

**Investigation on Soil Humus and Nitrogen
Dynamics Based on the Concept of
A. A. J. de 'Sigmund**

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The research work of Prof. 'SIGMOND was not only the basis of contemporary Hungarian soil science, but, at the same time, also the beginning of soil chemistry researches in our country. The importance of the determination of chemical soil properties was underlined in the works of 'SIGMOND. His researches [12] dealing with the adsorption complex of soils are generally very well known. The essence of his concept is the theory concerning the structure of the adsorption complex and the properties of soils saturated with cations [4].

The colloid fraction — named by 'SIGMOND as humus-zeolit complex — plays a considerable role in the development of soil types.

His concept is also important in illuminating the interactions of the inorganic — organic complex of the soil.

'SIGMOND summarized this concept in one of his works [13] as follows:

“The factor determining the chemical reaction of the soil is the above-mentioned and characterized humus-zeolit complex. It has not been possible as yet to characterize its chemical composition and structure but all our experiences indicate that it is a complex of various slight acids.

The complex with anionic character is able to absorb and to exchange various metallic ions and hydrogen ions in well determined equivalent quantities just like the characteristic chemical compounds”.

'SIGMOND's achievements [12, 18] showed that special attention should be paid to the investigations on soil humus complexes.

MADOS (KOTZMANN), one of the coworkers of 'SIGMOND, continued the investigation on the humus problem. MADOS elaborated a new approach to humus researches in the chapter dealing with soil organic matter problems in the textbook on soil science by 'SIGMOND [8].

The comparative determination methods of the soil's organic matter content according to MADOS and his method for the determination of the C-content of humic extracts with KMnO_4 played a basic role in Hungarian soil science for a long time [7, 8, 16]. This research work is actually the starting point in Hungarian humus researches. The whole concept of 'SIGMOND and his school placed the humus problem in the centre of soil chemistry problems. These investigations were also important in illuminating the interaction between humus quality and soil genetics.

“Our knowledge of the chemical structure of humus compounds is not so thorough as yet that we could recognize constitutional differences among the humus substances of various soil types. Further research along these lines

is among the tasks of the future. For the present we must be content with characterizing the different humus substances partly by the dispersity and the degree of saturation of humic acids, partly by numerical values — suitable for comparison — indicating the degree of humification.”

'SIGMOND [14, 15] studied the soil phosphorus and potassium problems and, in connection with the investigations on the adsorption complex, also the lime requirement of soils. The determination of nutrient requirement was carried out by 'SIGMOND's method, from the HCl extract of the soil. An important purpose of these extractions was to decompose the humus-zeolite complex of the soils. At that time the nutrient requirement of soils was determined only in general and it was not possible to have detailed information about the different N forms in the soil, nor about the N requirement.

Humus investigations and soil chemistry researches called attention to soil N conditions. From among 'SIGMOND's pupils K. PÁTER was the first who studied the C : N ratio of Hungarian soils. The results of PÁTER's investigations indicated that on the average the C : N ratio was about 11 : 1 [10]. These results called attention to the relationship between soil organic matter and soil nitrogen conditions. Later MADOS [9] began to study the hydrolysable N fraction of soils. He, quite rightly, was of the opinion that the determination of the availability of soil N is just as important as the determination of the availability of phosphorus and potassium.

When, under the direction of Prof. PÁTER, we started investigating the humus status of the main Hungarian soil types in 1952, we had at our disposal only some results obtained by SARKADI [11] in this field to rely on. The main purpose of our investigations was to characterize the connection between the soil genetical conditions and the improving of humus substances. In connection with our work some important relations in the case of brown forest soils and alkali soils were observed by STEFANOVITS and SZABOLCS, respectively [19, 20].

In 'SIGMOND's time, the GRANDEAU-method was commonly used for the investigation on humus substances. The first data on humus conditions in Hungary were obtained with this method, and 'SIGMOND [17] summarized them as follows:

Soil type Location	Active humus according to GRANDEAU	Equivalent effect of humus expressed in % of total effect of the adsorption complex
<i>Rendzinas</i>		
Budaórs	11.42	68.5
Ördögrom	8.96	70.8
Sopron	6.18	58.5
Bélapátfalva	7.02	60.9
<i>Chernozems</i>		
Mezőhegyes	2.13	32.0
Gyula	1.86	34.1
Békéscsaba	1.41	32.4

Materials and methods

For our investigations of humus quality we collected samples not only from the main soil types of Hungary but also from various raw organic matters, composts, manures, peats, earth mixtures and fossilic organic materials. At the same time we investigated also the N distribution and the organic N conditions in the samples.

We extended our investigations from the commonly employed method using one solution (e.g. the GRANDEAU-method or some investigations by SARKADI about $tg \alpha$ of humus extracts) in the line of applying a new method using two solutions. The method using two solutions takes into account the bounding of organic materials on the mineral complexes thereby supplementing with additional data the concept of 'SIGMOND.

When developing our new method [2] we summarized the action of the solutions as follows:

1% NaF dissolves humus substances of good quality with higher molecular weights which are humified to a higher degree; these are the real humus substances. 0.5 N NaOH dissolves raw humus substances humified to a lower degree, with lower molecular weights, which are acidic in character and much worse in quality. This method is suitable for the determination of the differences of humic substances under different genetical conditions.

The extraction of humic substances is carried out with 1 : 10 soil-solution ratio at room temperature. First the samples are shaken for 2-3 minutes, then they are left for 48 hours' extraction. After 48 hours the extracts are filtered on middle porous quantitative filter paper. If necessary, the solutions may be centrifuged. Then the light adsorption conditions are determined in Pulfrich photometer by measuring the extinction values on all of the filter wave lengths. By dividing the extinction value of the NaF extract with that of the NaOH extract and the total humus content, we can calculate the stability coefficient

$$K = \frac{E_{NaF}}{E_{NaOH} \cdot H}$$

The essence of our N investigations was to develop a method similar to the acid methods used by 'SIGMOND for the determination of the P and K status of soils. At the same time such methods should be suitable for the characterization of the N conditions with an as simple as possible process.

The method developed by the author [3] is based on the hydrolysis method of TYURIN and KONONOVA. The method developed by us consists of 7 successive steps; it is a continuous hydrolysis combined with oxidation. The first four grades are sequences of the same type of 0.5 N H_2SO_4 hydrolysis processes. As the 5th step an oxidative hydrolysis process with 3% H_2O_2 is applied for the determination of the potentially available N forms. The oxidation process yields a high amount of hydrolysable N which is very difficult to separate from the samples, so the 6th step is a repeated hydrolysis with 0.5 N H_2SO_4 for the evaluation of the released N forms. The hydrolysis is carried out in all the 6 steps with the same 20 g soil. Treatment is carried out in each case with 100 ml solution. After a short shaking (2-3') the acidic solution is left over the

sample for one night, then the supernatant is filtered on quantitative middle or small porous filter paper. The N content of the filtrates is determined by the microchromic method of TYURIN. 50 ml is taken from the extract. It is first treated with 0.5 g Zn-Fe mixture (pulverized) of 1 : 9 ratio. The solution is boiled very slightly. After cooling, 5 ml of cc. H_2SO_4 is added to one sample. As the last step they are heated in sand-bath till the appearance of white vapors. After a few minutes of cooling, 2 ml of 20% $K_2Cr_2O_7$ is added to the solution for oxidation.

The samples, covered with glass funnel, are boiled for 10 minutes to improve oxidation. After this the samples are ready for the determination of their N content. One by one they are placed into a Wagner-Parnass equipment and the determination of N is carried out in the usual way.

The various grades of the hydrolysis are carried out on the same samples. The soil which remains on the filter is washed with distilled water. It is left to dry for one or two days, then the sample is placed again into the bottle and the hydrolysis process takes place in the same way as before. As the last step, 10 g of the original sample is put in a reflux system and hydrolysed with 100 ml of 6 N HCl at 145 °C (in oil-bath) for 48 hours. The hydrolysates are filtered from the sample. Cl-residues must be carefully washed out of the soil and the total N content of this hydrolysed soil is determined in the usual way. The results of this N hydrolysis process yield data on the heterocyclic N content of the soils. This N we called "dead N" in soils because it is unavailable for plants not only practically but also theoretically.

Results of the investigations

Some characteristic results of our humus quality investigations carried out since 1955 are summarized in Table 1. It is clear from Table 1 that the values of humus stability coefficients are differing significantly from each other. The connection between humus quality and soil genetics is evident from the data. The results prove the rightness of the fundamental concept of SIGMOND according to which the changes in humus quality are closely related to the changes in soil genetics, and not only in connection with the adsorption of humus substances on the inorganic complex, but also depending on the genesis of humic substances. The results of a cooperation programme of Central European Countries demonstrated a considerable difference between the chernozems of Czechoslovakia, the German Democratic Republic and Poland on the one hand and those of Hungary, Rumania and Bulgaria on the other hand. The stability coefficients of these two great chernozem groups differ considerably. In the typical brown earths of various Central European countries the similarity is so striking that we must conclude that they developed under similar, very well characterizable conditions.

In order to characterize the interaction between the inorganic complex of the soil and humic substances, we investigated the effect of various extracts on humus substances. The data obtained by the various solutions showed that in general the stability numbers and stability coefficients change in a parallel way in the different horizons of various soil types. In spite of that we cannot estimate the differences among the stability coefficients obtained in different solutions by multiplying with a characteristic constant. The deviation, how-

Table 1

Stability coefficients for the characterization of different humus materials

Samples	Stability coefficient
<i>I. Fossilic humic substances</i>	
1. Brown-coal humic acid (Dudar)	0.0000410
2. Brown-coal humic acid (Balinka)	0.000413
3. Brown-coal humic acid (Várpalota)	0.001214
4. Humic acid from lignit (Petőfibánya)	0.00160
<i>II. Raw organic materials</i>	
1. Litter from brown forest soil (Gödöllő)	0.0027
2. Humified litter from brown forest soil (Gödöllő)	0.0041
3. A ₁ horizon (upper layer) from brown forest soil (Gödöllő)	0.0052
4. Manure	0.0110
5. Straw compost	0.0127
6. Manure-earth compost (Kertscher method)	0.0284
7. Acidic peat from West-Hungary (Osli)	0.0129
8. Humified acidic peat (Osli)	0.0192
9. Peat, calcareous (Hidegség)	0.0200
10. Indore compost	0.0434
<i>III. Moor soils</i>	
1. Well-humified horizon of moor soil (acidic) (Osli)	0.0250
2. Well-humified horizon of moor soil (calcareous) (Nagyberek)	0.342
<i>IV. Alkali soils</i>	
1. Meadow solonetz (Szarvas)	0.459
2. Solonetz (Hajdúszoboszló)	0.0780
3. Solonchak (Dinnyés)	0.0730
4. Meadow solonetz (Bánhalom)	0.148
<i>V. Meadow soils</i>	
1. Meadow soil alkali in deeper layers (Hajdúszoboszló)	0.364
2. Meadow soil (Vizesfás)	0.346
3. Meadow-moor soil (Bánhalom)	0.120
<i>VI. Forest soils</i>	
1. Pseudogleyic brown forest soil (Szentgyörgyvölgy)	0.070
2. Podsollic brown forest soil	0.109
3. Brown forest soil with clay illuviation	0.351
4. Brown earth (brown forest soil according to Ramann)	0.395
5. Brown earth (subtype rustbrown soil) (Gödöllő)	0.806
6. Brown earth (cultivated long ago) (Gödöllő)	0.916
7. Brown earth (cultivated long ago) (Gödöllő)	0.985
<i>VII. Chernozem soils</i>	
1. Leached chernozem soil (Karcag)	1.30
2. Leached chernozem soil (weakly leached)	6.75
3. Calcareous chernozem (lowland) (Csiribpuszta)	8.33
4. Calcareous chernozem (typical) (Csiribpuszta)	10.56

ever, from this parallelism and the differences express well the interaction between the organic and inorganic complexes of the soil.

By comparing the various stability coefficients, obtained by different extracts, we can estimate some characteristic numbers.

According to our experiences 1% NaF or 0.1 M $\text{Na}_4\text{P}_2\text{O}_7$ as well as 1% $\text{Na}_2(\text{COO})_2$ may be used as extractants. When determining the stability coefficients of such extracts the values by $\text{Na}_4\text{P}_2\text{O}_7$ are the largest. The stability coefficients by oxalates are somewhat smaller and the lowest stability coefficients were obtained with NaF which is, due to its chemical properties, the most neutral solvent.

In each case NaOH was used as the alkaline solution. To illustrate the deviations we introduced some relations

$$P/O = \frac{\text{stability coeff. in pyrophosphate}}{\text{stability coeff. in oxalate}}$$

$$P/F = \frac{\text{stability coeff. in pyrophosphate}}{\text{stability coeff. in fluoride}}$$

$$O/F = \frac{\text{stability coeff. of oxalate}}{\text{stability coeff. of fluoride}}$$

The values obtained for the different profiles of various soil types showed that the P/O values are more or less constant while the O/F and P/F values are ranging on a larger scale. The P/F and O/F values express well the variability of meadow solonetz and meadow (clay) soils within the whole profile. At the same time the P/O values are constant (Table 2).

Table 2
Ratio of humus stability coefficients obtained in different solutions

Soil type	Depth cm	P/O	P/F	O/F
Solonetz (Szarvas)	0-3	3.23	2.59	0.874
	3-15	3.22	3.43	1.16
	15-35	2.19	9.08	4.15
Chernozem (Kondoros)	0-15	—	2.03	—
	15-30	2.87	2.55	0.881
	30-45	3.14	2.58	0.820
Meadow soil	0-15	1.84	3.32	1.79
	15-25	1.76	6.57	3.72
	25-30	1.79	10.98	6.11

To explain these results we must presume a greater colloid content of these soils. The humus-clay mineral interaction may be very important in such soils, and it is influenced first of all by the adsorption of trivalent cations, such as Fe.

Table 3

N distribution in different soils (Fractions according to the HARGITAI-method)

Soil type, location	Total easily available N in % of total N	Potentially available N in % of total N released only		Heterocyclic N in % of total N insoluble in 6 N HCl
		by oxidation with 3% H ₂ O ₂	by 6 N HCl hydrolysis	
Pseudogleyic brown forest soil (Szentgyörgyvölgy)	9.00	67.00	6.00	18.00
Brown earth soil (Keszthely)	9.50	36.60	36.60	17.30
Brown earth (Gödöllő)	12.27	44.23	20.03	23.44
Chernozem (Kondoros)	8.23	33.45	35.90	22.42
Chernozem (Hajdúszoboszló)	5.97	13.73	65.80	14.50
Meadow soil (Vizesfás)	5.86	15.35	37.55	41.24
Solonetz (Szarvas)	4.95	19.28	65.33	10.44
Acidic low moor peat (Osli)	5.88	10.09	32.83	51.20

This is in accordance with the results of EVANS and RUSSELL [1] though to explain all these relations the above mentioned authors referred only to some of the basic points. When investigating the Fe : Al ratio of the extracts they obtained different values in the various extracts, for instance in Na₄P₂O₇ 16.4, in NaF 0.68. That means pyrophosphate dissolves a greater amount of Fe and the fluoride solutions dissolve more Al. It is clear that a greater change in the P/F ratio indicates the interaction with Fe ions in the adsorption complex. This fact also demonstrates the importance of iron in the development and change of humic substances.

The results of continuous N hydrolysis showed that with this method we can fractionate the easily available N forms from the N which is potentially available. The investigations also showed the average content of heterocyclic N in Hungarian soils, which is quite high [5, 6] (Table 3 and 4). That is the "dead N". The distribution of the N forms is also characteristic of the various soil types. The transformations of soil N forms are, according to our results, in close connection with the changes of the organo-mineral complexes of the soils.

Table 4

**The distribution of the N forms in pseudogley brown forest soil
(Hydrolysable N in mg/100 g soil determined by the HARGITAI-method)**

Soil sample	I.	II.	III.	IV.	I.—IV.	V.	VI.	V.—VI.	I.—VI.	Soil pH
31. Fallow, limed	17.8	7.1	7.3	3.3	35.5	107.7	31.7	139.4	174.9	5.54
32. Fallow, unlimed	15.0	2.0	3.2	3.6	28.8	115.0	36.0	151.0	174.8	5.02
35. Fallow, limed	21.0	9.6	5.1	3.4	39.1	108.0	24.9	132.9	172.0	5.62
36. Fallow, unlimed	14.8	9.3	5.8	2.0	31.9	108.3	31.9	140.2	171.1	4.95

I.—VI. are the steps of hydrolysis.

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