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Determination of Acid-Base Buffer Capacity of Soils

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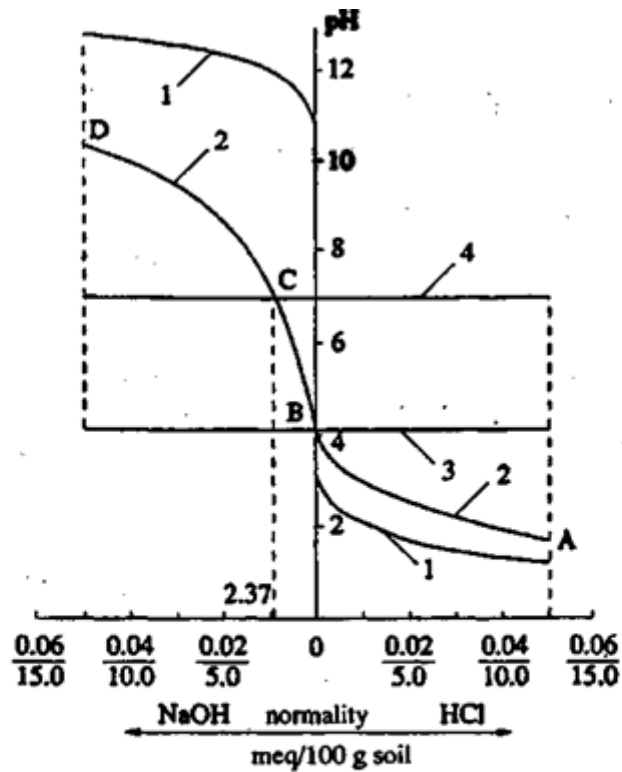
The buffer capacity and the neutralization index are suggested as objective quantitative parameters of acid-base soil buffering. They are estimated from buffer curves determined by the Arrhenius method with the maximum addition to a suspension of 12.5 meq of acid and alkali per 100 g of soil. A scale for evaluation of soil buffer capacity is proposed. The buffering properties of soils of different genesis have been determined.

Key words: Soil acid-base buffer, buffering properties of soils, Arrhenius method, anthropogenic pressure on soils

The intensification of agriculture, the broad use of chemical agents, and the impact of other technogenic factors result in considerable increase in anthropogenic pressure on soils. Cropping capacity is increasingly limited by the disturbance of the colloid-chemical properties by anthropogenic activities (5-15).

Therefore, attention is attracted to acid-base buffering as one of the principal indicators of soil absorption capacity [16,19]. It has significance for the problems of acidity of soils, evaluation of doses of lime and fertilizers [2], studies of gypsuming and desalinization of soils [4], and with the unfavorable impact of acid precipitations on soils and ecosystems [14]. Studies of buffer capacity are recommended for obtaining information on current soil processes and the genesis of soils [6].

The three modifications of the Arrhenius method by Jensen [20], Remezov [12], and Antipov-Karatayev and Firsova [3] are usually applied in research studies, although other methods are also known [1]. All these methods are based on the potentiometric determination of pH values of soil suspensions during additions of acids and alkali of various concentrations. The methods differ from each other mainly in terms of the qualitative and quantitative composition of the applied reagents, the duration and conditions of their reactions with soil, and on baseline readings.



Acid-base buffer of sod-Podzolic gley sandy loam soil. Horizon 0–12 cm (for explanations, see the text). Symbols: curve of relationship between pH values of HCl and NaOH solutions and the changes in concentration (1); buffer curve of sample (2); buffer curve of standard 1 (3); buffer curve of standard 2 (4).

The acid-base buffer capacity of soils is estimated through various indexes and characteristics obtained from buffer curves. Since Arrhenius's studies, the buffer properties have been expressed as the quantity of acid (or alkali) shifting pH value of the suspension by one unit. Buffer areas can also be used as scales of buffer capacity [15, 20]. Sometimes the estimations are based on the slopes of curves plotted in x- y coordinates, where the degree of saturation is given on the abscissa and pH values on the ordinate [21]. It has been suggested [10] that soils be characterized by their susceptibility to the effects of acid and alkali along with the soil buffer capacity.

Characteristic parameters of neutralization and absorption capacity expressed in meq/100 g soil are determined on buffer curves of CaCl₂ suspensions within the range of pH values from 5.0 to 8.0 [6]. The factors of «intensity» and «capacity» of buffer properties are used for estimations [16].

Although there are several methods of determining and evaluating buffer capacity of soils, limitations of studies of mechanisms and regularities of buffer properties and the presence of cer-

Table 1
Dependence of Calculated Value of Buffer Area on the Concentration Steps of Acid and Alkali
(23 samples analyzed)

pH of water suspension		Buffer area, cm ²		Error in calculation		
lim V	pH	lim V	S	Absolute, cm ²		Relative, %
				lim V	K	lim V
3.70-9.02	6.46	Acid interval		0.0.036	0.013	0-1.97
		0.47 - 36.14	13.93			
		0.47 - 36.20	14.01			
		Base interval		0.002-0.039	0.018	0.01 - 1.76
2.81 - 24.37	13.40					
		2.22 - 24.62	14.10			

Note. Calculated values of parameters: numerator with n measurements (concentration step 0,01); denominator with $2n$ measurements (concentration step 0.005).

tain difficulties in the elaboration of a convenient system of applicable indexes for objectively estimating buffer capacity of soils have been mentioned [11]. The buffer index, defined as the amount of acid (or alkali) required for shifting the pH value of soil suspension by one unit has been criticized by Kappen [7]. The biased character of buffer evaluations by means of buffer areas was pointed out in [7,13]. According to Nikol'skiy [10], the discrepancies between the methods are due to the different pH values of water suspensions of studied samples. To achieve correct and comparable results, Jensen [20] and Chernov [18] suggested that buffer areas be estimated within the same ranges of pH values.

Considering the importance of the problem, we studied the acid-base buffering in samples of soils with different properties and genesis seeking to find an objective diagnostic criteria of buffer capacity. The applicability of mathematical methods and the use of microprocessors for programmed computing of results was also tested. Some of the results have been published [8,9].

Our studies are based on potentiometric determination of the shift of pH with the addition of concentrations of acid (HCl) and alkali (NaOH) to the soil suspension. A 1:2-5 soil/solution ratio was used. The maximum concentrations of add and alkali used was 12.5 meq/100 g soil, allowing the buffer capacity of soils to be examined in the interval of pH values from 13 to 12.7.

The following analytical procedure, differing somewhat from modifications of the Arrhenius method [3,12, 20], was used. Ten gram samples of air-dried soil were placed into 13 conical flasks (100 ml volume). Twenty-rive milliliters of distilled water were added into one of the flasks, 25-ml aliquots of HCl solution were added into six flasks, and 25-ml aliquots of NaOH solution were added into the remaining flasks. The concentrations of the NaOH and HCl solutions

were 0.005, 0.01, 0.02, 0.03, 0.04, and 0.05 N. The solutions were prepared with CO₂-free distilled water. The capped flasks were agitated on a rotator for one hour and set aside for 24 hours. The suspensions were then shaken again for 10-15 minutes and the pH values were immediately tested using an EV-74 ion meter. In parallel, the pH values of the NaOH and HCl solutions used for preparing the suspensions were measured. The curves of relationships between pH values and concentrations (AC) of acid and alkali were plotted on millimeter paper. The values of concentrations were plotted on the abscissa using the scale 1 cm = 0.01 N; pH values were plotted on the ordinate with 1 cm s 1 pH unit. An additional scale is provided on the x axis for conversion of normality of the applied volumes of acid and alkali for the 10 g sample into meq/100 g soil (Figure). Estimations of buffer properties were based on analysis of buffer curves and buffer areas. The curve of the dependence of the potentiometric pH values on the concentration of acid and alkali in a standard with zero buffering was used as the baseline for the readings. Buffer areas of representative samples with absolute buffering within the studied ranges of concentrations of acid and alkali and having pH values of water suspensions equal to the values of the examined samples (standard 1) and to pH 7 (standard 2) were also used as standards for comparisons. They have straight buffer lines parallel to the abscissa and intersecting the ordinate at pH values of the examined sample and pH 7.

With the maximum (12.5 meq/100 g) addition of acid (or alkali) into the suspension and the use of the accepted scales, the buffer areas of acid and base intervals of standard 2 are equal to 26.32 cm². The buffer area of standard 1 depends on the pH value of its water suspension.

Buffer curves of studied samples with pH value of water suspension not equal to 7 are divided by the ordinate axis and the buffer line of standard 2 into 3 portions. The BC portion (Figure) lying outside the buffer scale limit of standard 2 was used for calculation of the neutralization ability of soils, expressed as the neutralization index (NI). The NI is numerically equal to the milli- equivalents of acid (acidic NI) or alkali (base NI) per 100 g soil required to reach neutral reaction of the soil suspension. NI values can be calculated based on the pH value of the suspension or measured on the plot. To achieve this, we drop a perpendicular from the intersection point of buffer lines of standard 2 and of the soil sample to the abscissa and take the reading from the denominator of the scale. We suggest that this index can be used as an additional parameter of buffer properties of soils and can be applied for estimations of the required doses of lime (or gypsum).

The natural buffer capacity (VB_n) and the reduced buffer capacity (VB_r) were used as the basic parameters of buffering. They were calculated from the following equations (in percent):

$$VB_n = \frac{S_a}{S_1} \times 100 \quad (1)$$

$$VB_r = \frac{S_a - \Delta S_a}{S_2} \times 100 \quad (2)$$

where S_a is the buffer area of the studied sample (cm²), S_1 is the buffer area of standard 1 (cm²), S_2 is the buffer area of standard 2 (cm²), and ΔS_a is the part of the buffer area of the studied sample beyond the buffer area of standard 2 (cm²).

Table 2
Buffer Properties of Some Soils and Rocks

Depth of sampling, cm	pH aqueous	Buffer area, cm ²		Neutralization index, meq/100 g		Buffer capacity, cm ²			
						Natural		Reduced	
		1	2	1	2	1	2	1	2
		Quartz sand							
	5.96	0.96	2.10	-	0.05	4.56	6.65	5.65	7.86
		Vermiculite							
	8.62	30.17	16.30	21.50	-	87.65	89.46	100.0	60.93
		Sodium montmorillonite							
	9.02	29.38	12.92	8.75	-	80.67	79.65	98.18	40.99
		Sod-Podzolic sandy soil							
0 - 20	5.60	3.13	2.20	-	0.38	16.20	6.60	11.89	7.94
		Soddy weakly developed sandy loamy soil							
0 - 10	4.52	2.02	9.27	-	1.10	14.51	23.94	7.67	33.09
		Gray Forest light loamy soil							
10 - 20	6.10	7.97	11.71	-	0.63	25.86	53.67	30.28	44.03
		Typical light loamy Chernozem							
		Ploughland							
0 - 10	6.18	9.97	16.91	-	1.13	44.87	55.59	37.88	63.49
		Strip of forest							
0 - 10	7.10	11.84	14.15	0.13	-	44.15	54.80	49.98	53.76
		Typical loamy Chernozem							
0 - 10	7.20	18.99	18.39	0.63	-	69.51	72.63	72.07	69.87
		Meadow Chernozemic loamy soil							
		Organic fertilizers							
0 - 25	8.05	25.64	9.23	5.50	-	81.21	43.81	93.01	35.07
		Organic and mineral fertilizers							
0 - 25	7.90	21.70	7.45	2.28	-	70.41	34.14	80.47	28.31
		Without application of fertilizers (control)							
0 - 25	8.12	24.33	5.79	5.00	-	76.22	27.94	88.18	22.00
		Soda Solonetz							
0 - 20	8.96	28.12	3.15	8.88	-	77.85	19.07	91.94	11.97
		Solonetz							
0 - 15	8.18	24.02	10.13	3.38	-	74.55	49.61	89.21	38.48
		Solonchak							
0 - 10	8.05	28.19	13.50	12.50	-	89.29	64.40	100.0	51.28
		Red Ferrosiallitic light loamy soil (Republic of Mali)							
0 - 15	5.52	1.75	9.08	-	0.62	11.62	26.93	8.36	33.85
		Red Ferrallitic heavy loamy soil (Cambodia)							
0 - 15	5.20	7.45	21.43	-	3.00	43.01	60.67	28.31	77.32
		Alluvial semihydromorphic light loamy soil (Cambodia)							
0 - 20	5.40	2.27	8.28	-	0.52	12.36	24.16	8.62	30.85

Note. Acid (1) and base (2) intervals.

It is obvious from Eqs. (1) and (2) and from the data in the figure that the buffer capacity indexes represent the relative parts of buffer scales of standards which correspond to buffer areas of studied samples within the proposed limits of pH values of acid (or alkali) solutions, and they also characterize the position of portions of the soil buffer curves in the buffer planes of standards.

The natural buffer capacity allows evaluation of the buffer properties of soils within the same pH values of water suspensions (pH 13 aqueous for the acid interval; pH 12.7 aqueous for the base interval) in relation to the absolute buffer standard. It seems to be possible to compare the buffer properties of all the studied soil samples using the buffer scale of standard 2 within fixed pH intervals, 1.3-7.0 for the acid interval and 7.0-12.7 for the base interval. In theory, the natural and reduced buffer capacities can vary from 0 to 100 percent.

The natural buffer capacity was used for diagnostics of buffer properties of soils with similar pH values. The neutralization index (NI) and the reduced buffer capacity were used for comparatively characterizing the buffering of soil samples with different pH values of water suspensions.

Buffer areas were evaluated by numerical integration according to the following transformed variants of Simpson's formula [17]:

$$S_a = \frac{h}{3} \sum_{j=0}^n C_j [f_2(X_j) - f_1(X_j)]$$

$$S_b = \frac{h}{3} \sum_{j=0}^n C_j [f_1(X_j) - f_2(X_j)]$$

(3; 4)

where S_a is the buffer area within the acid interval (cm^2); S_b is the buffer area within the base interval (cm^2); $C_j = 1, 4, 2, 4, 2, \dots, 4, 1$; $n = 2V$; $V = 1, 2, 3, 4, \dots$; $f_1(X_i)$ represents the pH of HCl (NaOH) solutions used in the analysis; $f_2(X_i)$ is the pH value of the soil suspension within the acid (or alkali).

The absolute errors of buffer areas calculated by numerical integration depend on the concentration step (A) of the acid (or alkali) used and can be expressed by the formula:

$$h = \frac{H_2 - H_1}{n} \quad (5)$$

where H_2 and H_1 are the minimal and maximal concentrations of acid (or alkali) and n is the number of tests of the analyzed sample.

Reducing the concentration step by a factor of two doubles, the required number of steps for the selected interval of concentrations of acid or alkali, it has been proven [17] that the error in the calculations directly depends on the number of steps (rt) and can be estimated according to the formula:

$$E_{2n} = \frac{|S_{2n} - S_n|}{15} \quad (6)$$

Table 3
Assessment Scale of Natural Acid-Base Buffer Capacity of Soils (percent)

Index assessment	Acid interval	Base interval
Very low	<15	< 10
Low	16-40	11-30
Medium	41-60	31-50
High	61-80	51-70
Very high	>81	>71

where S_n is the approximate buffer area determined in n steps and S_{2n} is the buffer area determined when the steps are one-half as large.

It was of interest to determine the optimal concentration step to be used in practice. For this purpose, we tested samples of rocks and soils with different properties, adding the maximum (1S meq/100 g) of acid (or alkali) into water suspensions. Titration curves were plotted and the buffer areas calculated by numerical integration using two concentration steps: 0.01 and 0.005. This enabled us to deal with even numbers of samples (6 and 12, correspondingly) for the add and base intervals, which is required for calculating buffer area by Simpson's formula of numerical integration.

The data (Table 1) shows that we must use concentration steps not exceeding 0.005 to ensure that the absolute error of the calculations will be less than 0.04 cm² (relative error 2 percent). With the maximal addition (12.5 meq/100 g) of 0.05 N acid (or alkali) into the soil suspension, this corresponds to 21 measurements. In practice, the 13 of them were obtained experimentally, the others being taken from the buffer curves.

Equations (3) and (4) were evaluated by computer. A brief description of the program "Integration of Tabulated Functions" for the Elektronika BZ-34 and similar models (MK-52, MK- 61, etc.) was presented earlier [9],

Table 2 presents the data on buffer properties of some samples of rocks and soils. The high level of buffer capacity of typical loamy Chernozem and of Solonetz soils within the acid interval attracts special attention.

The suggested indexes for buffer estimations are rather sensitive, and they allow the impact of the application of fertilizers on the acid-base buffer capacity of Meadow Chernozemic soil to be seen (Agronomic Experimental Station of the Ukrainian Agricultural Academy, stationary experiment).

The data show that the acid-base buffer capacity of real soil systems with limited quantities of added acid (or alkali) can be relatively low or high. The addition of 12J meq/100 g of acid (or

alkali) is not always sufficient to neutralize the soil solution. Thus additional studies and the use of higher concentrations of reagents may be required. For example, the neutralization index (NI) of vermiculite exceeded 12.5 meq/100 g sample (Table 2).

From studies and analysis of acid-base buffer capacity of soils of different genesis and properties, we elaborated a scale for evaluation of buffering by the natural buffer capacity index (Table 3).

The review of published data and our experiments show that we must use a complex approach to evaluation of buffer capacity. The buffer capacity can be sufficiently characterized by pH value of water suspension, the neutralization index, and the natural and reduced buffer capacities within the acid and base intervals and pH range studied.

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