering the ground under acid load. I suggested formulae to perform the calculations. Further on the appropriateness of the method and the correctness of the formulae need to be analysed in experiments with the appropriate amount of acidifying and alkalinizing agents.

The various acid-basis reducing ability of organic and mineral materials, the various buffering mechanisms have methodical significance for cultivating experiments as well. The comparative study of various media often explains setting the reaction to one level. Treatment with the same amount of alkalinizing or acidifying agents does not bring about correct results due to different buffering capacity. In case of organic or mineral materials with different characteristics the correct setting of the pH value to the same level, then the comparison and interpretation of the measured results is only possible when their buffering capacity and buffering mechanisms are known.

The study of the acid-basis buffering capacity of organic and mineral materials goes beyond the possibilities of horticultural application, it has enormous significance in researching the soil. The understanding of the numerous component functions of the soil is mostly only possible by simplifying a complex heterogeneous system and analysing each component separately. The individual study of organic and mineral materials, understanding and revealing the acid-basis neutralizing mechanism can elucidate the important role they play in the soil processes and in the soil in general. In soils there are no or few examples of extreme values that can be seen in mineral and organic materials. The connections revealed in our research draw attention to important regularities and enable the exact description of the processes.

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