Characterization and Properties of the Biochemical Threshold Range of Soils

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Soil processes in most of the cases are of very complex nature, especially biochemical ones. The biochemical phenomena in soils affect on one hand the dynamics of soil organic matter and on the other hand, the availability of plant nutrients. Our investigations during the last few years have been dealing with both of these questions of vital importance.

As per our investigations and also taking into consideration the work of some other authors [8] we could summarize the general factors affecting the availability of nutrients. All these factors are of complex nature, closely interrelated and can be defined as factor-groups.

This paper is dealing only with the effect of pH on one nutrient, on soil N. pH-range can be classed as one of the most important factors governing the availability of nitrogen. pH regulates not only the optimal range but also the extent of availability. The investigations of many researchers during the last few years in agreement with ours decisively show that the harmful effects of the pH in low pH range are the secondary ones and are the manifestations, for instance, of the high amounts of soluble toxic ions, Fe and Al, primarily Al [9, 10, 11]. One of the most important inhibitor of plant growth is the soluble Al in soils at low pH environment. The present investigation has primarily been aimed to offer a more clearcut and detailed understanding of the complex impact of pH on the availability of soil nitrogen.

It was also investigated that liming of soil and alteration of pH range influenced the dynamics of biochemical processes in the soil.

We could trace very interesting changes in the developement and properties of soil humic substances and also in the biochemical processes which have been noted to regulate the availability and dynamics of soil N.

Materials and methods

The soil samples were collected from the limed and unlimed plots of a long-term field experiment conducted by Belák [1] in Szentgyörgyvölgy, a pseudogleyic brown forest soil area, and thus they present the variation of pH in the same soil type.

The limed plots were treated with lime material at the rate of 50 q/ha. The lime material thus applied was only a one third of what calculated theoretically (according to hydrolytic acidity number) and in spite of this, the treatment was highly favourable, and the purpose of our investigations was also to acquire more informations about this favourable influence.

The availability of soil N was investigated by the method of the author. This is a continuous combined hydrolysis method through which, by virtue of repeated hydrolysis not only the actually available N but the potentially available one as well, can be determined. The main essence of the experimental method is a continuous hydrolysis of the same soil sample which is undertaken at first for four subsequent hydrolyses with 0,5 n H_2SO_4. This was followed by a fifth grade in which an oxidation was performed with H_2O_2 (3%) in a 0,5 n H_2SO_4 solution medium. Finally the sample is passed through the sixth hydrolysis similar to the first four. [6].

I—IV. grade in the whole is the "easily available" and V—VI. is the more combined form of soil N.

The availability of the toxic ions such as Al^3 and Fe^3 was measured by an EDTA method according to STEFANOVITS [12]. The ions were extracted from the soil through complexon (EDTA) and the content of soluble Fe and Al was determined by titration with $ZnCl_2$. Besides the above mentioned investigations, the quality of humic substances was analysed by the method of the author [4]. These analyses are based on the determination of the stability of humic acids in NaF and NaOH extracts.

The 1% NaF and 0,5% NaOH extracts are photometrically measured for extinction. Stability number of humic substances which is in correlation with the molecular weight, humification grade and precipitation properties of humic acids has been used to evaluate the quality of humic subtances.

$$Q = \frac{E_{\mathrm{NaF}}}{E_{\mathrm{NaOH}}}$$

The value for this coefficient is higher in the case of chernozem soils and the lowest in the case of raw organic matter.

According to our investigations the method determines not only the differences of soil genesis, but also the differences in the treatment, management and amelioration of soils. The stability number has been noted to increase with the action of favourable effects (e.g. liming) [3, 5].

Results and discussion

Considerably high changes were noted as regards the availability of soil N in pseudogleyic brown forest soils under small pH range. The data obtained are summarized in Fig. 1. It can be clearly seen that the solubility of N increased very suddenly in the pH range in question. The change in the distribution of nitrogen forms caused by liming was also investigated.

The main results of these investigations are summarized in Table 1. A very characteristic feature is expressed in the change of the distribution of N forms. A considerable increase in the amount of easily available N forms (I—IV) may be seen, total N content being the same. This signifies that the strongly combined forms are particularly changed to easily available ones as a result of liming. Thus, the data obtained clearly confirm the conception given by us. In some of our earlier papers we studied the actually and potentially available fractions of the total N. The later one is a form released by favourable biochemical processes. In the above mentioned critical range

Table 1

The distribution of N froms in pseudogleyic brown forest soils

Soil sample	Hydrolysable N in mg/100 g soil determined by the method of the author									
	I.	II.	III.	IV.	I.–IV.	V.	VI.	V.–VI.	I.–VI.	pH
31. fallow, limed 0—20 cm	17,8	7,1	7,3	3,3	35,5	107,7	31,7	139,4	174,9	5,54
32. fallow, unlimed 0—20 cm	15,0	2,0	3,2	3,6	28,8	115,0	36,0	151,0	174,8	5,02
35. fallow, limed 0—20 cm	21,0	9,6	5,1	3,4	39,1	108,0	24,9	132,9	172,0	5,62
36. fallow, unlimed 0—20 cm	14,8	9,3	5,8	2,0	31,9	108,3	31,9	140,2	171,1	4,95

I—IV. are the grades of hydrolysis

a change in the distribution of N forms is noted. In addition to above, the C : N ratio of the hydrolysed extracts was also calculated as biochemical processes determine to a high degree the amount of N released from humic substances. The microbiological activity, and all the organic matter decomposition processes are in a very close relation with the C : N ratio. Our investigations a few years ago demonstrated a gradual decrease in the C : N ratio with the number of consecutive hydrolyses.

As a result of such treatments a C/N ratio could be determined finally which is usually to be found only with amino acids of a very short chain.

Table 2 points to some very interesting features in this line.

Especially small and very constant values of C : N ratio have been noted. This fact leads to a point of great importance. It seems that the very constant C/N ratio has a close bearing on the stability of humic substances.

Concerning the toxicity in the acidic soils, according to the postulations of many researchers [2, 13], the most important limiting factor in such soils with a very low pH is the amount of soluble Al^3 and Fe^3 ions, especially the former. The process of liming decreases the amount of both ions in this very small pH range. Besides this, according to Peive and Peterbugszkij [11] the pH range in question is also the starting range of nitrification and of the activity of azotobacter.

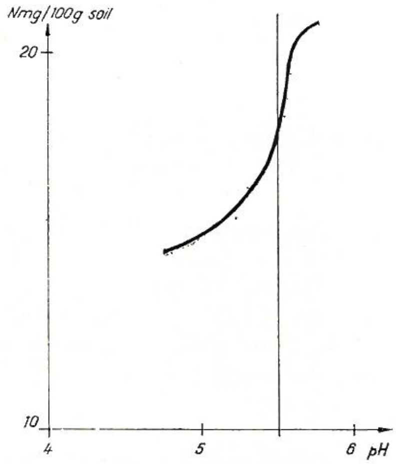

Figure 1
Relationship between pH of the soil and hidrolysable N

Considering all the above mentioned factors we have named this very characteristic, critical pH range as "the favourable biochemical threshold range" which is a new conception throwing light on the theory and practice of soil biochemical phenomena and soil liming problems.

Table 2

C : N ratio of the hydrolysates (pseudogleyic brown forest soil)

Soil sample	I.	II.	III.	IV.	VI.	pH
31. Fallow, limed 0—20	2,9	4,8	4,8	9,4	1,0	5,5
32. Fallow, unlimed 0—20	3,2	14,7	9,9	8,4	1,3	5,0
35. Fallow, limed 0—20	4,0	3,1	6,9	8,8	1,3	5,6
36. Fallow, unlimed 0—20	5,7	3,7	6,3	18,0	1,3	5,0

This new conception was introduced in 1965 and since that time we have systematically examined this critical range. On the basis of numerous data, we have dealt only with these two main directions: the quality of humus and the humic-nitrogen correlations as affected by liming. The determination of stability numbers of humic substances extracted through several extractants has shown that the properties of humic substances are governed by liming.

Table 3

Effect of liming on the content of soluble Al and Fe

Soil sample and treatment	pH	Al, mg	Fe, mg	Al eqv	Fe eqv
31 limed	5,54	43,2	97,0	4,8	5,0
32 not limed	5,02	90,0	131,0	10,0	6,8
45 limed (virgin grassland)	4,87	68,0	179,0	7,6	9,3
51 not limed (virgin grassland)	5,04	82,0	217,0	9,1	11,2

The data are expressed for 100 g soil.

Besides NaOH and NaF (frequently used by us), we treated the soils with $Na_2(COO)_2$ and $Na_4P_2O_7$ as well. The purpose of using the latter ones was to have some informations about the relation between the organic and inorganic components of soils.

Table 4

Changes in the stability numbers of the humic substances brought about by liming

Soil sample and treatment	Stability number of humic substances				Ratio between the stability numbers of limed and unlimed samples		
	pH	Q_{NaF}	$Q_{Na_2(COO)_2}$	$Q_{Na_4P_2O_7}$	R_{NaF}	$R_{Na_2(COO)_2}$	$R_{Na_4P_2O_7}$
27. limed	6,35	0,78	1,37	1,29	1,62	1,54	1,37
28. unlimed	5,27	0,48	0,89	0,94			
31. limed	5,54	0,64	1,10	0,90	1,49	1,24	2,09
32. unlimed	5,02	0,43	0,97	0,43			
35. limed	5,62	0,58	1,05	0,87	1,61	1,29	0,81
36. unlimed	4,96	0,50	0,81	1,08			
Average of the ratios					1,42	1,35	1,42

From Table 4 it is apparent that the stability numbers are in general increased with liming in this favourable threshold range, and in spite of the small change in pH values, the quality of humic substances was favourably influenced by liming. Tables 5, 6 show a few data of the solubility changes of N forms from free and combined humic substances, estimated in the solutions of the latter ones with various treatments.

Table 5

Effect of liming on soluble and humic N, extraced with different reagents
Soluble N in mg/100 g soil

Soil sample and treatment	NaOH			NaF			$Na_2(COO)_2$			$Na_4P_2O_7$		
	total	non-humic	humic	total	non-humic	humic	total	non-humic	humic	total	non-humic	humic
23 limed	26,5	6,2	20,3	22,9	2,3	20,6	24,4	3,6	20,8	19,5	4,7	14,8
24 not limed	72,8	5,7	67,1	25,8	2,2	23,6	19,3	2,3	17,0	35,1	3,1	32,0
27 limed	88,1	0,1	88,0	23,9	2,1	21,8	24,3	1,9	22,4	39,7	3,3	36,4
28 not limed	101,1	6,8	94,3	26,9	2,1	24,8	32,6	1,8	30,8	54,7	3,3	51,4
31 limed	29,7	8,8	20,9	22,0	2,8	19,2	33,9	2,5	31,4	23,5	1,9	21,6
32 not limed	118,0	1,2	116,8	41,7	4,2	37,5	41,4	4,2	37,2	64,8	1,3	63,5
35 limed	105,0	7,4	97,6	43,7	3,7	40,0	24,8	3,3	21,5	59,7	4,5	55,2
36 not limed	112,0	7,2	104,8	44,6	2,5	42,1	45,3	—	—	57,2	—	—

The differences between limed and unlimed soils are very characteristically demonstrated through the humus stability numbers.

In order to have exact data for a comparison between humic and N conditions in soils, we have calculated the solubility ratio of humic N components in the following way:

$$NQ_{fl} = \frac{\text{NaF soluble N}}{\text{NaOH soluble N}} \qquad NQ_{0x} = \frac{\text{Na}_2(\text{COO})_2 \text{ soluble N}}{\text{NaOH soluble N}}$$

$$NQ_{P_2O_7} = \frac{\text{Na}_4\text{P}_2\text{O}_7 \text{ soluble N}}{\text{NaOH soluble N}}$$

Considering that liming has brought forth these changes, the following two conclusions can be drawn:

1. The nitrogen solubility number is increased in many cases by liming;
2. The nitrogen solubility number estimated in NaF solution is very characteristically increased by liming.

The latter point (2) is probably also connected with the solubility of Al-humic complexes.

It can be assumed that the Al-complexes of humic substances are very common in acidic soils and possibly they are developed through various Al compounds in such soils. NaF dissolves Al-complexes very well. Recently some investigations (e.g. the results of WILLIAMS [13] and also ours) have been carried out, showing the importance of Al in the developement of humic complexes.

The metal-humic complexes are characterized by N-metal combination. It seems that such complex compounds are probably better developed in soils with high N content. The soluble Al content of soils is sharply decreased with

Table 6

Changes in the N solubility ratios in various extracts brought about by liming

Soil sample and treatment	pH	Solubility number of N			Ration between the N solubility numbers of limed and unlimed soils		
		NQ_{NaF}	$NQ_{Na_2(COO)_2}$	$NQ_{Na_4P_2O_7}$	NR_{NaF}	$NR_{Na_7(COO)_2}$	$NR_{Na_4P_7O_7}$
27 limed	6,35	0,272	0,275	0,450	1,02	0,850	0,833
28 unlimed	5,27	0,266	0,323	0,540			
31 limed	5,54	0,742	1,14	0,794	2,10	3,24	1,44
32 unlimed	5,02	0,353	0,351	0,550			
35 limed	5,62	0,417	0,237	0,570	1,05	0,586	1,13
36 unlimed	4,95	0,398	0,404	0,511			

liming, and probably the amount of Al-humic complexes are increased. The humic substances with a colloidic character and with higher N content are combined with Al with higher ease. The increase in pH is, at the same time, increasing the N solubility in NaF, because NaF very well dissolves the Al-humic complexes. This assumption invites further work to be done in this line.

Thus, all of these favourable effects are put in a very characteristic range, namely the favourable "biochemical threshold range". The knowledge of it seems to be very important from the point of view of liming practice.

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