

CONTRIBUTIONS OF SOIL ORGANIC MATTER  

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TO PRODUCTION POTENTIAL OF SOILS AND  

---

SOME PROPOSALS FOR PRACTICAL APPLICATION  

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Wolfgang FLAIG

Annex II

to the report of W. FLAIG

9 Lectures about: Contributions of soil organic matter to production potential of soils and some proposals for practical application.

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CONTRIBUTIONS OF SOIL ORGANIC MATTER

TO PRODUCTION POTENTIAL OF SOILS AND SOME PROPOSALS

FOR PRACTICAL APPLICATION

Wolfgang FLAIG

1973

## Preface

The increase of yield/ha is important for the food production of Indian Population. For this purpose firstly high yielding varieties of rice, wheat and other crops were bred. These demand a higher quantity of mineral fertilizers. Fertilization alone does not allow the realization of the full genetical potential of cereals. The inorganic ions of the fertilizers enhance also microbial activity. The microorganisms use the carbon from soil organic matter as source for energy and reproduction. As a consequence of decrease of soil organic matter unfavourable processes in soil, the substrate for production occur, which cause a reduction in plant production. Therefore an increase of yield by fertilization alone is limited.

Another way to overwhelm the biological border for the use of the genetical potential of cereals is to utilize the effect of bioregulators on plant metabolism, such as CCC, "Cycocel" to increase the resistance against lodging of wheat. There are some other substances in soil organic matter, which have bioregulating effects under unfavourable growth conditions. This influence of soil organic matter on yield is well known by the farmers as "humate-effect".

Therefore, it is evident, that special procedures for maintaining a critical status of soil organic matter should be followed. More research about humus is necessary. An intensive cereal production is then economical only, when yields are always maintained at a relatively high level. One should try to minimize the yield depressions by appropriate procedures.

The lectures are an introduction into the problems. The transfer of results of basic research into practice are mentioned and the experiences about the utilization of new findings are summarized.

I have to thank Mr. M.S. Sachdev (M.Sc.) for his indefatigable help, for the revision of the lectures and for compiling the references.

Wolfgang FLAIG

New Delhi, 29. September 1973

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Lecture - 8

CHARACTERIZATION OF HUMIC SYSTEMS  
IN DIFFERENT SOILS

1. Determination of similarity degrees of humic acids by light absorption.
2. Scheme for analysis of humic systems.
3. Example for characterization of humic systems in a morphosequence of soil.
4. Final remarks and Conclusions.

1. Determination of similarity degrees of humic acids by light absorption.

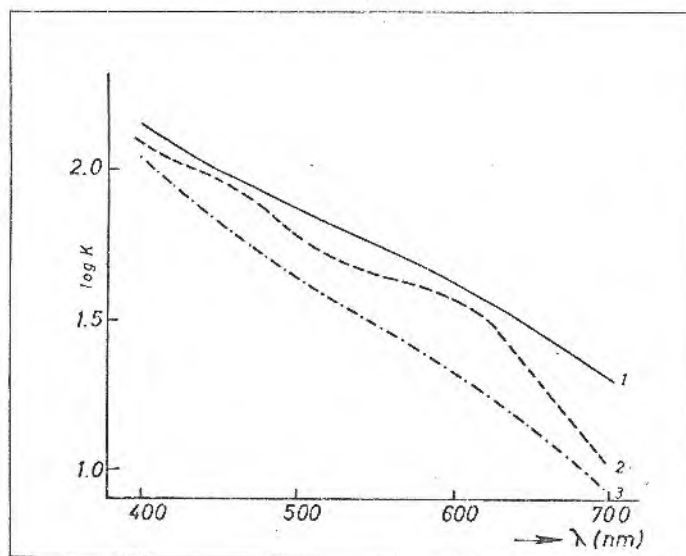


Fig. 1: Spectra of different humic acids. (1) Chernozem, (2) podzol B and (3) black peat in 0.1 N NaOH.

At first it must be established, that the spectra of humic acids are not linear, as the classical soil chemistry describes them. The spectra of humic acids are curved lines, which are different upon the origin of the humic acids. It shall be remembered, that the ratio of the quantities of phenols found after oxidative or

reductive cleavage depends on the origin of the humic substances, and that the content and ratio of amino acids differs also after acid hydrolysis.

Therefore the spectra cannot be characterized completely according to classical theory by means of only one quotient of two extinctions at about 400 and 600 nm = 4/6 ratio or by the differences of the logarithms of two extinctions e.g.  $\log 405 - 665$ .

To expand the possibilities for characterization of humic systems by means of spectrophotometric measurement, the extinction coefficients of three or more ranges of nm in the spectra have been used (SALFELD, 1972).

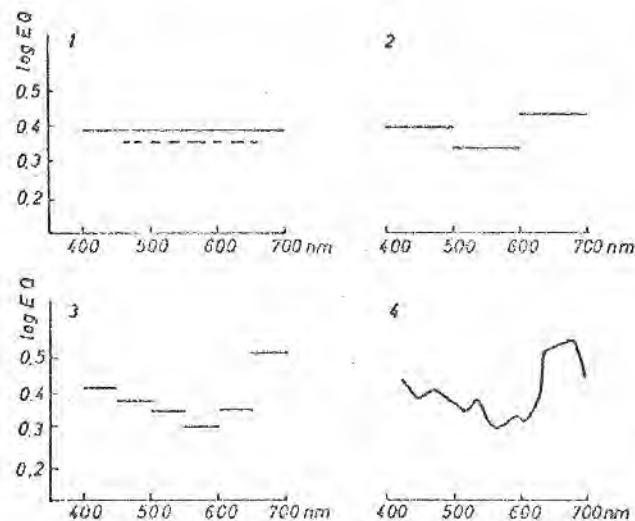


Fig. 2 Characterization of the spectra of the fraction of humic acids from a podzol by means of several extinction coefficients.



In the figure the number 1 represents the logarithm of extinction quotient  $E_{400/600}$ .

The number 2 represents the logarithm of the extinction quotients  $E_{400/500}$ ,  $E_{500/600}$  and  $E_{600/700}$ .

Number 3 are the logarithms of extinction quotients in a range of 50 nm and Number 4 in range of 10 nm.

The calculation of the differences of the extinction in smaller ranges of wavelengths  $\Delta \log K / \Delta \lambda$  - for instance in the range of 20 nm - results values, which give a better characterization of humic acids. Salfeld describes different humic acids by these "differential spectrograms", or the "differentiation of the spectra".

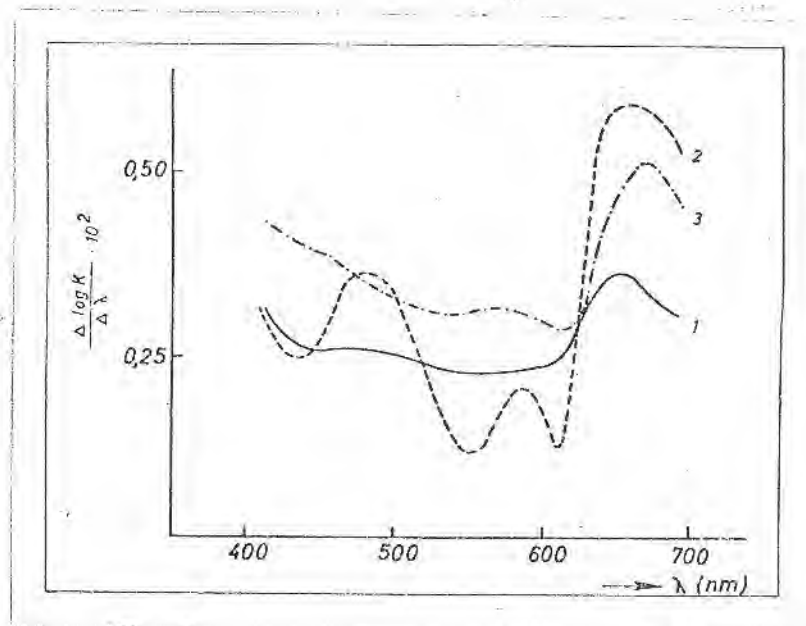


Fig.3: Differential spectrograms of humic acids in a range of 20 nm in 0.1 N NaOH (SALFELD 1965). (1) Chernozem, (2) podzol B and (3) black peat.

Fig. 3 demonstrates, that the spectra of humic acids are not straight lines with constant gradient, because the gradients change with the range of wavelengths and have minima and maxima between 500 and 600 nm for all 3 spectra. This means, that the spectra have a point of inflexion in this range. The changes of the gradient show remarkable quantitative differences. In the case of chernozem humic acids (1), the gradient decreases from lower to higher wavelengths at first only a little and then increases larger. The podzol humic acids (2) show at first a large decrease, a small maximum and then very large increase. In the case of humic acids from black peat (3) a larger decrease is followed by a larger increase.

The differential spectra vary in the different range of wavelength. Therefore it is not possible, that according to the theory at first fulvic acids, then hymatomelanic, then humic acids are formed. If the different acids would be formed in this sequence, the course of the curves should be the same in all 3 cases:

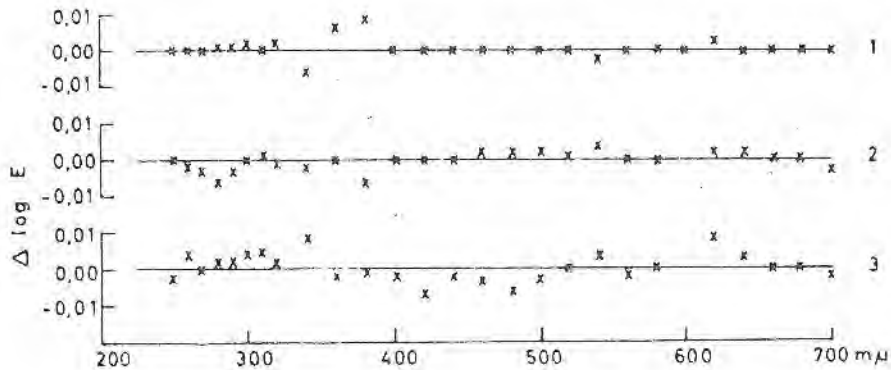


Fig. 4: Reproduceability of differences of logarithms of extinctions of different measurements with the same solution (1 and 2) and with different solutions (3) of the same preparation of chernozem.

To be able to use such measurements for a statistic of the characterization of isolated humic substances and their fractions or of systems of humic substances in soils, in cultures of microorganisms, in humification experiments or in the case of synthesis in vitro with various oxidation of phenols, the limits of reproduceability of the values must be known.

The graph shows the reproduceability of the measurements in the case of spectrum of humic acids from chernozem in 0.1 N NaOH. At first the same solution (1) and (2)

has been measured every 3 minutes two times and then a second new prepared solution of the same preparation of humic acids (3) has been measured. The differences of the logarithms of the measured extinctions is plotted against the wavelengths. The differences of the values are here smaller than in the measurements of the differential spectra.

To be able to place in order the humic substances themselves or their alteration products during different processes in a common system, the measured values for characterization of differences must be significant. The limits of reproduceability are not in all cases due to the method of isolation, but also due to the properties of the investigated materials. Because a voluminous material is necessary for such investigations, the methods for this purpose have to be automatized in regard to the apparatus as much as possible.

Investigations have been made, in which manner a larger number of samples of humic substances or systems could be compared by means of data of light absorption and could be sorted according to groups of similarity. Thus it was tried to compare and to classify groups of preparations of humic substances by means of the data, from spectra according to a method developed by SNEATH (1957).

As a measure for the similarity the ratio of the number of same properties to the number of the total regarded properties is defined. Each object is compared with each other. In this way diagrams of similarity are obtained; one example is demonstrated in the next graph with a group of 12 humic acids.

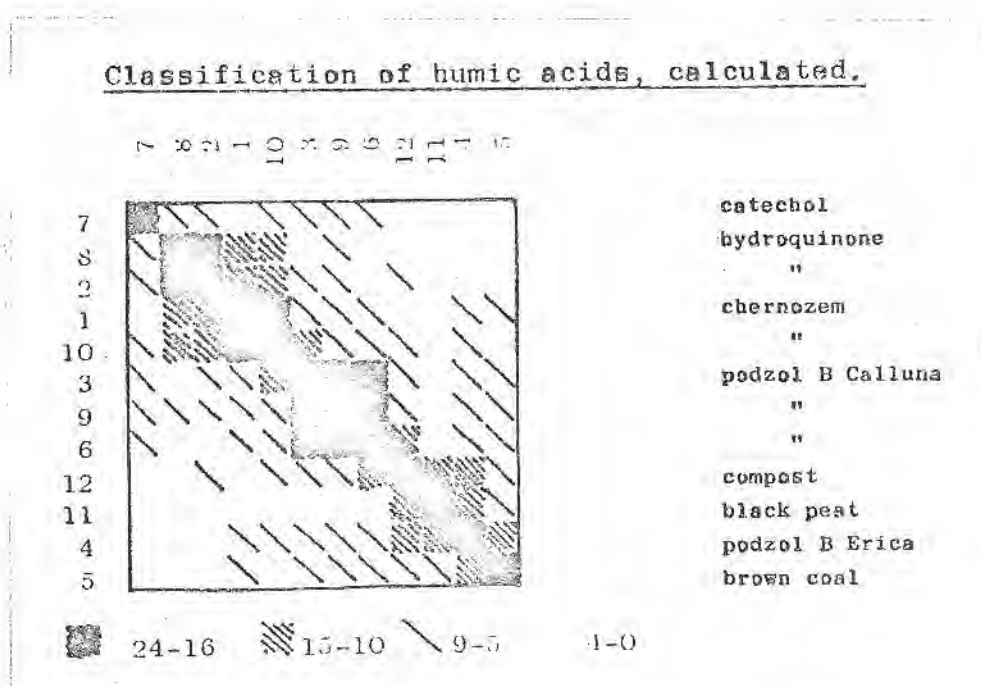


Fig. 5: Classification of humic acids, calculated.

In this example the spectra of 12 humic acids in 8 ranges of wavelengths are subdivided and the gradients as difference of logarithms of extinction are used as measured data. These data are transformed in an index number to simplify the representation. To compare the spectra the same index numbers of two spectra are

evaluated with 3 points, a difference between the index numbers of 1 with 2 points and a difference of 2 with 1 point. A number of 24 points for the similarity is obtained, when 2 spectra are identical, because 8 measured values with the same index numbers with an evaluation of 3 points is used. A complete dissimilarity is zero points.

For further simplification the decrease of similarity are subdivided in 4 groups /24 - 16/, /15 - 10/, /9 - 5/ and /4 - 0/. The more black the quadrats are, the more similar are the spectra of the humic acids. The preparations of humic acids at first marked with any number can be arranged (classified) mechanically or by calculation, so that the hydroquinone-, the chernozem- and the podzol humic acids (Calluna) are in each case in one group.

From the diagram also the similarities between humic acids it can be seen, which are not from the same origin. So No. 10, a humic acid from chernozem is relatively similar (degree of similarity 15 - 10) with hydroquinone humic acids No. 8 and No. 2 or with the podzol B Calluna humic acid No. 3, but very dissimilar (degree of similarity 4 - 0) with the humic acid from black peat No. 11.

This method is used especially in a suitable manner, when the objects are characterized by a larger number of

qualitative symptoms. If objects - in our case preparations of humic substances or their systems - are determined exclusively by measured data of properties, the similarity can be defined better as the distance of points in a n-dimensional space. For a group of objects, which are characterized by 3 measurable properties, a three-dimensional model can be easily realized. So it is possible to represent the humic acids by means of their spectra as points in a three-dimensional system of coordinates with the three extinction quotients  $E_{400/500}$ ,  $E_{500/600}$  and  $E_{600/700}$  as coordinates.

In this model 52 spectra of humic acids are presented as points with the coordinates of the extinction quotients of 3 different ranges of wavelengths. The position of the points in the space is a measure for the similarity. Three accumulations of points can be determined.

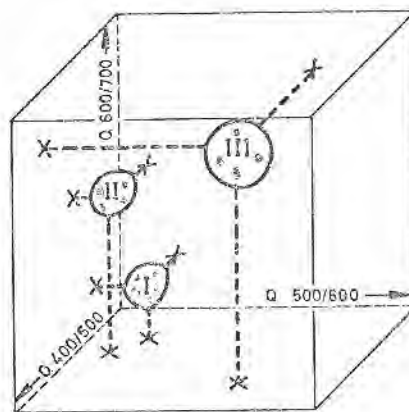


Fig. 6: Strongly schematized model of similarity of 52 humic acids by means of three extinction quotients ( $Q_{400/500}$ ;  $Q_{500/600}$  and  $Q_{600/700}$ ) (SALFELD 1968). The three groups of humic acids are marked with the numbers I, II, and III.

The closest accumulation contains the humic acids from chernozem (I), which is clearly separated from the humic acids from the podzol (II). A third accumulation is a group of preparations of humic acids (III) from different origin.

These remarks shall point out, that such possibilities of characterization exist and should be worked out to classify systematically the manifold experimental material for humic substances in order to draw more general conclusions. We characterize the fractions of humic substances in dependence of soil genetical and ecological symptoms, but also to find the correlations between the natural factors and those influenced by men during the formation and the decomposition of soil organic matter (SALFELD 1968, 1971, SALFELD and SOCHTIG 1969, SOCHTIG and SALFELD 1971).

Finally it might be also possible to correlate the productivity potential of soil with properties of soil organic matter. But this needs a strong cooperation with the agronomists and others and finally with the economists, because the best recommendations of chemists, biochemists, agronomists and soil scientists are useless, when the recommendations are not economical. Otherwise, the economists must learn, that one cannot calculate only with data based on the past year. A better understanding



of progress in biological science should enable them to give advices, if "drought resistance" or "inhibition of nitrification" is more important for the success of the farmers or the welfare of population.

To fulfil this task is only a question of ingenuity and directed cooperation.

Additional attempts have been made for characterization of humic systems by the use of other data of properties such as carbon and nitrogen content and different others.

The data in the literature cannot be used in the most cases to complete such investigations, because they do not correspond to the pretensions of the necessary reproduceability.

## 2. Scheme for analysis of humic systems

In the following, humic systems will be defined as the total complex of soil organic matter or chemically similar systems of organic substances, fractions of humic systems such as fulvic and humic acid fractions are in this sense also "humic systems".

In the following, a scheme of analysis of humic systems will be shown with which primary values are determined first. Then secondary values are derived

from these.

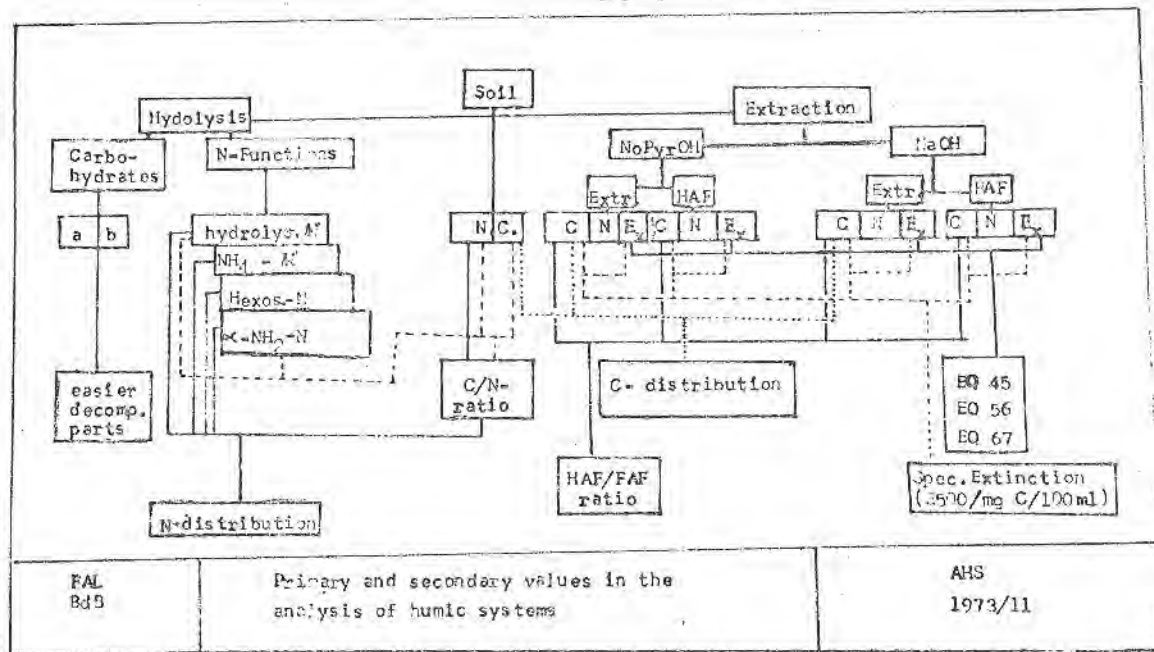


Fig. 7: Primary and secondary values in the analysis of humic systems.

Carbon and nitrogen content is determined in the soil. By hydrolysis with different concentrated acid easier degradable organic parts are determined for instance "carbohydrate fractions". The functions of nitrogen are determined according to Bremner (1965). The following determinations are made:

- 1) The part of nitrogen which is split off by hydrolysis totally;
- 2) the part of nitrogen N, which is split off NH<sub>3</sub> as during hydrolysis;
- 3) hexose amine-N and
- 4) α-amino-N.

The soil is extracted with two types of extractants:

- 1) a mixture of sodium pyrophosphate + sodium hydroxide, and
- 2) sodium hydroxide alone.

In the extract as well in the humic acid fractions precipitated with sulphuric acid at pH 1.0 and redissolved in sodium hydroxide, the following determinations were made:

- 1) carbon content
- 2) nitrogen content
- 3) extinction at 400, 500, 600, 700 nm.

From these primary values, secondary values are calculated.

- 1) The distribution of carbon in the different soil extracts and humic fractions. This relation leads to an estimation of the binding of humic substances on inorganic constituents.
- 2) The ratio of the fractions of humic acids and fulvic acids in the extract.
- 3) Specific extract of the humic system, this means the extinction is calculated based on carbon content in the same volume of extractant.
- 4) The ratio of the measured extinctions for characterising the spectra. This is also a key value of the slope.

Three ranges of the spectra are specifically divided up in ranges of 100 nm in each case.

5) The ratio of carbon to the differently bounded nitrogen.

6) The distribution of the different forms in which nitrogen is bound.

In the next five figures the scheme is divided up in tables to explain some singularities.

Tab. 1: List of methods for determination of values for analysis of humic systems.

No of method	No of apparatus	Methods
1	2	Pyrophosphat-NaOH-extract Extinction
2	2	" " Humic acids "
3	2	" " " "
4	2	" " " "
5	1	C-determination, Bichromate of method 1
6	1	" " " 2
7	1	" " " 3
8	1	" " " 4
9	1	" " " soil sample
10	1	N-determination, Kjeldahl "
11		
12		
13		
14	6	NH <sub>4</sub> -N in fresh soil samples
15	6	NO <sub>3</sub> -N " " " "
16	6	N-determination, total N, Kjeldahl, total hydrolysate 5
17	6	" " " NH <sub>4</sub> -N hydrolysate 5
18	6	" " " + Hexosamine-N hydrolysate 5
19	6	" " " + " + -NH <sub>2</sub> -N " 5
20	6	" " " Kjeldahl, solution method 1
21	6	" " " " " 2
22	6	" " " " " 3
23	6	" " " " " 4
24	6	Activity of dehydrogenase
25		
26	4	C-determination, soil sample combustion (Leco)
27	3	N-determination, " " (Heraeus)
28	1	Glucose-determination in hydrolysate (2 % HCl)
29	1	" " " " (72 % H <sub>2</sub> SO <sub>4</sub> )

Apparatus 1 = Braun Systematic, Analysensystem,  
 2 = Unicam SP 3000, 3 = Microrapid-N-, Heraeus,  
 4 = C-Determinator Leco, 5 = (in development),  
 6 = Digital pH-Meter Metrohm

In the first one the list of measured values for the determination of different values in the case of analysis of the humic systems is given.

Tab. 2: List of key values.

Normalized measured values of one method: In this list the normalized values (KM) of one method are given, which are calculated per units from the measured values.

KM 1	E 400	of method 1	Extinction of 10 ml solution/g soil
" 2	E 500	" "	" " " "
" 3	E 600	" "	" " " "
" 4	E 700	" "	" " " "
KM 5	E 400	of method 2	" " " "
" 6	E 500	" "	" " " "
" 7	E 600	" "	" " " "
" 8	E 700	" "	" " " "
KM 9	E 400	" method 3	" " " "
" 10	E 500	" "	" " " "
" 11	E 600	" "	" " " "
" 12	E 700	" "	" " " "
KM 13	E 400	" method 4	" " " "
" 14	E 500	" "	" " " "
" 15	E 600	" "	" " " "
" 16	E 700	" "	" " " "
KM 17		" method 5	mg/g soil
" 18		" " 6	"
" 19		" " 7	"
" 20		" " 8	"
" 21		" " 9	"
" 22		" " 10	"
KM 23		" " 11	"
" 24		" " 12	"
" 25		" " 13	"
KM 26		" " 14	"
" 27		" " 15	"
" 28		" " 16	"
" 29		" " 17	"
" 30		" " 18	"
" 31		" " 19	"
" 32		" " 20	"
" 33		" " 21	"
" 34		" " 22	"
" 35		" " 23	"
KM 36		" " 24	mg TPF <sup>+</sup> /10 g soil
" 37		" " 25	mg/g soil
" 38		" " 26	"
" 39		" " 27	"
" 40		" " 28	"
" 41		" " 29	"
" 42		" " 30	"

+ ) TPF = Triphenylformazan

Tab. 3: List of key values

Secondary values (KD). Difference from two different normalized measured values.

KD 1	Hexosamine-N	mg/g soil	KM 30	-	KM 29
KD 2	Amino-N	"	KM 31	-	KM 30
KD 3	Residual-N	"	KM 28	-	KM 31
KD 4	FAF-N	"	KM 32	-	KM 33
	in Pyrophosphate				
KD 5	FAF-N	"	KM 34	-	KM 35
	in NaOH-extr.				
KD 6	FAF-C	"	KM 17	-	KM 18
	in Pyr.-extr.				
KD 7	FAF-C	"	KM 19	-	KM 20
	in Pyr.-extr.				
KD 7	FAF-C	"	KM 19	-	KM 20
	in NaOH-extr.				

FAF = Fulvic Acids Fraction

One part of the secondary values is calculated as a difference from two different normalized values.

Tab. 4: List of key values

Secondary values (KQ). Quotient of two key values.

KQ	1	E 400/E 500	KM	1/KM 2	Pyr. extr.
"	"	E 500/E 600	"	2/KM 3	"
"	"	E 600/E 700	"	3/KM 4	"
"	4	E 400/E 500	"	5/" 6	HAF from extr.
"	5	E 500/E 600	"	6/" 7	"
"	6	E 600/E 700	"	7/" 8	"
"	7	E 400/E 500	"	9/" 10	Na OH-extr.
"	8	E 500/E 600	"	10/" 11	"
"	9	E 600/E 700	"	11/" 12	"
"	10	E 400/E 500	"	13/" 14	HAF from NaOH-extr.
"	11	E 500/E 600	"	14/" 15	"
"	12	E 600/E 700	"	15/" 16	"
KQ	13	C/N	"	21/" 22	total soil, Bichr./Kjel.
"	14	C/N	"	17/" 31	Pyroph. extr.
"	15	C/N	"	18/" 33	HAF in Pyr.
"	16	C/N	"	19/" 34	NaOH-extr.
"	17	C/N	"	20/" 35	HAF in NaOH
KQ	18	Specif. E. 400 nm, Pyr.		KM 1/KM 17	
"	19	" " 500 nm, "		" 2/" 17	
"	20	" " 600 nm, "		" 3/" 17	
"	21	" " 700 nm, "		" 4/" 17	
KQ	22	" " 400 nm HAF-Pyr.		" 5/" 18	
"	23	" " 500 nm "		" 6/" 18	
"	24	" " 600 nm "		" 7/" 18	
"	25	" " 700 nm "		" 8/" 18	
KQ	26	" " 400 nm NaOH		" 9/" 19	
"	27	" " 500 nm "		" 10/" 19	
"	28	" " 600 nm "		" 11/" 19	
"	29	" " 700 nm "		" 12/" 19	
KQ	30	" " 400 nm HAF-NaOH		" 13/" 20	
"	31	" " 500 nm "		" 14/" 20	
"	32	" " 600 nm "		" 15/" 20	
"	33	" " 700 nm "		" 16/" 20	

HAF = Humic Acids Fraction

Other values are calculated as a quotient of the key values.

Tab. 5: List of key values

Secondary values (KP). One key value in per cent of another key value.

KP	1	C-Pyrophosphate	in %	C-total	(KM 17, KM 21)
"	2	C-HAF Pyr.	"	"	" 18, " "
"	3	C-NaOH	"	"	" 19, " "
"	4	C-HAF NaOH	"	"	" 20, " "
"	5	C-HAF Pyr.	"	C-Pyr.	" 18, " 17
"	6	C-HAF NaOH	"	C-NaOH	" 20, " 19
"	7	N-Hydrolysate	"	N-total	" 28, " 22

HAF = Humic Acids Fraction

List of values in which secondary values are given as one key value in per cent of other key value.



These explanations demonstrate clearly, that such work can only be done with automatised instruments and electronic registration and evaluation of the values.

3. Example for characterisation of humic systems in a morphosequence of soil.

As an example to characterize humic systems some few results of an investigation of a black earth-griserde-morphosequence, will be mentioned. During the transition of a black earth to a griserde (gray brown, podzolic soil derived from black earth with clay migration) decalcification, clay formation and clay migration occurs. Simultaneously, the black earth-mull - 'A' horizon becomes more and more pale.

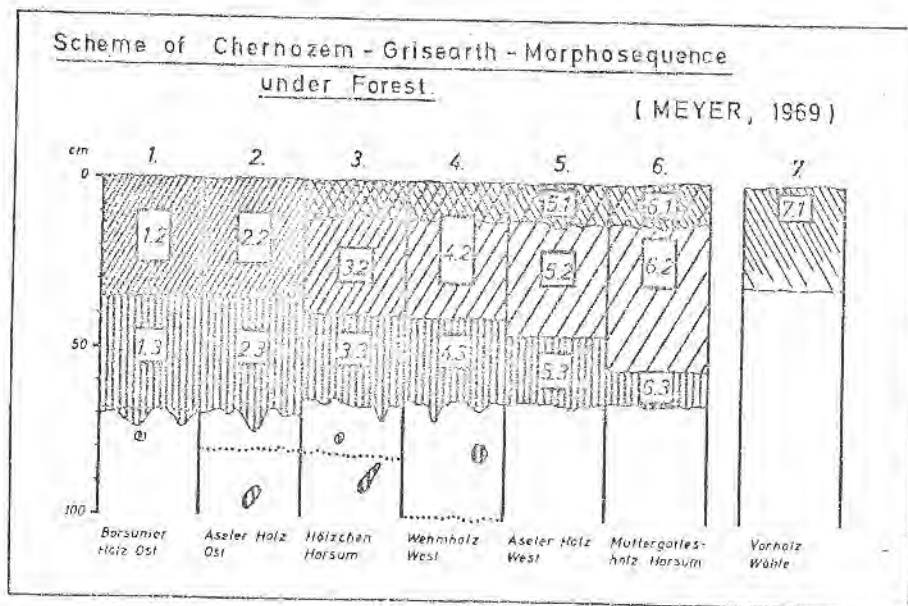


Fig. 8: Scheme of black earth-griserde-morphosequence under wood (profile number 1-6 and for comparison 'A'-horizon of gray brown podzolic soil on loss).

Six profiles had been chosen in which the bleaching in the sub-horizon  $A_2$  was increased. For comparison, 'A' horizon of a gray brown podzolic soil on loess was also investigated which is not derived from black earth. The visual differences of the six 'A' subhorizons have been also numbered.

1. Describes the subhorizons with recent humus formation:
2. Subhorizons with increasing leaching of the original 'A' horizon.
3. The old mull 'A' horizon.

All data mentioned in the scheme before have been determined. Only the results of the different solubility in sodium hydroxide and sodium hydroxide-pyrophosphate solution will be mentioned.

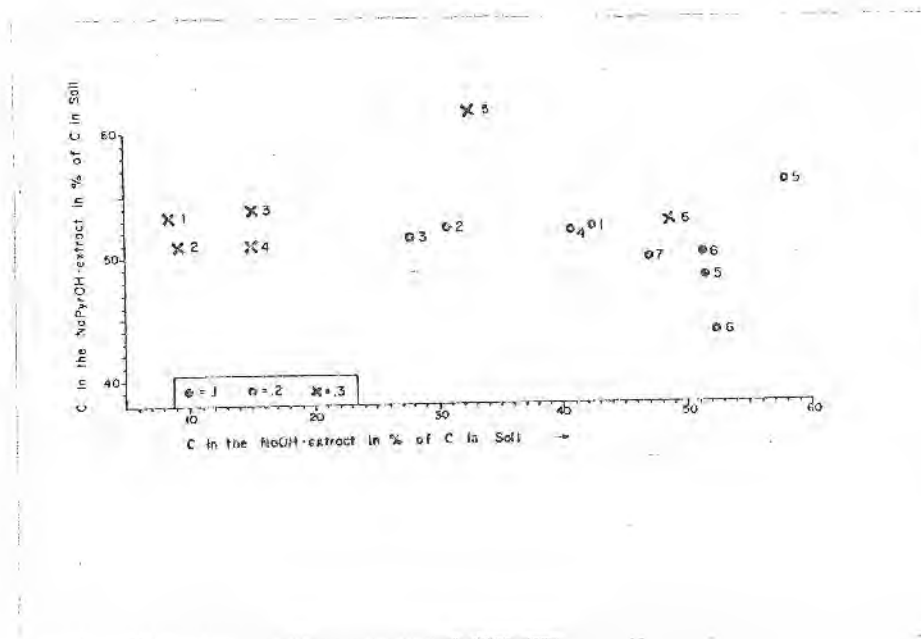


Fig. 9 : Carbon content in the extracts of sodium hydroxide and sodium hydroxide - pyrophosphate in dependence of total carbon content in soil.

The figure 9 shows the different solubility of humic substances in sodium hydroxide-pyrophosphate and in sodium hydroxide solution. In this figure the values for the humic systems from the subhorizons  $A_1$  are marked as points from subhorizon  $A_2$  as circles and from subhorizon  $A_3$  as crosses. Furthermore they are labelled by the numbers of the profile.

An average of 50% of the total C content were extractable with sodium hydroxide-pyrophosphate. This percentage is also the highest in the case of extraction with sodium hydroxide. Therefore, the conclusions about the humic systems represent only half of the total organic substances in the soil. This is not a particular case because nearly every investigation dealing with soil humic substances have been the similar drawback (KONONOVA, 1966). This fact one has to bear in mind in the case of characterisation of humic system in soil, but such data are not found in publications.

The solubility of humic substances in sodium hydroxide-pyrophosphate is nearly constant, while in sodium hydroxide this ranges from 10-60% of the total C in the different profiles.

Increasing solubility with sodium hydroxide indicates a decreased in the calcium linked portion of humic

substances and an increase of the free humic substances or those linked with mobile forms of sesquioxides. The humic substances of the subhorizons  $A_3$  of the profiles 1 - 4 are nearly totally connected to calcium, while those of subhorizons are nearly not connected with calcium. Those of subhorizon  $A_2$  of the profiles 1 - 4 are in between.

The humic substances of the intensive "bleached" profiles 5. and 6. are less connected with calcium than those of the not or moderately "bleached" profiles.

#### 4. Final remarks and Conclusions:

Not going in details, it will be only remarked that the combination of all these values is a useful tool for determination of properties of humic systems after statistical calculations with computers.

In the last part of the lecture, it will be reminded that only by the statistical methods determination of similarity or dissimilarity in the case of humic systems is possible. The arguments are the followings:

- 1) During humification processes "the initial material, the non-humic substances, are transformed in humic substances". This sentence reproduces only an imagination about humification, because a differentiation between non-humic and humic substances cannot be verified by experiments. It is not possible to separate humic substances

from non-humic substances completely by any method. The only possibility, which will exist, is to take out some fractions from soil organic matter which are either more similar to the fraction which are comparable in its properties with initial plant material or to this fraction which we call humic acids.

2) To make chemical statements as in similar systems of natural substances, one has to isolate chemically uniform substances from soil organic matter and to elucidate their constitution. Since the beginning of this century Schreiner and Shorey (1910) have done such work which was continued. One determined sugars, amino acids and also polycyclic hydrocarbons (Summarized FLAIG 1971)

The determination of numerous chemical compounds is of high value for special questions, for instance the phenol carboxylic acids with their influence on plant metabolism. But the low percentage of the determined organic compounds in soil in comparison to the total amount of carbon is not sufficient to elucidate chemical composition of the total complex of soil organic matter.

The results of many experiments contradict that important fractions with distinguished differences in their chemical compositions may be ever isolated. All results establish more or less that the fractions consist of numerous chemically similar individuals.

Therefore, only statistical statements can be made about the chemical structure of the components and above the chemical nature of the mixture.

3) To characterize the very complex system of humic substances as correctly as possible, many parameters are necessary. For special questions the number of parameters may be decreased. Furthermore the number of parameters increase, if these investigations concern not only chemical composition or chemical processes in the humic systems but also inter-actions with problems of soil science and plant production.

4) For exchange of information without loss, all the measured values as well as their evaluation must be documented on punch cards or other data registering procedures for the use of computers. This is important for over-regional cooperation. The mentioned system is compatible with other systems which are logically build up. Especially it can be fitted up in other corresponding systems.

The technical preposition are in principle known and fulfilled by automatization of the analytics and by electronic registration of the measured values and computerized evaluation of data. Only by this way evaluation of soil organic matter in relation to soil productivity and stabilization of the yield can be per-

formed at all places in the world. I believe this must be done in future, because in some decades the food production of the world population is no more a matter of the single countries as it is upto now.

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