

CONTRIBUTIONS OF SOIL ORGANIC MATTER

TO PRODUCTION POTENTIAL OF SOILS AND

SOME PROPOSALS FOR PRACTICAL APPLICATION

Wolfgang FLAIG

Annex II

to the report of W. FLAIG

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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- 2

Formation of Humic Substances from
plant residues

1. Introduction
2. Dependence of chemical composition and physical properties of humic systems on environmental conditions.
3. Degradation of plant constituents during humification.
4. Participation of different plant constituents on the formation of humic substances.
5. Special investigations with straw.
 - 5.1 Isolation of Lignin fractions and their elemental composition.
 - 5.2 Differences in the degradation of building blocks of lignin during humification.
6. Transformation of lignin fractions in humic substances.
 - 6.1 Alterations in elemental composition
 - 6.2 Functions of oxygen
 - 6.3 Functions of nitrogen.
 - 6.4 IR spectroscopic investigations.
7. Final Remarks.

1. Introduction

The processes of humification occur mainly under aerobic conditions. Soil animals may first reduce the size of the fresh organic residues. Further transformation are promoted by the activity of the enzymes of bacteria and fungi living in the soil. Cellulose, proteins and fats are readily available carbon sources for the microorganisms, while compounds such as lignin and other phenolic plant constituents are decomposed more slowly. These as well as some of the new substances which are formed through oxidation of phenolic units have toxic properties to different degrees. They can therefore serve as a carbon source only for special species of microorganisms. Generally the organic residues from higher animals and plants and many substances released by microorganisms can serve as carbon sources.

Certain species of microorganisms also synthesize phenolic or quinonoid metabolic products which decompose slowly by reason of their more or less markedly toxic properties or their sorption on inorganic soil constituents. I mention this, because different polycyclic compounds have

been isolated from soil; some of them are carcinogenic. In composts there is an enrichment of such compounds. An intensive discussion is going on about this fact.

The transformation of nitrogen containing substances plays an important role during humification. The micro-organisms use the proteins and their decomposition products derived from dead organisms, plants and animals, as a nitrogen source.

Some nitrogen components of humus serve as a slow releasing nitrogen source. They are the natural reservoir for the nitrogen nutrition of plants because this element is not supplied in significant quantities by the weathering of the rocks or the minerals of the soil. Furthermore the amount of nitrogen which reaches the soil in the rainwater and which is fixed by nitrogen fixing organisms is not sufficient for the annual plant growth in agriculture. The nitrogen containing organic compounds of the soil humus are, therefore, very important for the productivity of the soil under natural conditions. For economical yields, a high nitrogen supply by mineral fertilisers is necessary.

The humification process does not only involve the decomposition of high and low molecular weight plant, animal

and microbial cell constituents and transformation products but also the synthesis of low and high molecular weight compounds, which are not all formed within living cells, but must be considered as typical organic soil constituents formed by humification processes. These compounds are dark coloured and are called humic substances. They can be separated in different fractions from the other substances of the humus by their characteristic solubility or dispersability.

The composition of the different humic fractions from a single soil sample depends to a considerable degree on the methods used. The composition of one humic fraction by isolation with a standardized procedure from different soils is also variable. The names "Fulvic acids", "Hymatcmelanic acids", "Humic acids", "Humins" are therefore only designations or symbols for fractions of substances, which are isolated and separated with conventional methods. The similarity or dissimilarity obtained by one isolation procedure depend upon the values of different factors and is therefore only statistical.

2. Dependence of chemical composition and physical properties of humic systems on environmental conditions.

As an example about the influence of climatic

conditions on formation of humic substances, the investigations of KONONOVA (1961) are as follows. The amounts of fulvic and humic acids of the soils of the UdSSR from North to South were investigated with a standardized procedure and their elemental composition determined.

Tab.1: Elemental composition of humic acids (I) and fulvic acids (II) of the main soils of the UdSSR (as percentage of absolute weight of ash-free material according to KONONOVA, 1961).

Soils		C	H	O	N	C:H
Northern podzol under forest; humus illuvial horizon 16-24 cm; arkhangel region	I	58.11	5.37	32.00	4.52	10.82
	II	52.37	3.53	42.89	1.21	14.84
Sod-podzolic soil, arable; 0-20 cm; Moscow region	I	57.63	5.23	35.33	4.81	11.02
	II	42.63	5.05	44.60	4.12	9.15
Dark-gray forest soil under oak; 12-19 cm; Shipov forest Voronezh region	I	61.20	3.60	31.32	3.88	17.00
	II	47.46	3.64	45.87	3.03	13.04
Ordinary chernozem, arable; 0-20 cm; Kamennaya Steppe, Voronezh region	I	62.13	2.91	31.38	3.58	21.35
	II	44.84	3.45	49.36	2.35	13.00
Chestnut soil; virgin land; 0-20 cm; Valuisk Exp. Sta. Stalingrad region	I	61.74	3.72	30.62	3.92	16.60
	II	43.19	3.61	51.43	1.77	11.96
Light serozem, arable; 0-20 cm; Pakhta-Aral, Kazakhsk SSR	I	61.94	3.93	29.46	4.67	15.76
	II	45.80	4.30	46.00	3.90	10.65
Krasnozem under farn; 0-20 cm; Anaseuli, Georgian SSR	I	59.65	4.37	31.54	4.44	13.65
	II	49.82	3.35	44.33	2.50	14.87

I represents humic acids
II represents fulvic acids

The percentage of the elements depends upon the conditions of formation of the humic substances. Humic acids have a higher C and N content but a smaller oxygen content than the fulvic acids.

In the following scheme nine soils of U_dSSR from the North to the South are arranged. In the same direction the average temperature of the year increases from 2° to 11° C and the yearly rainfall decreases from about 600 mm to 100 mm. The values were collected from the book of KONONOVA (1966).

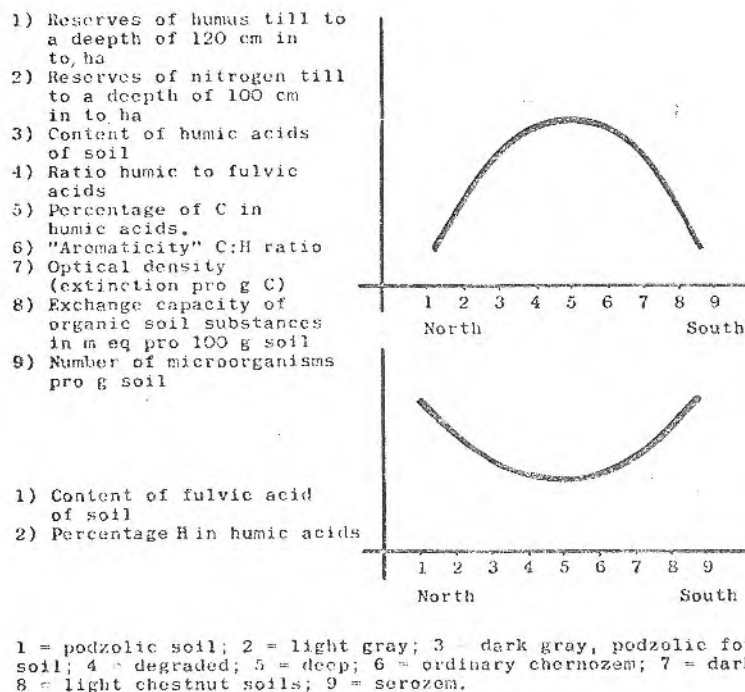


Fig. 1. Measurement of properties of soil organic matter of different soil types of U_dSSR (according to KONONOVA 1966).

The course of the curves of the different properties of soil organic matter shall only indicate, that a maximum or ~~minimum~~ exists for the data in the case of chernozem.

The different environmental factors and the inorganic initial materials lead in each case by the different ecological conditions to various biological processes, which finally influence the quantity and the properties of humic substances. These differences have again an influence on soil productivity by the interaction with the inorganic soil constituents.

It is clearly evident from these investigations that the amount as well as the physical properties and the chemical composition of the fractions named fulvic or humic acids differ dependent on the inorganic constituents of the soils.

3. Degradation of plant constituents during humification.

The humification of plant material of different composition has been investigated primarily in the laboratory (KOLENBRANDER 1955, SPRINGER 1944, 1945, 1955, SPRINGER and LEHNER 1952 a,b, SPRINGER and SEISCHAB 1961). WAKSMAN and TENNEY (1927, a,b) call attention to the fact

that young plants with a low methoxyl lignin content decompose easier than older ones with a higher methoxyl content.

Some details of decomposition of different materials are summarized in the following figures. All values are under humid climate. They are nearly the same, but differ only by the effect of different soil types.

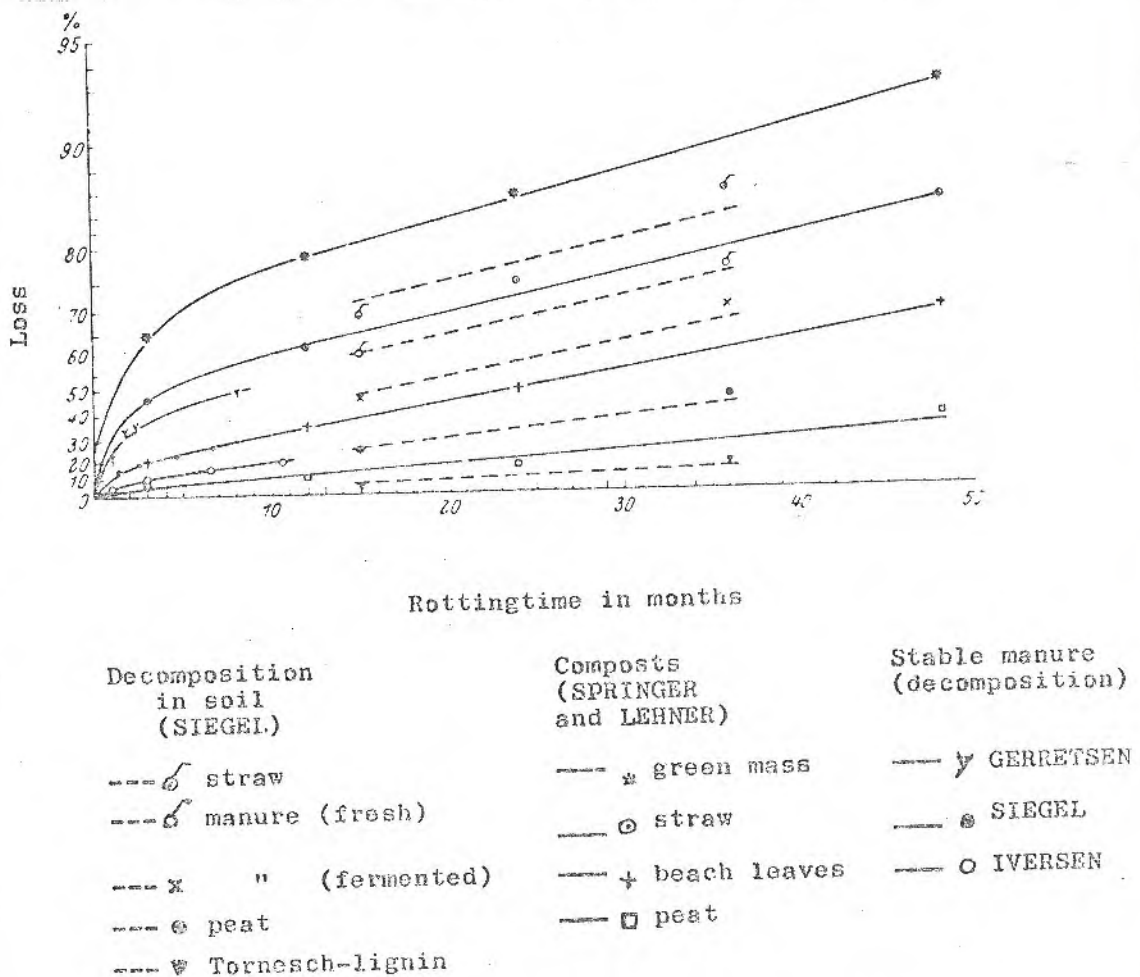
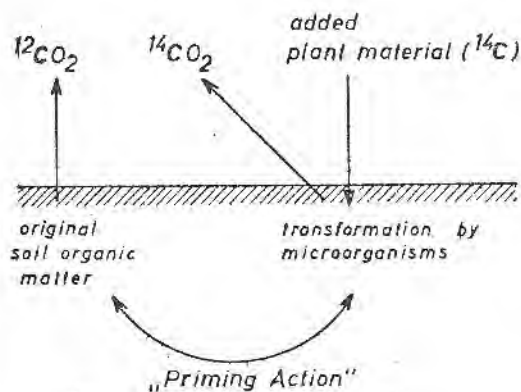


Fig.2: The losses of organic fertilizers on organic substances and dry matter during decomposition in soil, in composts and stable manures (KOLENBRANDER 1955).

Similar investigations were made with over-all labelled plant material by SAUERBECK (1968, a, b, c), JENKINSON (1965, 1966 b 1968), OBERLANDER and ROTH (1968) SAUERBECK and FUHR (1968, 1970), JANSSON and PERSON (1968). In principle the curves are the same, but it could be shown, that after 2 years about 30% of labelled plant carbon remains in the soil and upto 4% carbon are found in humic acids.

Fig. 3: Balance between increase and degradation of soil organic matter.



By addition of uniformly labelled plant material with carbon- 14 the formation and the decomposition of organic material especially of humic substances have been

investigated. By measuring the labelled carbondioxide in comparison with the unlabelled not only the transformation of added plant material by the action of microorganisms could be followed during a longer period of time, but also the simultaneous decomposition of the organic matter, which has been in the soil before. The turnover of organic matter depends upon the climatic conditions, the system of agriculture, the plant associations, the pH values and the mechanical composition of the soil.

The so called "Priming Action" is caused by the accelerated decomposition of soil organic matter which was originally in the soil. This effect occurs only when easily decomposable labelled plant material or manure is added to the soil. Experiments of this type have been made by different authors (JANSSON and PERSON, 1968, JENKINSON 1965, 1966, a,b,c, 1968, OBERLANDER and ROTH, 1968, SAUERBECK 1968 a,b,c, SAUERBECK and FUHR, 1968, 1970 and others).

A short remark must be made about labelling of plant material with carbon-14. The assimilation of $^{14}\text{CO}_2$ cannot be made only for a short time. For experiments to rot plant materials it has to be taken into consideration, if plants were grown for a short or a long time in a

$^{14}\text{CO}_2$ -atmosphere. Only during long time growth in the CO_2 -atmosphere plants were uniformly labelled in all carbon atoms. FUHEMANN (1964) showed in his short growth experiments, that in the lignin not all carbon atoms were uniformly labelled; the methoxyl groups were higher labelled than the other carbon atoms.

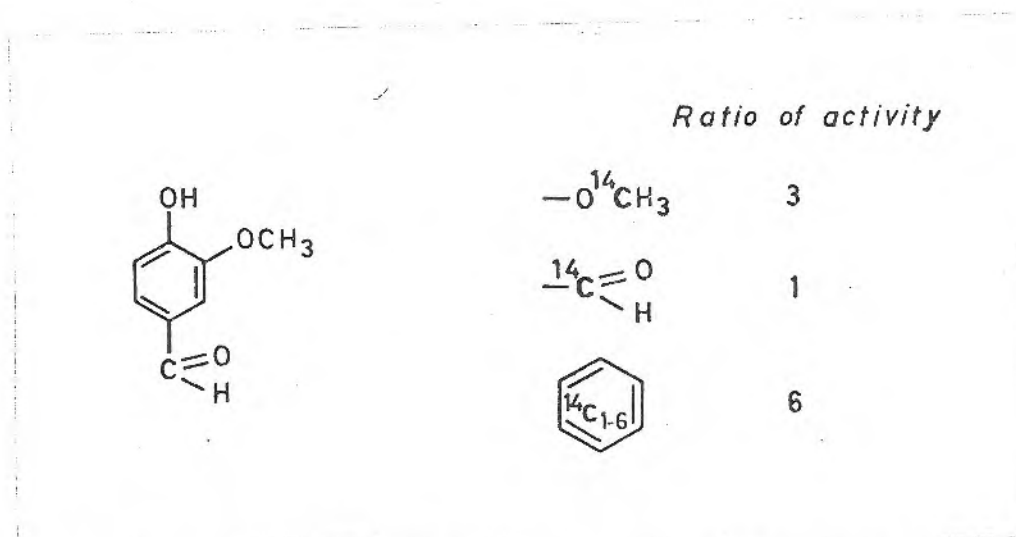


Fig. 4: Ratio of activity in vanillin from lignin of a short time experiment.

For instance vanillin was isolated after oxidation of the spruce lignin with sodium-*m*-nitrobenzene-sulfonate in alkaline solution. The distribution of the activity in the carbon atoms of the carbonyl-, of the methoxyl groups and in the 6 carbon atoms of the aromatic ring has been determined as 1:3:6 this means, that the activity of the

carbon atom of the methoxyl group is three times higher than in the carbon atom of the carbonyl group or on average the same in one of the carbon atoms of the aromatic ring.

These observations are important for experiments dealing with the so-called "Priming Action". Only by the use of statistically uniformly labelled plant materials conclusions are allowed for the decomposition of the unlabelled native organic matter in the soil.

Thus many factors are included in the processes of turnover of organic matter in soil and consequently in the formation of humic substances.

JENKINSON (1966 a) has given a summary of these problems. He reports also a mathematical model for the turnover of soil organic matter:

$$\frac{dX}{dt} = A - rX \quad (1)$$

$$X = \frac{A}{r} + \left(X_0 - \frac{A}{r} \right) e^{-rt}$$

Assuming that all parts of X are equally decomposable, then if r is the fraction of X decomposed per year, A the annual addition of organic matter to unit area of soil sampled to depth d and t time.

SAUERBECK (1968 b) investigated the stability of recently formed humic fractions in the soil. He incubated

labelled straw for 50 days with a low carbon soil and isolated the humic fractions with 0.1 NaOH. The decomposition of each fraction was followed in soil for 120 days. Non-dialysed fulvic acids lost 42% of their carbon content, humatomelanic acids 20%, gray humic acids about 6 and brown humic acids about 2%. From these experiments it can be concluded, that also the freshly formed humic acids formed by the decomposition of plant material in the soil are relatively stable products, whilst the fulvic acids undergo a quicker transformation.

The interrelations between decomposition of various labelled plant residues and loss of soil organic matter have also been investigated by J.H. SMITH (1966). He comes to similar results as the other authors and suggests, that the protective effect on indigenous organic matter sometimes observed is caused by substances, that are in plant material and toxic to the soil microorganisms. By these substances the decomposition of added plant material would be limited for a time and also the rate of decomposition of the indigenous soil organic matter would be reduced.

With other investigations it could be shown with ^{14}C -labelled humic acids by MAYAUDON and SIMONART (1960) that humic acids flocculated with calcium ions are very much stabilized against microbial attack in the soil, whilst an

addition of protein to the not flocculated humic acids increases the decomposition rate about 50%.

The isotopes have become an important tool for the dynamics of the fractions of soil organic matter. SCHARPENSEEL (1960 a,b) labelled humic acids by means of the Wilzback-technique with tritium. By labelling with tritium and carbon-14 it is possible to show the transformation of one humic acid fraction into another one. Another way for synthesis of ^3H -labelled humic acids is to rot plant material which is added to a soil moistened with ^3H -labelled water. Also model humic acids have been made from tritiated purpurogalline by oxidation in the presence of a phenoloxydase. SCHARPENSEEL and BECKMANN (1964) add ^{14}C -labelled humic acids to soils and investigate the release of carbondioxide under different conditions. In a summarizing paper SCHARPENSEEL (1966 a) discusses the different possibilities of labelling and the distribution of labelled material in soil organic matter; he reports 70 papers and makes new proposals for this purpose.

4. Participation of the different plant constituents on the formation of humic substances.

The decomposition of uniformly labelled plant material in the soil gives only an idea about the extent of its participation on the formation of soil organic matter, but

does not allow to estimate the importance of the single plant constituent for the formation of humic substances. Therefore it is necessary for the elucidation of the formation and for the chemical properties of humic substances to report more details especially in the field of chemistry and biochemistry.

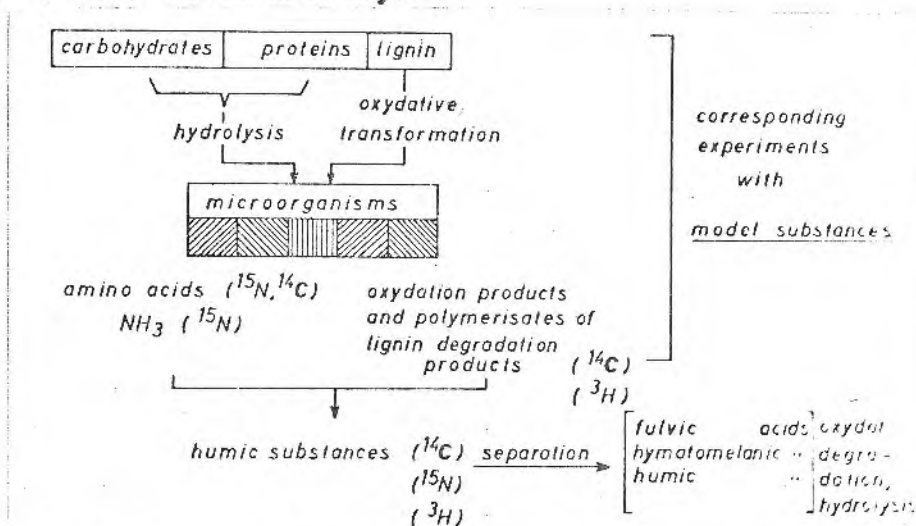


Fig. 5: Use of isotopes in soil organic matter studies.

The highmolecular plant constituents cellulose and proteins can be hydrolysed to their monomers by the enzymes of soil microorganisms, whilst lignin is not hydrolysable. So far it is known, it is degraded by oxidative processes, whereby oxidising enzymes may be involved.

The activity of the microorganisms in the soil is therefore an essential factor for the humification of plant residues. Otherwise an extensive activity of the microorganisms can only be observed, when organic materials are in the

soil to a sufficient amount for the energy supply of the microbial metabolism.

The lignin degradation products are oxidized to compounds such as phenols or quinones, which are very reactive. Both types of compounds polymerise to polymers of different composition.

By the use of plant material labelled with ^{14}C or ^{15}N labelled degradation products or by further oxidation reaction products are formed which are also labelled. Finally the formation of humic substances occurs by the reaction between the degraded lignin, the lignin degradation products, other phenolic substances synthesized by plants or microorganisms or their oxidation products, and the proteins from the plants and from the microorganisms or from other compounds formed by hydrolysis and further transformation. In this way it is possible, that labelled humic acids are formed, which are isolated and separated by the usual procedures in the fractions of fulvic, humatomelanic and humic acids. By further oxidative or reductive degradation, hydrolysis and other reactions several informations are obtained about the chemical constitution of the isolated humus components. The different possibilities of labelling with ^{14}C , ^{15}N , ^3H have been used. In many cases the use of labelled plant materials is not always sufficient. Therefore it has been necessary to make corresponding experiments with labelled model substances.

First of all the extent of the participation of the plant constituents on the formation of humic substances has been studied. (MAYAUDON and SIMONART 1958, 1959 a, b, 1961, SIMONART and MAYAUDON 1958 a,b,1966, SIMONART, MAYAUDON and BATISTIC 1959, SRENSSEN 1963, 1966 and others).

To study the participation of carbohydrates on formation of humic substances labelled cellulose, hemicelluloses or glucose were added to soils and incubated for several days. During incubation the released carbon dioxide has been absorbed in sodium hydroxide solution and measured its activity.

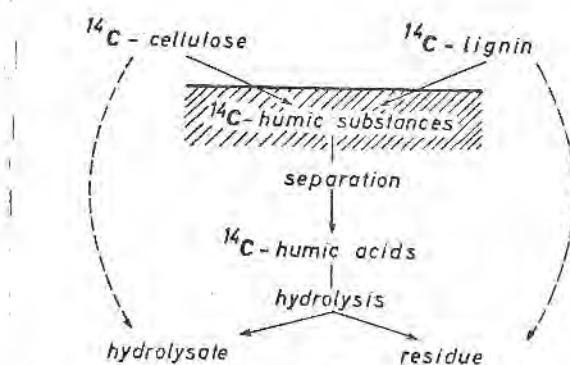


Fig. 6: Decomposition of distinct plant constituents.

Glucose is not immobilized in the soil as such. It is decomposed more rapid than hemicellulose and this more rapid than cellulose. The decomposition rate depends upon the environmental conditions used by the different authors. After the extraction and fractionation of the humic substances the humic acids have been hydrolysed. The major

part of the activity has been in the hydrolysate. By paper chromatography it could be shown, that this was located in the amino acids. The carbohydrates have been transformed through the metabolism in the microorganisms to proteins, which reacted with other constituents of soil organic matter to humic acids. On the other hand if labelled lignin is added to the soil the larger part of the activity is in the residue of the hydrolysis of the humic acids' fraction. Lignin decomposes more slowly than cellulose; this can be determined by the production of labelled carbondioxide.

Also lignin degradation products, such as p-hydroxy-benzaldehyde, vanillin and syringeldehyde is chiefly concentrated in the nonhydrolysable fractions of humic acids. (FUHR 1962, FUHR and SAUERBECK, 1966, MAYAUDON and SIMONART 1958, 1959 a,b, SIMONART and MYAUDON 1958 a,b, SIMONART, MAYAUDON and BATISTIC 1959, SRENSSEN 1963).

Some special results about the participation of lignin degradation products in formation of humic substances and about the occuring reaction mechanisms will be reported in lecture 5.

5. Special investigations with straw:

The most intensive studies on the processes of humification have been made with straw, a plant material, which is relatively rich in cellulose and lignin and poor in

protein (BARTLETT and NORMAN 1938, BARTLETT, SMITH, BROWN 1937, BROADBENT 1954, FLAIG, SCHOBINGER and DEUEL 1959, KAILA 1952, MAEDER 1960, MOHTADI 1962, PHILLIPS 1934, REINHARDT, 1961, SCHOBINGER 1958, SMITH, STEVENSON, BROWN 1930, SPRINGER and LEHNER 1952 a,b, WAKSMAN, TENNEY and DIEHM 1929).

Since the content of available nitrogen may be a limiting factor for the activity of the microorganisms and therefore also for the rate of humification, the addition of nitrogen to low nitrogen residues accelerates decomposition.

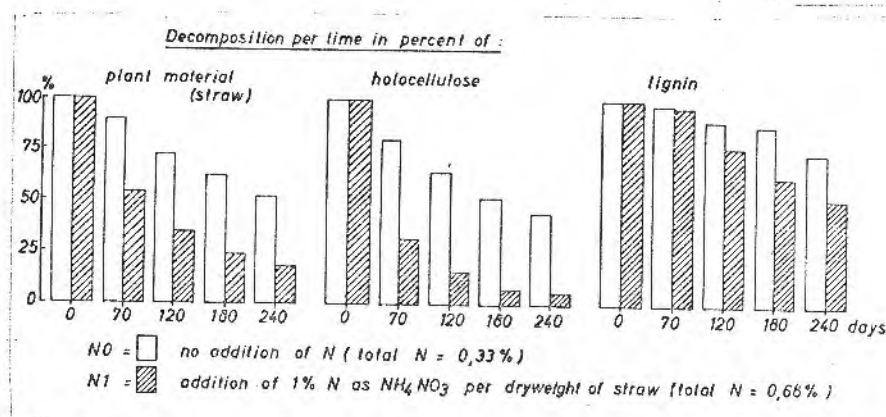


Fig. 7: The decomposition of plant material (straw) of Holocellulose and of lignin in per cent during rotting time (MAEDER, 1960)

From the figure can be seen, ^{an} addition of 1 per cent nitrogen in the form of ammoniumnitrate per dry weight of straw accelerates the bio-chemical degradation of plant materials. The degradation of holocellulose is faster than that of lignin by addition of available nitrogen (MAEDER 1960)

During these processes the possibility exists that lignin degradation product participate directly in formation of humic substances (Flaig, 1962).

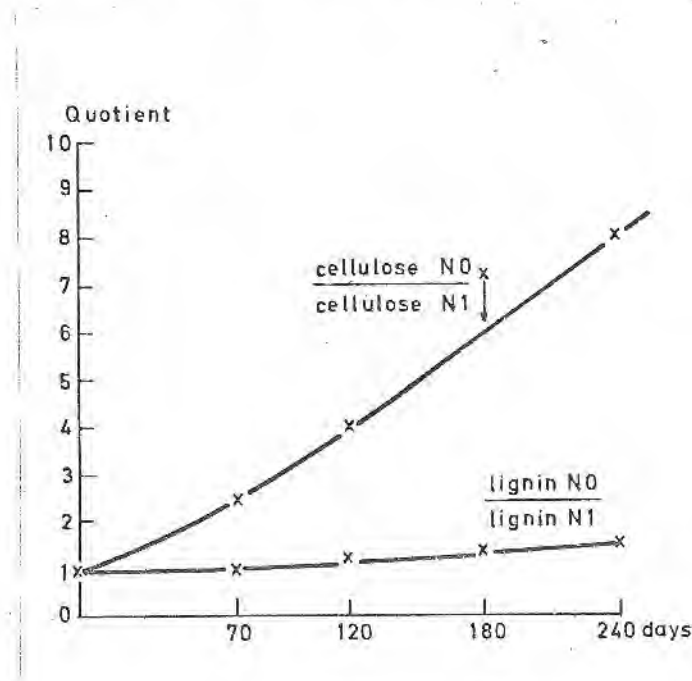


Fig. 8: Acceleration of the degradation of cellulose and lignin of rye straw by addition of nitrogen during 240 days. N 0 = no nitrogen added; N 1 = 1 % N as NR_4 , NO_3 per dry weight of straw (according to MAEDER 1960).

The quotient of the amount of the cellulose remaining after a given time without addition of nitrogen divided by the amount of the cellulose remaining with addition of nitrogen increases more rapidly than that of lignin (Fig. 8). This means that the degradation of cellulose is accelerated much more than that of lignin by added nitrogen (FLAIG 1962).

Thus curves are characteristic for different decomposing materials, conditions and addition of nitrogen.

5.1. Isolation of lignin fractions and their elemental composition.

The conditions for the isolation of different lignins from different plant species and the necessary precautions for good yields with the sulphuric acid procedure, are described by PLOETZ (1940). Different methods for the isolation of lignin from rotted straw have been checked in extensive investigations (FLAIG, SCHOBINGER and DEJEL 1959).

The most useful values were obtained with the 72% sulfuric acid method by careful treatment of the rotted straw (MAEDER 1960) "Sulfuric Acid" lignins can be obtained with a sulfur content of 0,6 to 0,8 % and an ash content of 8 to 11%.

The "lignin fraction", which can be isolated from straw during its humification, differ in their elemental composition from the original lignin. Therefore, it is incorrect to call them "lignin", it is better to speak about "lignin fractions". The alterations in carbon and oxygen content are not as pronounced as the value for nitrogen and methoxyl content (Table 2) even when the lignin fractions are isolated with dioxane (Tab.3) according to the method of BJORKMAN (1954, 1956), compare also: BARTLETT and

NORMAN 1938, BARTLETT 1939, BROADBENT 1954, FLAIG 1960, FLAIG, SCHOBINGER and DEUEL 1959, NEHRING and SCHIEMANN 1952 a,b, STOCKLI 1952, WAKSMAN and SMITH 1934.

Tab.2: Elementary analysis of the lignin fractions of rye straw from experiments with and without added nitrogen calculated for ash-free substances (MAEDER 1960).

Days nitrogen	C %	H %	O % (Diff.)	N %	S %	OCH ₃ %	ash %
0	62.73	5.48	30.55	0.53	0.55	17.08	6.15
70 ^{ON*)}	62.73	5.48	31.20	0.54	0.49	15.53	7.65
1N**)	61.42	5.25	30.20	1.44	0.69	12.76	9.00
120 ^{ON}	62.13	5.42	31.41	0.56	0.48	14.99	8.62
1N	60.93	5.41	31.20	1.68	0.78	11.33	10.02
180 ^{ON}	62.20	5.41	31.30	0.56	0.53	14.37	9.31
1N	60.94	5.38	31.15	1.74	0.79	10.95	11.24
240 ^{ON}	62.14	5.27	31.03	0.56	0.97	13.46	9.36
1N	59.61	5.13	32.77	1.88	0.61	13.46	11.69

ON*) = no nitrogen added,
1N**) = 1 % N as NH₄NO₃ per dryweight of straw

Tab.3: Elementary analysis of isolated "sulfuric acid" and "Bjorkman" lignin fractions of wheat straw (Addition of 0,5% N as NaNO₂ per dry weight of straw)(SCHOBINGER 1958)

Days of humification	C %	H %	O % (Diff)	N %	S %	OCH ₃ %
H ₂ SO ₄ -Lignin	0 58,59	5,60	31,37	0,54	3,9	15,33
	70 58,78	5,93	29,48	2,01	3,8	11,14
	180 58,67	5,91	29,15	2,37	3,9	9,06
	340 54,97	5,96	32,09	3,08	3,9	8,57
Bjorkman-Lignin	0 60,68	5,79	33,11	0,42		16,76
	70 59,75	7,35	30,93	1,97		10,84
	180 58,81	6,56	31,27	3,36		8,19
	340 57,37	6,95	31,14	4,54		7,50

Tables 2 and 3 show that the conditions during humifi-

cation and the composition of the initial material (rye and wheat straw) influence the transformations of the lignin. But in all cases the methoxyl content decreases and of the nitrogen content increases (FLAIG 1960 a).

The products formed are dark coloured and have physico-chemical properties (spectra, solubility, cation exchange capacity) which are comparable to those of humic acids (FLAIG 1963, FLAIG, SCHOBINGER and DEUEL 1959). The products formed from lignin decomposition have a methoxyl content, which is higher than that of humic acids from manures or composts (NEHRING and SCHIEMANN 1952 a,b).

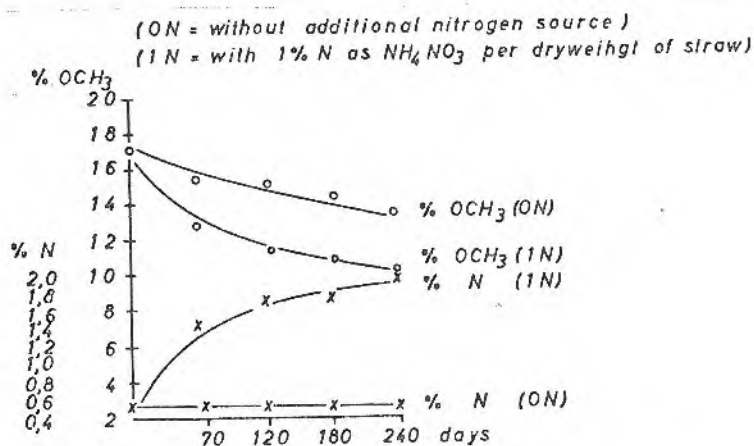


Fig.9: Alterations of the content of nitrogen and methoxyl of the lignin fractions of straw during humification.

If one isolates the lignin fractions from rotted plant material for instance straw with sulphuric acid, the content of methoxyl groups decreases and the nitrogen content

increases concurrently with the time of rotting (BARTLETT 1939, BARTLETT and NORMAN 1938, BROADBENT 1954, FLAIG, 1960 a, FLAIG, SCHOBINGER and DEJEL 1959, NEHRING and SCHIEMANN 1952 a,b, RITTER, SEBORG and MITCHELL 1932, STOCKL 1952, WAKSMAN and SMITH 1934). This suggests that the cleavage of the methoxyl group proceeds the introduction of nitrogenous groups (FLAIG 1960 b).

The fixation of nitrogen compounds after alteration of several groups, especially demethylation, in the lignin preserves the high molecular structure of lignin fractions. The nitrogen becomes partly less available for microorganisms by these procedures.

5.2. Differences in the degradation of building blocks of lignins during humification.

It was also investigated, if the different building blocks of different lignin types are decomposed with the same rate during humification.

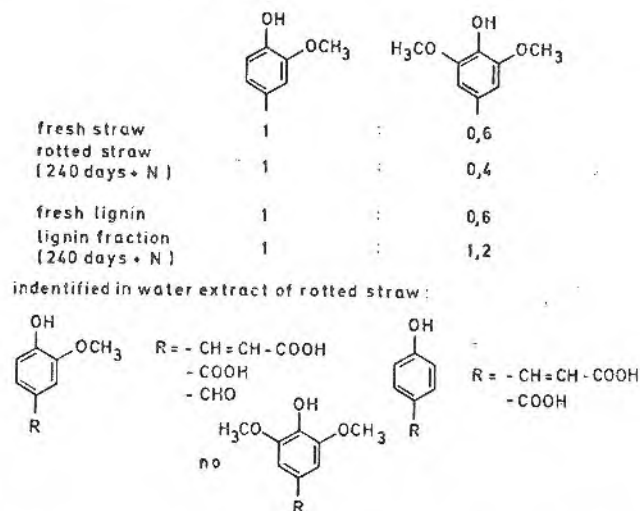


Fig.10: Alterations of the content of the guaiacyl-

or syringyl - component of rye straw during humification (according to KRATZL and CLAUS 1962).

KRATZL and CLAUS (1962) found by ethanolysis of rotted rye straw that the ratio of guaiacyl to syringyl component is shifted from 1:0,6 to 1: 0,4 after 240 days (1% N per dry weight of straw was added as NH_4NO_3). This means that the guaiacyl component is enriched in the rotted straw; this may be caused by a favoured degradation of the syringyl component. Syringyl components seem to be more utilized by the microorganisms than the guaiacyl components. (Remember the lignins of different plants are differently composed). The ratio of guaiacyl to syringyl component changed from 1:0,6 to 1: 1,2 in the lignin fraction of rye straw after humification. The guaiacyl component seems to be split off more than the syringyl component or, if the guaiacyl component remains in the lignin molecule, it is demethylated to a larger extent. The differential degradation of various lignins seems to be connected with the linkages of the monomers in the lignin molecule. It is suggested, that the linkages occur mainly through the carbon atom 2 of the side chains. The type of linkages may be prevalent in lignins containing sinapyl alcohol units, because both positions of the hydroxyl group in the ring are substituted with methoxyl groups and therefore the

linkages between the rings and the side chains or between two rings might be rare (comp. scheme of lignin structure Introductory lecture p.13.).

In water extracts of rotted straw only guaiacyl components such as ferulic acid, vanillic acid or vanillin but never syringyl compounds could be identified. Furthermore p-hydroxybenzoic acid and its aldehyde were found (MAEDER 1960). Lignin degradation products were also isolated by investigations of other humified materials (JACQUIN 1963, BRUCKERT, JACQUIN and METCHE 1967). But syringic acid could be isolated only from soils and peat.

6. Transformation of lignin fractions in humic substances.

6.1. Alterations in elemental composition.

Table 4: Elemental composition of lignin, humified lignin, humic and fulvic acids. (According to FREUDENBERG and HARKIN 1964, MAEDER 1960(1), KONONOVA(2), Dregunov 1948 (3).)

		% C	% H	% O	% OCH ₃	% N
<u>Lignin</u>						
1) Beech (Fagus silvaticus)	$C_9H_6.5O_2(H_2O)_{0.64}(OCH_3)_{1.41}$	61,87	6,03	32,10	21,65	
2) Spruce (Picea exelsa)	$C_9H_7.12O_2(H_2O)_{0.40}(OCH_3)_{0.92}$	65,08	5,88	29,04	12,87	
3) Peat-moss (Sphagnum)	$C_9H_7.96O_2(H_2O)_{0.90}(OCH_3)_{0.25}$	61,67	5,89	32,44	4,36	
4) Rye straw	$C_9H_6.15O_2(H_2O)_{1.05}(OCH_3)_{1.13}N_{0.08}$	63,10	5,92	30,67	17,20	0,54
<u>Humified lignin</u>						
5) Rye straw decomposed 180 days	$C_9H_5.45O_2(H_2O)_{1.42}(OCH_3)_{3.68}N_{0.24}$	61,15	5,42	32,42	11,05	1,75
<u>Humic acids</u>						
<u>Fulvic acids</u>						
6) Northern podsol under forest		58,11	5,37	32,00	-	4,52
		57,37	3,33	42,89	-	1,21
7) Podzolic soil		57,94	5,79	31,41	1,54	4,86
8) Ordinary chernozem, arable		67,13	2,91	31,38	-	3,58
		44,84	3,45	49,36	-	2,33
9) Chernozem		57,32	4,25	34,39	1,17	4,04

The elementary analysis of lignin and humic acids (Table 4) demonstrates that the carbon content of the lignin of different plants is higher than that of humic acids. The decrease of carbon content and the increase of oxygen content show, that oxidative processes play an important role during the transformation of lignin into humic substances. Furthermore the content of nitrogen is increased, whilst the content of methoxyl groups decreased remarkably during humification.

KRATZL et al. (1964, 1966) conclude by their investigations of sulphite liquors of cellulose production from coniferous wood, that demethylation occurs through semi-quinone formation during oxidation in alkaline medium. Thereby the methylether group reacts like an ester and is saponified by alkali. Reactive groups are formed by demethylation, which is important for further reactions of lignin with other reactive compounds such as amino acids finally for the degradation which occurs in nature by enzymatic processes.

6.2. Functions of the oxygen.

BARTLETT and NORMAN (1938) and BROADBENT (1954) have found, that the number of hydroxyl groups tends to decrease upon degradation. The content of carboxylic groups and the

cation exchange capacity progressively increase with humification.

Also the titration of lignin fractions, isolated from wheat straw according to the method of BJORKMAN, in ethylenediamine with ethanalamine according to BROCKMANN and MEYER (1953) shows a decrease in equivalent weight with increasing time of humification.

Table 5: Transformation of lignin fractions of wheat straw at different periods of humification according to FLAIG, SCHOBINGER and DEUEL (1959).

	equivalent weight	acidic groups equiv./100 g	readily decarboxylated groups in mol CO ₂ /100 g	CO ₂ -formation in % of the acidic groups
fresh straw	560 ± 13	178	10.6	6
70 days rotted	677 ± 11	173	14.5	8
180 days rotted	429 ± 7	233	30.4	13
340 days rotted	412 ± 9	243	-	

The titration curves indicate, that an increase of acidic groups occurs, which is due primarily to carboxylic groups. A portion of these new acid groups can be split off with 12% hydrochloric acid to form carbondioxide. This may also originate from the side chain of the oxidised lignin building blocks or from acids, which are formed by the cleavage of the ring. The lignin of the fresh straw is altered by treatment with strong acids, whereby ring condensations occur (BRAUNS and BRAUNS 1960, p.516-518). The products formed are decomposed by oxidation to benzene polycarboxylic acids.

The formation of carbon dioxide can be explained by these reactions as well as by the decomposition of pentosanes which might be included. According to the investigations of DEUEL and DUBACH (1958 a,b) and DEUEL, DUBACH and BACH (1958) ketocarboxylic acids, unsaturated heterocyclic and aromatic hydroxycarboxylic acids are decarboxylated by treatment with 12% HCl.

The appreciable increase in exchange capacity is, according to BARTLETT and NORMAN (1938), not associated with proteins, which might be coprecipitated during the isolation of the lignin fractions. An addition of egg albumin to lignin isolated from fresh wheat or oat straw, in an amount equivalent to the nitrogen content of rotted straw lignin had little effect on the exchange capacity. Furthermore the authors believe that the increase in the exchange capacity of the lignin fractions isolated from the humified straw is not caused by the condensation of nitrogen compounds with the transformed lignin.

Further investigations on functional oxygen in the lignin fractions isolated from wheat straw according to BJORKMAN showed an increase in carbonyl content from 0,3% in the fresh straw to 0,47% and 0,59% after 70 and 410 days respectively. Carbonyl content was determined with 2,4-dinitrophenylhydrazone (TRAYNARD and EYMERY 1956). This increase may be due to an increase of the carbonyl groups

in the side chains and perhaps also to an oxidation of phenolic hydroxyl groups to quinones during humification. STEELINK and TOLLIN (1962) have demonstrated, that free radicals increase in the lignin fractions during humification and that the free radicals were probably related to the presence of quinonoid groups.

Tab. 6: Methylation of lignin fractions of wheat straw isolated by the Bjorkman method (SCHOBINGER 1958).

		N-content
Lignin from fresh straw	16.76 % OCH ₃	0.42 % N
Lignin from fresh straw, methylated	21.76 % OCH ₃	
Lignin 70 days rotted	10.84 % OCH ₃	1.97 % N
Lignin 70 days rotted, methylated	13.97 % OCH ₃	

The decrease of the methoxyl content of the lignin fractions during humification could theoretically lead to an increase of phenolic hydroxyl groups by cleavage of the methyl ether. But as the ratio of the methoxyl content before and after methylation is in both cases about 3:4, no increase in the number of free phenolic hydroxyl groups in the lignin fractions occurred. The increase of nitrogen from 0,42% to 1,97% shows that the phenols have reacted with nitrogen compounds. Model investigations with 1-hydroxy-2-methoxybenzene compounds demonstrated, that methoxyl containing phenols do not condense with primary amino compounds such as amino acids (HAIDER, FREDERICK and FLAIG 1965).

6.3 Functions of nitrogen.

Tab.7: Distribution of the nitrogen of the lignin fractions of wheat straw in percent after different periods of humification (calc. for ash-free substances) (FLAIG, SCHOBINGER and DEUEL 1959).

Days of humification	Residue of hydrolysis	Total N in %	In % of total-N(=100) before hydrolysis				Loss of weight by Hydrolysis
			α -amino nitrogen in the Hydrolysate	In residue of hydrolysis		Sum of α -NH ₂ -N + NH ₃ -N + "residual"-N	
				as NH ₃	as "residual"-N		
Lignin fractions (isolated with sulfuric acid)							
0	44,0	0,55	58,1	40,0	0	98,1	17
70	44,6	2,09	39,2	27,8	18,7	85,5	20
180	55,7	2,46	21,1	25,2	18,7	65,0	24
260	42,4	3,26	20,8	17,2	25,1	63,1	24
340	52,1	3,20	20,3	25,6	26,5	72,4	32

It is noted in this table, that for fresh straw the sum of nitrogen determined as α -amino-nitrogen and that which remains in the hydrolysate as NH₃-N and in the residue after hydrolysis is more than 90%, while the sum is always lower for the rotting straw. This result may be explained by the investigations of GALE (1946), who found that certain amino acids are decarboxylated to amines by the action of microorganisms and therefore, cannot be determined by the titrimetric method with ninhydrin (van SLYKE, MC FADYEN and HAMILTON 1941). Thirteen amino acids could be identified in some cases with paper chromatography in the hydrolysates of fractions, in which α -amino-nitrogen was found.

An oxidative deamination of amino acids can occur in

in oxidising medium by α -diphenols or quinones which are formed from the lignin degradation products by cleavage of the methylethers. The continuous increase in the nitrogen content of the residues after hydrolysis or of the $\text{NH}_3\text{-N}$ determined in a fusion with potassium hydroxide and sodium acetate under reducing conditions (BREYHAN 1956) and of the residual-N indicates, that the nitrogen is bound in such a way, that it can be split off only under the drastic conditions of the alkali fusion ($\text{NH}_3\text{-N}$) or is no longer hydrolysable ("residual"-N). Indol compounds could also be detected (FLAIG and BREYHAN 1956).

A considerable loss of weight is observed upon recovery of the residues after hydrolysis which cannot be explained on the basis of hydrolysable amino acids. Therefore other reactions must occur during the hydrolysis with 6 N hydrochloric acid, which are unknown.

6.4 IR-Spectroscopic investigations.

The transformation of the lignin fractions during humification has also been investigated by infrared spectroscopy (FLAIG, SCHORINGER and DEJEL 1959, FLAIG 1958, 1964 a, FLAIG and BEUTELSPACHER 1968, FAIMER and MORRISON 1960 and others).

The lignin fractions of fresh wheat and rye straw show the same bands in the region between 5,8 - 7,75 μ . The method of isolation whether with 96% alcohol according to BRAUNS (1939), with 90% dioxane according to BJORKMAN (1954, 1957), with sulfuric acid according to a modified method

of Klason (RITTER, SEBORG and MITCHELL 1932), or with thioglycolic acid according to HOLMBERG (1934), does not change the pattern. The C = O-valency vibrations of carboxyl groups at 5,8 μ are caused by the thioglycolic acid, if this acid is used for the isolation. Changes in the bands at 8-9 μ occur when sulfurnic acid is used for isolation. These changes may be related to acid catalysed ring condensation similar to those which occur with coniferous lignin (BRAUNS AND BRAUNS 1960).

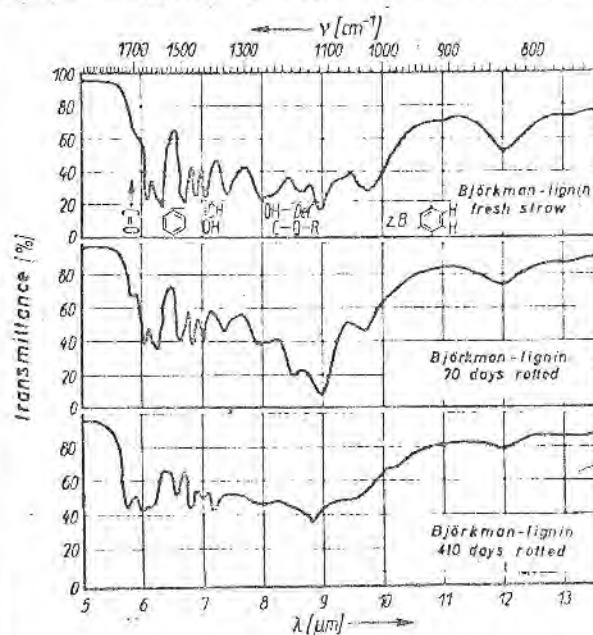


Fig.11: Alterations of IR-spectra of lignin fractions during humification.

An increase of the intensity of the C = O-band at 5,85 μ with increases of time of humification may be due to an increase of carboxyl groups because the consumption of alkali increases during titration (FLAIG, SCHOBINGER and DEUBL 1959, BROADBENT 1954). The number of carboxyl

groups determined by chemical methods also increases (BROADBENT 1954).

The absorption of the C = C-valency vibrations at 6,25 and 6,65 μ may be caused chiefly by the aromatic parts of the lignin molecules and does not change very much with time.

The increasing background absorption may be explained by the assumption that with time a greater variety of aromatic components is present, although the total quantity may remain the same. The steady decrease of the methoxyl content of the lignin fractions, the increase of the syringyl component, and the increase of non-hydrolyzable nitrogen supports this explanation.

The alterations of the C-H-deformation vibrations at 6.85 and 7 μ may be connected with alterations in the side chains. The strongly marked bands at 7.95 μ and 8.95 to 9.10 μ are due to arylalkyl and other ether linkages based on investigations with model substances. The strong absorption of the other bands at 8,95 μ in the case of the lignin fractions of fresh or rotted straw, but which are weak for polymers of guaiacol may be caused by syringyl components (FLAIG 1964 a).

The absorption at 6,1 upto 6.20 μ increases with the

increased nitrogen content of the lignin fractions during humification. In this region not only C = C bands but also the N-H-deformation and C = N-valency vibrations occur. The latter may be due to heterocyclic compounds.

The spectra of lignin fractions isolated with sulphuric acid from the same humified straw samples to which different amounts of nitrogen were added, but which had the same nitrogen content, were identical in the region from 5.8 to 8.8 μ (FLAIG 1964 a).

7. Final remarks.

In this lecture some facts about biochemical transformations of dead plant material in humic substances have been reported. It was special intention to consider in details. Some of the reaction mechanisms, which have been elucidated with labelled compounds, are reported later on.

It is established that soil organic matter plays an important role for plant production specially in relatively hot climates. Its importance for soil productivity became evident in connection with the use of higher quantities of mineral fertilizers which the high yielding varieties need.

To increase soil organic matter content in soil will not be possible, but it is very important to maintain or stabilize the level of soil organic matter. Even the

stabilization will be a difficult task, because by the increasing use of mineral fertilizers the possibility of an accelerated decomposition of soil organic matter is likely, if by the addition of the fertilizers a not enough increased root production is caused. Increased root production is biochemically under same environmental conditions a function of:

1. Plant type.
2. Variety of plant species.
3. Acceleration of root growth by physiologically active substances.

To improve soil structure by larger amount of organic material seems to be possible only under certain conditions but not in all cases.

Work with labelled plant material gives in India only other data about its half life time in soil according to other climatic or reaction conditions respectively, especially by the higher temperature, but no new results in principle.

By the basic research about decomposition of straw as organic material, the most important processes are known. Some differences occur in connection with differences in chemical composition and reaction conditions.

The investigation of transformations of straw in humic substances show clearly the importance of nitrogen . Therefore one should combine experiments still conducted with ^{15}N fertilizers for yield formation with those of organic matter formation, transformation and decomposition. For the first step labelling with ^{15}N and the knowledges from the literature seem to be sufficient.

References:

- ACERBO, R., H. KASTORI, H. SOCHTIG, H. HARMS and K. HAIDER: Effect of boron in synthesis and transformation of lignin precursors in Zea Mays. *Zeitschr. f. Pflanzenphysiologie*, 69, 306-317 (19).
- ALEXANDER, M. Biochemical ecology of soil microorganisms. *Ann. Rev. Microbiol.* 18. 217-252 (1964).
- BAILEY, N.T., G.G. BRIGGS, G.J. LAWSON, J.M. SCHWTON and S.G. WARD: Observation on the structure of humic acid. 6. Intern. Kohlenwiss. Tagung, Münster, W., 1.-3.6.1965. Beitrag Nr. 3, 1. (1965).
- BARTLETT, J.B.: The effect of decomposition of the lignin of plant materials. *Iowa State Coll. J. Sci.* 14, 11-13 (1939).
- BARTLETT, J.B., F.P. SMITH and P.E. BROWN: Lignin decomposition in soils. *Proc. Iowa Acad. Sci.* 44, 97-101 (1937).
- BARTLETT, J.B., and A.G. NORMAN: Changes in the lignin of some plant material as a result of decomposition. *Soil Sci. Soc. Amer., Proc.* 3, 210-216 (1938).
- BELAV, L: Chemische Untersuchungen heimischer Torfbildner ein zur Kenntnis der umwandlung von pflanzenstoffen unter natürlichen und künstlichen Bedingungen. Dissertation Rostock (1967).
- BERLING, J., K. BARZ, H. HARMS and K. HAIDER: Degradation of phenolic compounds in plant cell cultures. *FEBS LETTERS*, 16(2), 141-146 (1971).
- BIELAWSKI, J., T.E. THOMPSON and A.L. LEHNINGER: The effect of 2,4-dinitrophenol on the electrical resistance of phospholipid bilayer membranes. *Biochem. and Biophys. Res. Comm.* 24, 948-954(1966).
- BJORKMAN, A.: Isolation of lignin from finely divided wood with neutral solvents. *Nature* 174, 1057 (1954).
- BJORKMAN, A.: Lignin and Lignin-Carbohydrate Complexes. Extraction from wood meal with neutral solvents. *Ind. Eng. Chem.* 49, 9 1395-1398 (1957).
- BLOIS, M.S.: Random polymers as a matrix for chemical evolution. In: *The origins of prebiological systems*, edit. by Sidney W. Fox, Academic Press New York-London 1965, 19-38.
- BONDIETTI, E., J.P. MARTIN and K. HAIDER.: Influence of nitrogen source and clay on growth and phenolic polymer production by *Stachybotrys* species, *Hendersonula toruloidea* and *Aspergillus sydowi*. *Proc. Soil Sci. Soc. Am.* 35(6), 917-922(1971).

- BONDIETTI, E., J.P. MARTIN and K. HAIDER: Stabilization of amino sugar units in humic type polymers. Proc. Soil Sci. Soc. Am. 36, 597-602 (1972).
- BRAUNS, F.E.: Native Lignin. I. Its isolation and methylation. J. Amer. Chem. Soc. 61, 2120-2127 (1939).
- BRAUNS, F.E. and D.A. BRAUNS: The chemistry of lignin; supplement volume: Covering the literature for the years 1949-1958. New York and London, Academic Press 516-518, (1960).
- BREMNER, J.M.: "Organic forms of nitrogen". Ch. 85 Methods of Soil Analysis. (Agron. Monographs 9) ASA Madison 1965.
- BREMNER, J.M., W. FLAIG and E. KÜSTER: Zur Kenntnis der Huminsäuren. IX. Mitteilung. Der Gehalt an Aminosäuren in Streptomyceten-Huminsäuren. Z. Pflanzenernähr., Düng., Bodenkunde 71, 58-63 (1955).
- BREMNER, J.M. and T. HARADA: Release of ammonium and organic matter from soil by hydrofluoric acid and effect of hydrofluoric acid treatment on extraction of soil organic matter by neutral and alkaline reagents. J. Agric. Sci. 52, 2 (1959).
- BREYHAN, Th.: Eine Mikromethode zur Stickstoffbestimmung. Z. analyt. Chem. 152, 412-417 (1956).
- BROADBENT, F.E.: Modification in chemical properties of straw during decomposition. Soil Sci. Soc. Amer., Proc. 18, 165-169 (1954).
- BROCKMANN, H. and E. MEYER: Äquivalent- und Molekulargewichtsbestimmungen durch potentiometrische Mikrotitration in nicht-wässrigen Lösungsmitteln. Chem. Ber. 86, 1514-1523 (1953).
- BRUCKERT, S.F., F. JACQUIN and M. METEHE: Contribution a l'etude des acides phenols presents dans les sols. Bull. de l'Ecole Nationale Supérieure Agronomique de Nancy, IX, 73-92 (1967).
- BURGES, A. and P. LATTE: Decomposition of humic acid by fungi. Nature 186, 4722, 404-405 (1960).
- BURGES, N.A., H.M. HURST and B. WALKDEN: The phenolic constituents of humic acid and their relation to the lignin of the plant cover. Geochim. Cosmochim. Acta 28, 1547-1554 (1964).
- CHAMINADE, R.: Action de l'acide humique sur le developpement et la nutrition minerale des vegetaux. VI. Int. Soil Sci. Congr. Vol. D. Paris, 443 (1956).
- CHAMINADE, R.: Effet physiologique des constituants de la matière organique des sols, sur le metabolisme des plantes, la croissance et le rendement. In: The use of isotopes in soil organic matter studies. Report of the FAO/IAEA Technical Meeting. Pergamon Press Ltd. Oxford 1966, 35-47.

- CHoudRI, M.B. and F.J. STEVENSON: Chemical and physicochemical properties of soil humic colloids. III. Extraction of organic matter from soils. Soil Sci. Soc. Amer., Proc. 21, 508-513 (1957).
- CHRISTEWA, L.A.: Die stimulierende Wirkung der Huminsäuren auf die Lebenstätigkeit höherer Pflanzen und die Effektivität der Humindünger in südlichen Gebieten der Ukraine, SSR. Int. Soil Sci. Congr. Vol. II, Comm. II u. IV. Hamburg 46-55 (1958).
- CHRISTEWA, L.A.: Theorie und Praxis der Humindüngeranwendung in der Ukraine. Der Internationale Torfkongress, UdSSR Leningrad (1963) (russ.).
- COFFIN, D.E. and W.A. DELONG: Extraction and characterization of organic matter of a podzol B-horizon. 7th. Int. Congr. of Soil Sci. Madison, Wisc. USA Vol. II, 91-97 (1960).
- CONN, H.J. and J.F. CONN: The stimulative effect of colloides upon the growth of certain bacteria. J. Bact. 32, 99-100 (1940).
- CROMARTIE, R.I.T. and H. MASON: The structure of tyrosine melanin. Chem. Ind., 972-973 (1953).
- DAMBROTH, M.: Einfluß von N-lignin auf Ertrag und wertbestimmende Merkmale von Sommergerste, Z. Pflanzenern., Düng. Bodenk. (1972).
- DEUEL, H. and P. DUBACH: Decarboxylierung der organischen Substanz des Bodens. II. Nachweis von Uronsäuren. Z. Pflanzenernähr., Düng., Bodenkunde 82, 97-106 (1958)a.
- DEUEL, H. and P. DUBACH: Decarboxylierung der organischen Substanz des Bodens. III. Extraktion und Fraktionierung decarboxylierbarer Humusstoffe. Helv. Chim. Acta 41, 1310-1321 (1958 b).
- DEUEL, H., P. DUBACH and R. BACH: Decarboxylierung der organischen Substanz des Bodens. I. Decarboxylierung der gesamten Humusstoffe. Z. Pflanzenernähr., Düng., Bodenkunde 81, 189 (1958).
- DUBACH, P. and N.C. MEHTA: The chemistry of soil humic substances. Soils Fertilizers XXVI, 293-300 (1963).
- DUBACH, P., N.C. MEHTA and H. DEUEL: Extraktion von Huminstoffen aus dem B-Horizont eines Podsols mit ADPE. Z. Pflanzenernähr., Düng., Bodenkunde 25, 119-123 (1961).
- DUBACH, P., N.C. MEHTA and H. DEUEL: Schonende Extraktion von Huminstoffen und Isolierung der Fulvosäure-Fraktion aus verschiedenen Bodentypen. Z. Pflanzenernähr., Düng., Bodenkunde 102, 1-7 (1963).

- FARMER, V.C. and R.I. MORRISON: Chemical and infrared studies on phragmites peat and its humic acid. Sci. Proc. Roy, Dublin Soc. Series A 1, 85-104 (1960).
- FARMER, V.C. and R.I. MORRISON: Lignin in Sphagnum and phragmites and in peats derived from these plants. Geochim. Cosmochim. Acta 28, 1537-1546 (1964).
- FILIPS, Z.: The influence of small supplements of bentonite on the development of certain groups of microorganisms in a soil culture. Rostlinna Vyroba (Prague) 14, 209-216 (1968 a).
- FILIPS, Z.: Development of microorganisms and humus substance formation in media with different content of bentonite. Pochvovedeniye (Moscow) 9, 55-61 (1968 b).
- FILIPS, Z.: Characteristic of humic substances in a soil incubated with additions of bentonite. Rastlinna Vyroba (Prague) 15, 377-390 (1969).
- FILIPS, Z., K. HAIDER, W. FLAIG, H. BEUTELSPACHER, E. KUSTER u. J.P. MARTIN: Einfluß der Tonminerale auf die Huminstoffbildung einiger Bodenpilze. Landbauforschung Völkenrode, 21, 97-102 (1971).
- FILIPS, Z., K. HAIDER and J.P. MARTIN: Influence of clay minerals on growth and metabolic activity of *Epicoccum Nigrum* and *Stachybotrys Chartarum*. Soil Bio. Biochem. 4, 135-145 (1972a).
- FILIPS, Z., K. HAIDER and J.P. MARTIN: Influence of clay minerals on the formation of humic substances by *Epicoccum Nigrum* and *Stachybotrys chartarum*. Soil Biol. Biochem. 4, 147-154 (1972 b).
- FLAIG, W.: Zur Bildungsmöglichkeit von Huminsäuren aus Lignin. Holzforschung 9, 1-4 (1955).
- FLAIG, W.: Zur Chemie der Huminsäuren und deren Modellsubstanzen. Vle. Congres Internat. de la Science du Sol. Paris, 2, 471-478 (1956).
- FLAIG, W.: Die Chemie organischer Stoffe im Boden und deren physiologische Wirkung. Verhandl. d. II. und IV. Komm. d. Internat. Bodenkundl. Ges., Hamburg, Vol. II (1958).
- FLAIG, W.: Einige Reaktionen der Benzochinone und ihre Absorptionsspektren. Angew. Chem. 69, 723 (1957).
- FLAIG, W.: Chemie der Humusstoffe. Suomen Kemistilehti A 33, 229-251 (1960 a).

- FLAIG, W.: Comparative chemical investigations on natural humic compounds and their model substances. *Sci. Proc. Roy. Dublin Soc. Ser. A* 1, 4. 149 (1960 b).
- FLAIG, W.: Zur Umwandlung von Lignin in Humusstoffe. *Freiberger Forschungshefte A* 254, 39-56 (1962).
- FLAIG, W.: Über den Einfluß von Humusstoffen auf den Stoffwechsel der Pflanzen. *Der internationale Torfkongress UdSSR Leningrad 1963*.
- FLAIG, W.: Chemische Untersuchungen an Humusstoffen. *Z. Chem.* 4, 253-265 (1964 a).
- FLAIG, W.: c) Humusstoffe. *Handbuch der Pflanzenernährung und Düngung. Bd. II: Boden und Düngemittel 1966*, S. 282-458, Springer-Verlag Wien.
- FLAIG, W.: Uptake of organic substances from soil organic matter by plant and their influence on metabolism. *Pontificiae Academiae Scientiarum Scripta Varia* 32, 723-770 (1968).
- FLAIG, W.: Contribution a la connaissance de la constitution et de la synthese des acides humiques. *Extrait de "Sciences du Sol"*, Supplement au Bulletin de l'Association Francaise pour l'Etude du Sol, No. 2, 39-72 (1970).
- FLAIG, W.: Organic compounds in soil. *Soil Sci.* 111, 19-33 (1971).
- FLAIG, W. and H. BEUTELSPACHER: Investigations of humic acids with the analytical ultracentrifuge. In: *Isotopes and radiation in soil organic matter studies*. International Atomic Energy Agency, Vienna 1968, 23-30.
- FLAIG, W. and Th. BREYHAN: Über das Vorkommen von Indolverbindungen in Schwarzerde-Huminsäuren. *Z. Pflanzenernähr., Düng., Bodenkunde* 75, 132-135 (1956).
- FLAIG, W. and K. HALDER: Reaktionen mit oxydierenden Enzymen aus Mikroorganismen. *Planta Medica, Z.f. Arzneipflanzenforsch.* 9, 123-139 (1961 a).
- FLAIG, W. and K. HALDER: Die Verwertung phenolischer Verbindungen durch Weißfäulepilze. *Arch. Mikrobiol.* 40, 212-223 (1961 b).
- FLAIG, W. and K. HALDER: Über die Beteiligung von Phenolen am Aufbau von Huminsäuren. - 9th International Congress of Soil Science Transactions III, 175-182 (1968).

- FLAIG, W. and W. de JONG: Untersuchungen über die Wirkung von p-Benzochinonderivaten auf den aeroben und anaeroben Stoffwechsel der Hefe (*Saccharomyces cerevisiae*). Arch. f. Mikrobiol. 37, 355-368 (1960 a).
- FLAIG, W. and W. de JONG: Vergleich der Wirkung von Thymochinon und Thymohydrochinon mit der von 2,4-Dinitrophenol auf den Stoffwechsel der Hefe (*Saccharomyces cerevisiae*). Arch. f. Mikrobiol. 37, 369-378 (1960 b).
- FLAIG, W. and H. RIEMER: Polarographische Untersuchungen zum Verhalten von Trihydroxytoluolen bei der Reaktion mit Glycin unter Oxydierenden Bedingungen. Justus Liebig's ANNALEN DER CHEMIE 246, 81-85 (1971).
- FLAIG, W. and E. SAALBACH: Zur Kenntnis der Huminsäure. XIII. Untersuchungen über die Beeinflussung der Anfangs-entwicklung von Getreide in Neubauerschalen durch Thymohydrochinon als Modellsubstanz von Vorstufen bzw. Abbauprodukten von Huminsäuren. Z. Pflanzenernähr. Düng. Bodenk. 72, 7-15 (1956)-Beziehungen zwischen Kalium, Wasser und Boden, Kalium-Symposium (1958).
- FLAIG, W. and Chr. SALFELD: UV-Spektren und Konstitution von p-Benzochinonen. Liebigs Ann. Chem. 618, 117-139 (1958).
- FLAIG, W., K. SCHARNER and G. SCHOLL: Humic acids XVI. The effect of Thymohydroquinone as model substance of humic matter on the activity of various enzymes in rye. Z. Pflanzenernähr. Düng. 76, 201-209 (1957 a).
- FLAIG, W., K. SCHARNER and G. SCHOLL: Humic acids XVII. The effect of Thymohydroquinone as model substance of humic matter on the phosphorus uptake by rye seedlings. Z. Pflanzenernähr. Düng. 76, 210-212 (1957 b).
- FLAIG, W. and G. SCHMID: Über den Wirkungsmechanismus stoffwechsellaktiver Substanzen. In: Eigenschaften und Wirkungen der Gibberelline, Symposium der Oberhessischen Gesellschaft für Natur- und Heilkunde, Naturwissenschaft. Abt. zu Giessen vom 1.-3. Dez. 1960, S. 25-27 (Herausg. R. Knapp). Springer-Verlag Berlin-Göttingen-Heidelberg 1962.
- FLAIG, W., U. SCHÖBLINGER and H. DEWEL: Umwandlung von Lignin in Huminsäuren bei der Verrottung von Weizenstroh. Chem. Ber. 92, 1973-1982 (1959).
- FLAIG, W. and G. SCHOLL: Hacia el conocimiento de los ácidos húmicos. XVIII. Comunicación "Influencias de la timohidroquinona sobre la economía del agua en plantas de interés agrícola. Anales de Edafología y Agrobiología XIX, 251-259 (1960).

- FLAIG, W. and H. SÖCHTIG: Einfluß organischer Stoffe auf die Aufnahme anorganischer Ionen.- *Agrochimica* 6, 251-264 (1962).
- FLAIG, W., F. SCHEFFER and B. KLAMROTH: Zur Kenntnis der Huminsäuren. VIII. Zur Charakterisierung der Huminsäuren des Bodens. *Z. Pflanzenernähr., Düng., Bodenkunde* 71, 33-37 (1955).
- FREUDENBERG, K.: Forschung am Lignin, *Fortschr. Chem. org. Naturstoffe* 20, 41 (1962).
- FREUDENBERG, K.: Entwurf eines Konstitutionsschemas für das Lignin der Fichte, *Holzforsch.* 18, 3-9 (1964 a).
- FREUDENBERG, K.: Ergänzung des Konstitutionsschemas für das Lignin der Fichte, *Holzforschung* 18, 166 (1964 b).
- FREUDENBERG, K. and J.M. HARKIN: Ergänzung des Konstitutionsschemas für das Lignin der Fichte. -*Holzforsch.* 18, 166-168 (1964).
- FREUDENBERG, K. and A.C. NELSH: Constitution and biosynthesis of lignin. Springer-Verlag Berlin-Heidelberg, New York 1968.
- FRÖMEL, W.: Über Absorptionsspektren von Huminsäuren in Lösungen. *Bodenkunde und Pflanzenernähr.* 6, 93-119 (1938 a).
- FRÖMEL, W.: Über UV-Absorptionsspektren von Huminsäuren in Lösungen. *Bodenkunde und Pflanzenernähr.* 11, 129-144 (1938 b).
- FRÖMEL, W.: Über Fulvosäuren. *Bodenkunde und Pflanzenernähr.* 25, 345-358 (1941).
- FÜHR, F.: Untersuchungen zur Aufnahme von Kohlendioxid und Strohabbauprodukten durch die Pflanzenwurzel. Dissertation Bonn 1962.
- FÜHR, F. and D. SAUERBECK: Über die Aufnahme und Translokation ¹⁴C-markierter organischer Rotteprodukte bei *Raphanus sativus*. *Z. Pflanzenernähr., Düng., Bodenkunde* 105, 136 (1964).
- FÜHR, F. and D. SAUERBECK: Die räumliche und chemische Verteilung durch die Wurzel aufgenommener organischer Rotteprodukte bei *Daucus carota*. - *Z. Landw. Forsch.* 19, Sonderheft 153-163 (1965).
- FÜHR, F. and D. SAUERBECK: The uptake of straw decomposition products by plant roots. In: "The use of isotopes in soil organic matter studies". Report of the FAO/IAEA Technical Meeting. Oxford Pergamon Press Ltd., 73-83 (1966).
- FÜHR, F. and D. SAUERBECK: The uptake of colloidal organic substances by plant roots as shown by experiments with ¹⁴C-labelled humus compounds. *Isotopes in plant nutrition and physiology*. International Atomic Energy Agency, Vienna 1967, 317-328.

- GALE, E.F.: The bacterial amino acid decarboxylases. *Advan. Enzymol* 6, 1-32 (1946).
- GRABBE, K. und K. HAIDER: Die Huminstoffbildung und die Stickstoffverteilung bei der Strohhrotte in Beziehung zur mikrobiellen Phenolbildung. *Z. Pflanzenern., Bodenkunde* 129, 202-216 (1971).
- GRABBE, K. and K. HAIDER: *Z. Pflanzenernähr., Bodenkunde* (1971) in press.
- GREAVES, M.P. and M.J. WILSON: The adsorption of nucleic acids by montmorillonite. *Soil Bio. Biochem.* 1, 317-323 (1969).
- GREENLAND, D.J.: The adsorption of sugar by montmorillonite II. Chemical studies. *J. Soil-Sci.* 2, 329-334 (1956).
- GROSS, S.R., R.D. GAFFORD and E.L. TATUM: The metabolism of protocatechuic acid by *Neurospora*. *J. Bio. Chem.* 210, 781-796 (1956).
- GUMINSKA, Z. and J. SULEJ: The effect of sodium humate and sodium versenate upon sprouting of seed. *Biuletyn Instytutu Howowli i Aklimatyzacji. Roslin* Nr. 3 29 (1964).
- HAIDER, K.: Untersuchungen über den mikrobiellen Abbau von Lignin. *Zbl. Bakteriol. Parasitenkunde Infektionskrankh. und Hygiene*, 198, 308-316 (1965).
- HAIDER, K. and J.P. MARTIN: Synthesis and transformation of phenolic compounds by *Epicoccum nigrum* in relation to humic acid formation. *Proc. Soil Sci. Soc. Am.* 31(6), 766-772 (1967).
- HAIDER, K., J.P. MARTIN: The role microorganisms in the formation of humic acids. - In: *Isotopes and radiation in soil organic matter studies. Proceedings of the Symposium on the use of isotopes and radiation in soil organic matter studies.* Intern. Atomic Energy Agency, Vienna 1968, 188-195.
- HAIDER, K., Z. FILIPS, and J.P. MARTIN: Einfluss von Montmorillonit auf die Bildung von Biomasse und Stoffwechselzwischenprodukten durch einige Mikroorganismen. *Arch. Mikrob.* 73, 201-215 (1970).
- HAIDER, K. and J.P. MARTIN: Humic acid-type phenolic polymers from *Aspergillus sydowi* culture medium. *Stachybotrys* spp. cells and autoxidized phenol mixtures. - *Soil Biol. Biochem.* 2, 145-156 (1970).
- HAIDER, K., L.R. FREDERICK and W. FLAIG: Reactions between amino acid compounds and phenols during oxidation. - *Plant and Soil* XXII, 49-64 (1965).
- HAIDER, K., S. LIM and W. FLAIG: Untersuchungen über die Einwirkung von Mikroorganismen auf ¹⁴C-markierte phenolische Verbindungen, *Landw. Forschung* 15, 3/4, 1-9 (1962).

- HAIDER, K., S. LIM and W. FLAIG: Experimente und Theorien über den Ligninabbau bei der Weißfäule des Holzes und bei der Verrottung pflanzlicher Substanz im Boden. *Holzforsch.* 18, 81-88 (1964).
- HAMILTON, G.L.: Mechanismen of two- and four-electron oxidations catalysed by some metalloenzymes in "Adv. in Enzymology", 32, 55-96 (1969) Intersciences Publishers, New York, London, Sydney, Toronto (1969).
- HANF, M.: Pflanzenschutzentwicklung i. J. 1946-1971. BASF-Mitteilg. f. d. Landbau, Pflanzenschutz März 1972.
- HANSEN, E.H. and M. SCHNITZER: The alkaline permanganate oxidation of Danish illuvial organic matter. *Proc. Soil Sci. Soc. Am.* 30, 745-748 (1966).
- HANSEN, E.H. and M. SCHNITZER: Zn-dust distillation and fusion of a soil humic and fulvic acid. *Soil Sci. Soc. Amer. Proc.* 33, 29-36 (1969).
- HARMS, H.: Untersuchungen zur Aufnahme von phenolischen Ligninspaltstücken durch die Wurzeln von Weizenkeimpflanzen. Dissert. Justus-Liebig-Universität Giessen (1967).
- HARMS, H. und I. PRIESS: Positionsspezifische O-Demethylierung von Benzoesäuren in Weizenkeimpflanzen. *Planta* 109, 307-315 (1973)
- HARMS, H., H. SÖCHTIG and K. HAIDER: Untersuchungen zur Aufnahme und Umwandlung C^{14} -markierter Phenole durch die Pflanze. I. Aufnahme von C^{14} -carboxylmarkierter p-Hydroxy-benzoe-, Vanillin- und Syringasäure durch die Wurzeln von Weizenkeimpflanzen und Verteilung der Aktivität über die Pflanze. *Plant and Soil* XXXI, No. 1 129-142 (1969 a).
- HARMS, H., H. SÖCHTIG and K. HAIDER: Untersuchungen zur Aufnahme und Umwandlung C^{14} -markierter Phenole durch die Pflanze. II. Die Umwandlung von p-Hydroxy-benzoesäure, Vanillinsäure, sowie Syringasäure nach der Aufnahme durch die Wurzeln von Weizenkeimpflanzen.- *Plant and Soil* XXXI, No. 2, 257-272 (1969 b).
- HARMS, H., H. SÖCHTIG and K. HAIDER: Aufnahme und Umwandlung von unterschiedlichen Stellungen C^{14} -markierter Phenolcarbonsäuren in Weizenkeimpflanzen.- *Z. Pflanzenphysiologie* 64, Heft 5, S. 437-445 (1971).
- HARMS, H., K. HAIDER, J. BERLIN, P. KISS and W. BARZ: Über O-demethylierung und Decarboxylierung von Benzoesäuren in pflanzlichen Zellsuspensions-kulturen. *Planta* 105, 342-351 (1972).

- HOLLECK, L. and D. BECHER: Untersuchungen über den Einfluß der Leitsalzen auf die polarographische Reduktion aromatischer Nitroverbindungen in Acetonitril und Dimethylformamid. *J. electroanal. Chem.* 4, 321-331 (1962).
- HOLMBERG, B.: Thioglykolsäure als Ligninreagenz. *Ing. Ventenskaps Akad. Handl. No.* 131, 5-15 (1934).
- HOLMBERG, B. : Hypobromite lignin. -- *Ber.* 75, 1760-1764 (1942).
- ISHIWATARI, R. : An estimation of aromaticity of lake sediment humic acid by air oxidation and evaluation of it. *Soil Sci.* 107, 53-57 (1969).
- JACQUIN, F. : Chromatographic study of various types of humic acids. *C. R. hebd. Seances Acad. Sci.* 250, 1892-1893 (1960).
- JACQUIN, F. : Contribution a l'étude des processus de formation et d' evolution des divers composés humiques. Thèse Docteur des Sciences. *Bull. ENSAN V*, 1-156 (1963).
- JANSSON, S.L. and J. PERSON: Co-Ordination of humus chemistry and soil organic matter biology by isotope techniques. In: *Isotopes and radiation in soil organic matter studies*. International Atomic Energy Agency, Vienna 1968, 111-123.
- JENKINSON, D.S.: The turnover of organic matter in soil. In: *The use of isotopes in soil organic matter studies*. Report of the FAO/IAEA Technical Meeting. Pergamon Press. Ltd. Oxford 1966 a, 187-197.
- JENKINSON, D.S.: The priming action. In: *the use of isotopes in soil organic matter studies*. Report of the FAO/IAEA Technical Meeting. Pergamon Press, Ltd., Oxford 1966 b, 199-208.
- JENKINSON, D.S.: Experimental techniques for using carbon-14 in studies of soil organic matter. In: *The use of isotopes in soil organic matter studies*. Report of the FAO/IAEA Technical Meeting. Pergamon Press. Ltd. Oxford 1966 c, 365-369.
- JENKINSON, D.S.: Studies on the decomposition of plant materials in soil I-III. *J. Soil Sci.* 16, 104-115 (1965; 17, 280-302 (1966 b); 19, 25-39 (1968).
- KAILA, A. : Humification of straw at various temperatures. *Acta agral. fenn. Helsinki* 28, 3-32 (1952).
- KANG, K.S. and G.T. FELBACK: A comparison of the alkaline extracts of tissues of *Aspergillus niger* with humic acids from soils. *Soil Sci.* 99, 175-181 (1965).
- KASATOCHKIN, V.I. and O.I. ZILBERBRAND: X-ray and infrared spectroscopy applied to the study of the structure of humic substances. *Pochvovedenie No.* 5, 80-85 (1956).

- KASATOCHKIN, V.I., M.M. KONONOVA and G.I. ZILBERBRAND: Infrarotspektren von Huminsäuren des Bodens. Dokl. Akad. Nauk 119, 785-788 (1958). (russ.)
- KASTORI, R., H. HANAS, H. SÖCHTIG and K. HAIDER: Untersuchungen zur Aufnahme und Umwandlung C^{14} -markierter Phenole durch die Pflanze. III. Die Aufnahme, der Transport und die Umwandlung von C^{14} -markiertem Thymohydrochinon durch Weizenkeimpflanzen. *Plant and Soil* 33, 597-611 (1970).
- KHAN, S.U. : Distribution and characteristics of organic matter extracted from the black solonchic and black chernozemic soils of Alberta; the humic acid fraction. *Soil Sci.* 112, 401-409 (1971).
- KHAN, S.U. and F.J. SOWDEN: Distribution of nitrogen in the black solonchic and black chernozemic soils of Alberta. *J. Soil Sci.* 51, 185-193 (1971).
- KHAN, S.U. and F.J. SOWDEN: Distribution of nitrogen in fulvic acid fraction extracted from the black solonchic and black chernozemic soils of Alberta. *Can. J. Soil Sci.* 52, 116-118 (1972).
- KLEIST, H. and D. MUCKE: Stabile freie Radikale in Huminsäuren. *Experientia* 22, 136-137 (1966).
- KLEIST, H. : 4. Torf-Kolloquium DDR-VR Polen 1/4 Rostock (1967).
- KOLENBRANDER, G.J.: Die Verluste an organischer Substanz im Stalldünger. *Z. Pflanzenernähr., Düng., Bodenkunde* 69, 125-134 (1955).
- KONONOVA, M.M.: Humus der Hauptbodentypen der UdSSR, seine Natur und Bildungsweisen. *Rapports VI. Congr. Internat. de la Science du Sol, Chemie du Sol*, S. 5, Moskau (1956) (russ.)
- KONONOVA, M.M.: Soil organic matter. Its nature, its role in soil formation and in soil fertility. Pergamon Press Oxford, London, New York, Paris (1961).
- KONONOVA, M.M.: Gedanken zur Nomenklatur der im Boden vorhandenen organischen Stoffe. 8th Internat. Congr. of Soil Sci. Transaction, Vol. III, Bucharest-Romania, 401-404 (1964). Discussions regarding the terminology in the field of humus, 405-413.
- KONONOVA, M.M.: Soil organic matter, its nature, its role in soil formation and in soil fertility. Pergamon Press, Oxford, London, Edinburgh, New York, Toronto, Sydney, Paris, Braunschweig, (1966).
- KRATZL, K. and P. CLAUS: Zur quantitativen Bestimmung der monomeren Athenolysenprodukte aus dem Lignin monocotylar und dicotylar Angiospermen, *Monatsh. Chem.* 93, 219-229 (1962).

- KRATZL, K., and E. RISNYOVSKY: Zum Mechanismus der alkalischen Hydrolyse der Ligninsulfosäure. *Chimie et Biochimie de la Lignine de la Cellulose et des Hemicelluloses. Actes du Symposium International de Grenoble, Juillet (1964).*
- KRATZL, K., G. BILLIK, E. KLEIN, K. EUTSCHER: Über das Verhalten von markiertem Coniferin in der verholzenden Pflanze. *Monatsh. f. Chemie* 88, 721-734 (1957).
- KRATZL, K., E. RISNYOVSKY, P. CLAUS and E. WITTMANN: Über den Mechanismus der alkalischen Hydrolyse von Guajacylglycerin- β -guajacylather- α -sulfosäure. I. Mitteilung, Modellversuche zur Fragmentierung der Ligninsulfosäure in alkalischem Medium. *Holzforschung* 20, 21-27 (1966).
- KRATZL, K., W. SCHAFER, P. CLAUS J. GRATZL and P. SCHILLING, Zur Oxydation von ^{14}C -markierten Phenolen (Ligninmodellen) *Mh. Chemie* 98, 891-904 (1967).
- KUBISTA, K.: The influence of bentonite and of aeration on the dynamics of the development of microorganisms during the decomposition of lucerne in a sand culture. *Rostlinna Vyroba (Prague)* 15, 221-228 (1969).
- KUMADA, K.: Studies on the colour of humic acids. Part. I. On the concepts of humic substances and humification. *Soil Sci. and Plant Nutr.* 11, 11-16, (1965).
- KUMADA, K. and A. AIZAWA: The infrared spectra of humic acids. *Soil and Plant Food* 3, 1 2-159 (1958).
- KUMADA, K. and K. AIZAWA: The infra-red absorption spectra of soil components. *Soil and Plant Food* 4, 101-188 (1959).
- KÜSTER, E.: Umwandlung von Mikroorganismen-Farbstoffen in Huminstoffe. *Z. Pflanzenernähr., Düng., Bodenkunde* 57, 51-57 (1952).
- KÜSTER, E.: Humusbildung und Phenoloxidasen bei Streptomyceten. *Z. Pflanzenernähr., Düng., Bodenk.* 69, 137-142 (1955).
- KÜSTER, E.: Beiträge zur Physiologie der Streptomyceten. VI. *Congres International de la Sci. du Sol. Paris* 3, 67-72 (1956).
- KYUMA, K.: A fractional precipitation technique applied to soil humic substances. *Soil Sci. Plant Nutr.* 10, 33-35 (1964).
- LANTZ, R. and H. MICHEL. Action de l'ammoniaque en des amines primaires sur le benzene substitué en 1,3 et par des groupes amino ou hydroxyles, non substitués ou substitués. *Bull. Soc. Chim. France* 12, 2402-2408 (1961).
- LAATSCH, W., L. HOOPS and O. BIENECK: Über Huminsäuren des Pilzes *Spicaria elegans*. *Z. Pflanzenernähr., Düng., Bodenkunde* 58, 258-268 (1952).

- LEVESQUE, M. and M. SCHNITZER: Organo-metallic interactions in soils: 6. Preparation and properties of fulvic acid-metal phosphates. *Soil Sci.* 103, 183-190 (1967 b).
- LIM, S.: Beiträge zur Aufklärung der Zusammenhänge zwischen dem mikrobiellen Abbau des Lignins und der Bildung von Humusstoffen. Dissertation der Rheinischen Friedrich Wilhelms-Universität Bonn (1965).
- LYINCH, D.L., L.M. WRIGHT and L.J. COTNOIR: The adsorption of carbohydrates and related compounds on clay minerals. *Proc. Soil Sci. Soc. Amer.* 20, 6-9 (1956).
- LYNCH, D.L., L.M. WRIGHT and L.J. COTNOIR: Some factors affecting the adsorption of cellulose compounds, pectins and hemicellulose compounds, on clay minerals. *Soil Sci.* 84, 113-126 (1957).
- MAEDER, H. : Chemische und pflanzenphysiologische Untersuchungen mit Rottestroh. Diss. Justus Liebig Universität Giessen (1960).
- MARSHALL, K.C.: Methods of study and ecological significance of Rhizobium-clay interactions. In methods of study in Soil Ecology. (J. Phillipson, Ed) Proceedings of UNESCO and IBP, Paris 1970. pp. 107-110. UNESCO, Paris (1967).
- MARTIN, A.E. and R. REEVE: The extraction of organic matter from podzolic B-horizons with organic reagents. *Chem. and Ind.* 1955, 356.
- MARTIN, A.E. and R. REEVE: Chemical studies on podzolic illuvial horizons. I. The extraction of organic matter by organic chelating agents. *J. Soil Sci.* 8, 268-270 (1957 a).
- MARTIN, A.E. and R. REEVE: Chemical studies on podzolic illuvial horizons. II. The use of acetylacetone as extractant of translocated organic matter. *J. Soil Sci.* 8, 279-286 (1957 b).
- MARTIN, A.E., P. DUBACH, N.C. MEHTA and H. DEJEL: Bestimmung der funktionellen Gruppen von Huminstoffen.-Z. Pflanzenernähr., Düng., Bodenkunde 103, 29-39 (1963).
- MARTIN, J.P. and K. HAIDER: Phenolic polymers of *Stachybotrys atra*, *Stachybotrys chartarum* und *Epicoccum nigrum* in relation to humic acid-formation. *Soil Sci.* 107, 260-270 (1969).
- MARTIN, J.P. and K. HAIDER: Microbial activity in relation to soil humus formation. *Soil Science* 111, No. 1, 54-63 (1971).
- MARTIN, J.P., S.J. RICHARDS and K. HAIDER: Properties and decomposition and binding action in soil of humic acid synthesized by *Epicoccum nigrum*. *Soil Sci. Soc. Amer. Proc.* 31, 657-662 (1967).

- MASON, H.S: Chemistry of melanin. III. Mechanism of oxidation of 3¹⁴-dihydroxyphenylalanine by tyrosinase. *J. Bio. Chem.* 172, 83-99 (1948).
- MAYAUDON, J. and P. SIMONART: Etude de la decomposition de la matière organique dans le sol au moyen de carbone radioactif. II. Decomposition du glucose radioactif dans le sol. A. Répartition de la radioactivité dans fractions humiques du sol. *Plant and Soil* IX, 376-380 (1958).
- MAYAUDON, J. and P. SIMONART: Etude de la decomposition de la matière organique dans le sol au moyen de carbone radioactif. III. Decomposition des substances solubles dialysables des protéines et des hemicelluloses. *Plant and Soil* XI, 170(1959 a).
- MAYAUDON, J. and P. SIMONART: Etude de la décomposition de la matière organique dans le sol au moyen de carbone radioactif. V. Decomposition de cellulose et de lignine, *Plant and Soil* XI, 181-192 (1959 b).
- MAYAUDON, J. and P. SIMONART: Stabilité de l'humus du sol étudiée à l'aide d'humus marqué au ¹⁴C-*Arch. Internat. de Phys. et de Biochim.* 68, 512 (1960).
- MAYAUDON, J. and P. SIMONART: Decomposition of cellulose C¹⁴ and lignin C¹⁴ in the soil. *Ecology of Soil Fungi* (1961).
- MAZUMDAR, B.K., S.K. CHAKRABARTTY and A. LAHIRI: Aromaticity and oxidation of coal. *Sci. Ind. Res. (India)* 16, B. 275 (1957).
- McCALLA, T.M.: The adsorbed ions of colloidal clay as a factor in nitrogen fixation by *Azotobacter*. *Soil Sci.* 48, 281-286(1939).
- McCALLA, T.M.: Physico-chemical behavior of soil bacteria in relation to the soil colloid. *J. Bact.* 40, 33-43 (1940).
- McLAREN, A.D. and G.H. PETERSON: Introduction to the biochemistry of terrestrial soils. In *Soil Biochemistry* (A.D. McLaren and G.H. Peterson, Eds.) pp. 1-15, MarcelDekker, New York(1967).
- MEYER, B.: Exkursionsführer zur Jahrestagung 1969 in Hannover. *Mitt. Deutsche Bodenkundl. Ges.* 9, 104 u. 105 (1969).
- MIGITA, N. and M. KAWAMURA: Studies on lignin. I. A comparison between the insoluble and soluble portions of lignin sulfate isolated from various trees.- *J. Agr. Chem. Soc. Japan* 20, 348-352 (1944 a).
- MITCHELL, L.P.: Chemiosmotic coupling in oxidative and photosynthetic phosphorylation. *Bio. Rev. Cambridge philos. Soc.* 41, 445-502 (1966).
- MITSCHERLICH, E.A: An der Grenze der Ertragssteigerung. *Z. Pflanzenernähr., Düng., Bodenkunde* 40, 193-200 (1948).

- MOHTADI, S.: Beitrag zur Isolierung von pflanzenphysiologisch wirksamen Stoffen während der Rotte von Stroh. Dissertation Giessen (1962).
- MORRISON, R.I.: Products of the alkaline nitrobenzene oxidation of soil organic matter. *J. Soil Sci.* 14, 201-216 (1963).
- MOSCHO PEDIS, S.E.: *Fuel*, 31, 425 (1962).
- MUSSO, H.: Über Phenol-Oxydationen. - *Angew. Chem.* 75, 965-977(1963).
- MUSSO, H., U.V. GIZYCKI, H. KRAMER and H. DOPP: Über Orceinfarbstoffe. XXIV. Über den Autoxydationsmechanismus bei Resorcinderivaten. *Chem. Ber.* 98, 3952-3963 (1965).
- NAUMOVA, A.N. and E.P. GROMYKO: The influence of gumbrin on the micro-organism of gray-soil. *Mikrobiologiya.* 22, 1 (1953).
- NEHRING, K. and R. SCHIEMANN: Untersuchungen zum Humusproblem. I. Mitt. Beiträge zur Kenntnis der Vorgänge bei der Rotte von Stallmist und Komposten sowie zur Kenntnis der Huminsäuren. *Z. Pflanzenernähr., Düng., Bodenkunde* 57, 97-113 (1952 a).
- NEHRING, K. and R. SCHIEMANN: Untersuchungen zum Humusproblem. I. Mitt. Beiträge zur Kenntnis der Vorgänge bei der Rotte von Stallmist und Komposten sowie zur Kenntnis der Huminsäuren. 2. Teil Beiträge zur Kenntnis der Huminsäuren. *Z. Pflanzenernähr., Düng., Bodenkunde* 57, 193-215 (1952 b).
- NICOLAUS, R.A.: Biogenese der Melanine. *Conf. VII Corso chim. Acad. naz. Lincei, Milano* (1962).
- NOVAK, B.: Contribution to the Theory of microbial formation of humus. *For. Social Agri. Sci. (Prague)* 12, 401-418 (1963).
- NOVAKOVA J.: The effect of different amounts of bentonite and kaolinite on the decomposition of glucose. In *Studies about Humus. Trans. Intern. Symp. "Humus et planta IV"*, Prague:185-188 (1967).
- NOVAKOVA J.: The influence of different quantities of bentonite and kaolinite on glucose mineralization. *Rostlinna Vyroba(Prague)* 15, 215-220 (1969).
- OBERLANDER, H.E. and K. ROTH: Transformation of ^{14}C -labelled plant material in soils under field conditions. In: *Isotopes and radiation in soil organic matter studies. International Atomic Energy Agency, Wien 1968*, 251-264.
- ORLOV, D.S. and N.M. GRINDEL: Spectrophotometric determination of the humus content in soil. *Pochvovedenie Nr. 1*, 112-122(1967) (russ.)

- ORLOV, D.S., O.H. ROZANOVA and S.G. MATYUKHINA: Infrared absorption spectra of humic acids. Pochvovedenie Nr. 1, 17-25 (1962) (russ.)
- OTTEY, L., E.L. TATUM: Protocatechuic acid oxidase of Neurospora. J. Biol. Chem. 223, 307-311 (1956).
- PEOVER, M.E. and J.D. DAVIES: Einfluß der Ionenassoziation auf die Polarographie der Chinone in Dimethylformamid.-J. electroanalyt. Chem. 6, 46-53 (1963).
- PHILLIPS, M: The chemistry of lignin. Chem. Rev. 14, 103-170 (1934).
- PLOETZ, Th.: Beiträge zur Ligninbestimmung mit starker Schwefelsäure. Cellulosechemie 18, 49-57 (1940).
- PLOETZ, Th.: Polymere Chinone als Huminsäuremodelle.-Z. Pflanzenernähr., Düng., Bodenkunde 69, 50-58 (1955).
- PLOTHO, O.v.: Die Humusbildung der Mikroorganismen. Z. Pflanzenernähr., Düng., Bodenkunde 51, 212 (1950).
- PLOTHO, O.v.: Weitere Untersuchungen zur Humusbildung der Mikroorganismen. Z. Pflanzenernähr., Düng., Bodenkunde 55, 151-169 (1951).
- POSNER, A.M.: The humic acid extracted by various reagents from a soil. Part. I. Yield, inorganic components, and titration curves. J. Soil Sci. 17, 65-78 (1966).
- POSNER, A.M., B.K.G. THENG and J.R.H. WAKE: The extraction of soil organic matter in relation to humification. 9th Internat. Congr. Soil Sci., Adelaide, Australia, Transaction III, 153-162 (1968).
- RAPER, H.S.: Die Einwirkung von Tyrosinase auf Tyrosin. Fermentforschung 9, 206 (1927).
- RAPER, H.S.: The aerobic oxidases. - Physiol. Rev. 8, S.245-248 (1928).
- REINHARDT, G.: Untersuchungen über die Einwirkung von Lignin und dessen Abbauprodukten auf das Wachstum und den Stoffwechsel von Pflanzen. Dissertation Universität Giessen 1961.
- RIEMER, H.: Polarographische Untersuchungen über Beziehungen zwischen Struktur und Reaktivität bei Benzochinonen. Dissertation TU Braunschweig 1970.
- RIFFALDI, R. and M. SCHNITZER: Electron spin resonance spectrometry of humic substances. Proc. Soil Sci. Soc. Am. 36, 301-305 (1972).

- RITTER, G.J., R.M. SEBORG and R.L. MITCHELL: Factors affecting quantitative determination of lignin by 72 percent sulfuric acid method. *Ind. Eng. Chem. Analyt. Edit.* 4, 202 (1932).
- RUHEMANN, H.: Untersuchungen zur Auftrennung physiologisch aktiver Stoffe aus Lignin unter Anwendung von Radiokohlenstoff. Dissertation Th Braunschweig 1964.
- RUIZAMIL, M. and W. FLAIG: The effect of Thymohydroquinone on the organic-acid metabolism and the respiration of plants. *An. Edafol. Agrobiol.* 19, 1-9 (1964).
- RUIZAMIL, M. and W. FLAIG: Influence de la timohidroquinona sobre el metabolismo de carbohidratos en algunas dicotiledoneas. *Annles de Edafologia y Agrobiologia XIX*, 1, 11-22 (1960 b).
- SAALBACH, E.: Zur Kenntnis der Huminsäuren, XIV. Mitt. Einfluß von Modell-substanzen von Humusstoffen auf den Stoffwechsel von Getreide, *Landw. Forsch.* 9. Sonderheft 95-100 (1957).
- SAGAVE, B.: Grundzüge der Abschätzungslehre. P. Parey, Berlin 125-131 (1934).
- SALFELD, J. Chr.: Zum Reaktionsmechanismus der Purpurogallinbildung. *Angew. Chem* 69, 723-724 (1957).
- SALFELD, J. Chr.: Fraktionierung eines Huminstoffpräparates mit wasserhaltigen Lösungsmitteln. *Landbauforsch. Völknerode* 14, 131-136 (1964).
- SALFELD, J. Chr.: Die Charakterisierung von Huminstoffen durch Differenzen-Spektrogramme. *Mitt. Dtsch. Bodenkundl. Ges.* 4, 289-290 (1965).
- SALFELD, J. Chr.: Untersuchungen zur Klassifizierung der organischen Bodensubstanz. *Mitt. Dtsch. Bodenkundl. Ges.* 8, 133-135 (1968)
- SALFELD, J. Chr.: Optical measurements on humic systems. *Symposium Humus at Planta V, Prag* (1971), 257-266.
- SALFELD, J. Chr. and E. BAUME: Über die Oxydation von Pyrogallol und Pyrogallolderivaten. IV. Die Konstitution der Purpurogallin-carbonsäure -(9). *Chem. Ber.* 97, 307-311 (1964)
- SALFELD, J. Chr. and H. SÖCHTIG: Ergänzung zum Exkursionsführer der Jahrestagung der Dtsch. Bodenkundl. Ges. in Hannover (1969).
- SAUERBECK, D.: Stability of recently formed humus compounds in soil. In: *Isotopes and radiation in soil organic matter studies. International Atomic Energy Agency, Vienna 1968 b*, 57-66.
- SAUERBECK, D.: Die Umsetzung markierter organischer Substanzen im Boden in Abhängigkeit von Art, Menge und Rottegrad. *Landwirtsch. Forsch.* 21, 91-102 (1968 a).

- SAUERBECK, D.: Comparison of plant material and animal manure in relation to their decomposition in soil. In: Isotopes and radiation in soil organic matter studies. International Atomic Energy Agency, Vienna 1968 c, 219-225.
- SAUERBECK, D. and F. FÜHR: Alkali extraction and fractionation of labelled plant material before and after decomposition - a contribution to the technical problems in humification studies. In: Isotopes and radiation in soil organic matter studies. International Atomic Energy Agency, Vienna 1968, 3-11.
- SAUERBECK, D. and F. FÜHR: Die Umsetzung von markiertem Pflanzenmaterial im Boden unter Feldbedingungen. Mitt. Deutsche Bodenkundl. Gesellsch. 10, 174-177 (1970).
- SCHARPENSEEL, H.W.: Herstellung und Reinigung von tritiummarkierten Graublau Braun/Huminsäurepräparaten sowie von Tritium-Purpurgallin. -Z. Pflanzenernähr., Düng. und Bodenkunde 91, 131-146 (1960 a).
- SCHARPENSEEL, H.W.: Untersuchungen mit radioaktiv markierten Huminsäuren und Vorstufen. 2. Teil.-Z. Pflanzenernähr., Düng. und Bodenkunde 91, 193-202 (1960 b).
- SCHARPENSEEL, H.W.: Labelling of soil organic matter. In: The use of isotopes in soil organic matter studies. Report of the FAO/IAEA Technical Meeting, Pergamon Press. Ltd. Oxford 1966a, 351-364.
- SCHARPENSEEL, H.W.: Aufbau und Bindungsform der Ton-Huminsäurekomplexe. Teil IV. Z. Pflanzenernähr. Düng. V. Bodenk. 55, 151-169 (1970).
- SCHARPENSEEL, H.W. and W. ALBERSMEYER: Infrarotspektroskopische Untersuchungen an Huminsäuren, Huminsäureaufschlüssen und phenolisch-chinoiden Vergleichssubstanzen. Z. Pflanzenernähr. Düng., Bodenkunde 88, 3, 203-211 (1960).
- SCHARPENSEEL, H.W. and H. BECKMANN: Untersuchung zur Kohlendioxid-Entbindung des Bodens. II. Teil. Spezielle Studien unter Verwendung radioactiver Tracer.-Z. Pflanzenernähr., Düng. Bodenkunde 104, 110-119 (1964).
- SCHARPENSEEL, H.W. and R. KRAUSSE: Aminosäureuntersuchungen an verschiedenen organischen Sedimenten, besonders Grau- und Braunhuminsäurefraktionen verschiedener Bodentypen (einschließlich C^{14} -markierter Huminsäuren). Z. Pflanzenernähr., Düng. Bodenkunde 26, 11-34 (1962).

- SCHARPENSEEEL, H.W., E. KÖNIG and E. MENTHE: Infrarot- und Differentialthermo-Analyse an Huminsäureproben aus verschiedenen Bodentypen, aus Wurmkot und Streptomyces, Z. Pflanzenernähr., Düng., Bodenkunde 106, 134-150 (1964).
- SCHIEFFER, F. and B. ULRICH: Lehrbuch der Agrikulturchemie und Bodenkunde. III. Teil. Humus und Humusdüngung 1, Enke Stuttgart, pp. 266 (1960).
- SCHIEFFER, F., O.v. PLOTHO and E. WELTE: Untersuchungen über die Bildung von Humusstoffen durch Actinomyceten. - Landwirtschaftl. Forsch. 1, 81-92 (1950).
- SCHMID, G. and W. FLAIG: Pflanzenstoffwechsel und Wirkstoffe. Landbauforsch. 12, 51-56 (1962).
- SCHNITZER, M.: The application of infrared spectroscopy to investigations on soil humic compounds. Canad. Spectroscopy 10, No. 5, 121-127 (1965).
- SCHNITZER, M. and J.G. DESJARDINS: Molecular and equivalent weights of the organic matter of a podzol. Soil Sci. Soc. Amer., Proc. 26, 362-365 (1962).
- SCHNITZER, M. and J.G. DESJARDINS: Carboxyl and phenolic hydroxyl groups in some organic soils and their relation to the degree of humification. Can. J. Soil Sci. 45, 257-264 (1965).
- SCHNITZER, M. and I. HOFFMAN: Thermogravimetry of soil humic compounds. Geochim. Cosmochim. Acta 29, 359-370 (1965).
- SCHNITZER, M. and SU. KHAN: "Humic substances in the Environment". Marcel Dekker Inc. New York. (1972).
- SCHNITZER, M. and S.I.M. SKINNER: Organo-metallic interactions in soils: 3. Properties of iron- and aluminium-organic matter complexes, prepared in the laboratory and extracted from a soil. Soil Sci. 98, 197-203 (1964).
- SCHNITZER, M. and S.I.M. SKINNER: Organo-metallic interactions in soils: 4. Carboxyl and hydroxyl groups in organic matter and metal retention. Soil Sci. 99, 278-284 (1965 a).
- SCHNITZER, M. and S.I.M. SKINNER: The carboxyl group in a soil organic matter preparation. Soil Sci. Soc. Amer., Proc. 29, 406-405 (1965 b).
- SCHNITZER, M., D.A. SHEARER and J.R. WRIGHT: A study in the infrared of high molecular weight organic matter extracted by various reagents from a podzolic horizon. Soil Sci. 87, 252-257 (1959).

- SCHNITZER, M. and U.C. GUPTA: Some chemical characteristics of the organic matter extracted from the C and B2 horizons of a gray wooded soil. Proc. Soil Sci. Soc. Am. 28, 374-377 (1964).
- SCHNITZER, M. J.R. WRIGHT and J.G. DESJARDINS: A comparison of the effectiveness of various extractants for organic matter from two horizons of a podzol profile. Can. J. Soil Sci. 38, 49-53 (1958).
- SCHOBINGER, U. : Chemische Untersuchungen über die Umwandlung von Weizenstrohlignin im Laufe der Verrottung.- Dissertation, ETH Zurich (1958).
- SCHREINER, O. and E. SHOREY: Chemical nature of soil organic matter. U.S. Dept. Agric. Bureau of Soils Bull. 74, 5-48 (1910).
- SIMONART, P. and J. MAYAUDON: Etude de la décomposition de la matière organique dans le sol au moyen de carbone radioactif. I. Cinétique de l'oxydation en CO₂ de divers substrats radioactifs. Plant and Soil 9, 367-375 (1958 a).
- SIMONART, P. and J. MAYAUDON: Etude de la décomposition de la matière organique dans le sol au moyen de carbone radioactif. II. Décomposition du glucose radioactif dans le sol. B. Répartition de la radioactivité dans l' a-humus. - Plant and Soil 9, 381-384 (1958 b).
- SIMONART, P. and J. MAYAUDON: Etude des transformations de la matière organique du sol au moyen du carbone-14. In: The use of isotopes in soil organic matter studies. Report of the FAO/IAEA Technical Meeting. Pergamon Press. Ltd. Oxford 1966, 245-258.
- SIMONART, P., J. MAYAUDON and L. BATISTIC: Etude de la décomposition de la matière organique dans le sol au moyen de carbone radioactif. IV. Décomposition des pigments foliaires. Plant and Soil 11, 176-180 (1959).
- SKUJINS, J.J.: Enzymes in soil. In soil Biochemistry (A.D. Melaren and G.H. Peterson, Eds.) pp. 371-414, Marcel Dekker, New York. (1967).
- SLYKE, D.D. van, D.A. MacFAYDEN and P. HAMILTON: Determination of free amino acids by titration of the carbon dioxide formed in the reaction with ninhydrin. J. Biol. Chem. 141, 671-680 (1941).
- SMITH, J.H.: Some inter-relationships between decomposition of various plant residues and loss of soil organic matter as measured with carbon-14 labelling. In: The use of isotopes in soil organic matter studies. Report of the FAO/IAEA Technical Meeting. Pergamon Press. Ltd. Oxford 1966, 223-233.

- SMITH, F.B., W.H. STEVENSON and P.E. BROWN: The production of artificial manures. Agr. Exp. Sta. Res. Bul. 126, (1930).
- SNEATH, P.H.A.: The application of computers to taxonomy. J. Gen. Microbiol. 17, 201-226 (1957).
- SÖCHTIG, H.: Beeinflussung des Stoffwechsels der Pflanzen durch Humus und seine Bestandteile und die Auswirkung auf Wachstum und Ertrag. - Landbauforschung Völkenrode 14, 9-16 (1964)
- SÖCHTIG, H.: Ein Pflanzentest zur Feststellung der Wirkung stoffwechselaktiver Substanzen, Methodik und Erfahrungen. Deutsch-Polnisches Torf-Kolloquium DDR-Polen in Rostock 1967.
- SÖCHTIG, H.: Über den einfluß von N-Lignin auf die Nitrifizierung im Boden sowie den Ertrag und den Nitratgehalt der Pflanzen - Qual. Plant. Mater. Veg. XX, 1-2, 137-150 (1970).
- SÖCHTIG, H.: (1972) In press.
- SÖCHTIG, H. and H. HARMS: Über den Einfluß von Torf auf Keimung und Anfangs-wachstum von Pflanzen.- Landw. Forsch. 26/II (1971)
- SÖCHTIG, H. and F. MACIAK: Bindung des Stickstoffs und Vorkommen phenol-ischer Verbindungen im Torf. Telma, Band 1, 49-61 (1971).
- SÖCHTIG, H. and J. Chr. SALFELD: Characterization of humic systems in a black earth-Griserde-morphosequence in the area of Hildesheim. Symposium Humus et Planta V, Prag 1971, 247-256.
- SØRENSEN, H.: Studies on the decomposition of ¹⁴C-labelled barley straw in soil. Soil Sci. 95, 45-51 (1963).
- SØRENSEN, H.: Formation of soil organic matter during decomposition of plant components. In: The use of isotopes in soil organic matter studies. Report of the FAO/IAEA Technical Meeting. Pergamon Press. Ltd. Oxford 1966, 271-274.
- SOWDEN, F.J. and H. DEJEL: Fractionation of fulvic acids from the B-horizon of podzol. Soil Sci. 91, 44-47 (1961).
- SPRINGER, U.: Stoffabbau und Humusaufbau untersucht an einem Strohmis und Strohlignin ist (Laboratoriumsversuch). Prakt. Blätter f. Pflanzenbau u. Pflanzenschutz 21/22, 1-57(1944/45).
- SPRINGER, U.: Über Komposthuminsäuren aus verschiedenen pflanzlichen Ausgangsstoffen.-Z. Pflanzenernähr., Düng., Bodenkunde 69, 66-71 (1955).

- SPRINGER, U., and A. LEHNER: Stoffabbau und Humusaufbau bei der aeroben und anaeroben Zersetzung landwirtschaftlich und forstwirtschaftlich wichtiger organischer Stoffe. I. Z. Pflanzenernähr., Düng., Bodenkunde 58, 193-231 (1952 a).
- SPRINGER, U. and A. LEHNER: Stoffabbau und Humusaufbau bei der aeroben und anaeroben Zersetzung landwirtschaftlich und forstwirtschaftlich wichtiger organischer Stoffe. II. Z. Pflanzenernähr., Düng., Bodenkunde 59, 1-27 (1952 b).
- SPRINGER, U. and F. SELSCHAB: Zur Kenntnis der bei der Kompostbereitung auftretenden stofflichen Veränderungen. Mit Ergebnissen eines dreijährigen Gefäßversuches. Bayr. Landw. Jahrbuch 38, 250-300 (1961).
- STAHLER, R.Y. and J.L. INGRAHAM: Protocatechuic oxidase.- J. Biol. Chem. 210, 799-808 (1954).
- STEELINK, C.: Free radical studies of lignin, lignin degradation products and soil humic acids. Geochim. Cosmochim. Acta 28, 1615-1622 (1964).
- STEELINK, C. and G. TOLLIN: Stable free radicals in soil humic acid. Biochim. Biophys. Acta 59, 25-34 (1962).
- STEELINK, C., J.W. BERRY, A.HO and H.E. NORDBY: Alkaline degradation products of soil humic acid. Sci. Proc. Roy. Dublin Soc. Ser. A 1, 59-67 (1960).
- STEINMETZ, A.: Modellversuche zur Beteiligung von Polyphenoloxidasen bei der Bildung natürlicher Huminsäuren. Dissertation TH Braunschweig (1956).
- STOCKLI, A.: Über den Abbau von Lignin, Cellulose und Hemicellulose durch Pilze. Versuche mit Streumaterialien, Holz und Ligninsulfonsäure. Promotion ETH Zurich (1952).
- STOTZKY, G.: Influence of clay minerals on microorganisms. II. Effect of various clay species, homoionic clays, and other particles on bacteria. Can. J. Microbiol. 12, 831-843 (1966).
- STOTZKY, G.: Clay minerals and microbial ecology. Trans. N.Y. Acad. Sci. Ser II, 30, 11-21 (1967).
- STOTZKY, G. and L.T. REM: Influence of clay minerals on microorganisms. I. Montmorillonite and Kaolinite on bacteria. Can. J. Microbiol. 13, 1535-1550 (1967).
- SUNDMAN, W., K. HARO: On the mechanism by which cyclolignolytic agro-bacteria might cause humification. Finiska Kemists Med. 75, 11-118 (1966).

- SWABY, R.: Soil organic matter. -8th, 9th, 10th C.S.I.R.O. Annual Reports. Government Printers, Sydney. (1956-1958).
- THENG, B.K.G. and A.M. POSNER: Nature of the carbonyl groups in soil humic acids. *Soil Sci.* 101, 199-201 (1967).
- TINSLEY, J. and A. SALAM: Extraction of soil organic matter with aqueous solvents. *Soils and Fertilizers* 24, 81-84 (1961).
- TOKUDOME, S. and I. KANNO: Nature of the humus of some Japanese soils. 9th Internat. Congr. Soil Sci., Adelaide, Australia, Transactions III, 163-173 (1968).
- TRAYNARD, Ph. and A. EYMERY: Delignification par les solutions hydro-tropiques. II. Etude des lignines hydrotropiques. *Holzfor-schung* 10, 6-11 (1956).
- TRIPPETT, S., S. DAGLEY and D.A. STOPHER: Bacterial oxidation of pro-tocatchuic acid. *Biochem. J.* 76, 9p (1960).
- TSCHAPEK, W. and A.J. GARBOSKY. The principles of adsorption of the Azotobacter, Transactions of the Fourth International Con-gress of soil science, Proceedings, Amsterdam 3, 102-104 (1950).
- WAKSMAN, S.A. and J.W. SMITH: Transformation of methoxyl group in lig-nin in the process of decomposition or organic residues by microorganisms. *J. Amer. Chem. Soc.* 56, 1225 (1934).
- WAKSMAN, S.A. and F.G. TENNEY: The composition of natural organic materials and their decomposition in the soil. I. Methods of quantitative analysis of plant materials. *Soil Sci.* 24, 275-283 (1927 a).
- WAKSMAN, S.A. and F.G. TENNEY: The composition of natural organic materials and their decomposition in the soil. II. Influence of age of plant upon the rapidity and nature of its de-composition - rye plants. *Soil Sci.* 24, 317-333 (1927 b).
- WAKSMAN, S.A., F.C. TENNEY and R.A. DIEHM: The chemical and microbiolo-gical principles underlying the transformation of organic matter in the preparation of artificial manures. *J.A.S.A.* 21, 533-545 (1929).
- WHITEHEAD, D.C. and J. TINSLEY: Extraction of soil organic matter with dimethylformamide. *Soil Sci.* 27, 34-42 (1964).
- WIESEMÜLLER, W.: Untersuchung über die Fraktionierung der organischen Bodensubstanz. *Albrecht Thaer Archiv* 9, 419-436 (1965).
- WINTER, A.G.: Untersuchungen über die Aufnahme von Penicillin und Streptomycin durch die Wurzeln von *Lepidum sativum* und ihre Beständigkeit in natürlichen Boden. *Z. Bot.* 40, 153 (1952)

- WINTER, A.G., H. PREUSS and F. SCHÖNBECK: Untersuchungen über die Aufnahme organischer Substanzen durch die Wurzeln höherer Pflanzen. I. Phenolische Verbindungen. *Naturwissensch.* 46, 536-537 (1959).
- WRIGHT, J.R. and M. SCHNITZER: Oxygen containing functional groups in the organic matter of the Ao and Bh-horizon of a podzol. 7th Internat. Congr. Soil Sci. Madison, Wisc. USA 2, 120-121 (1960).
- WRIGHT, J.R. and M. SCHNITZER: An estimate of the aromaticity of the organic matter of a podzol soil. *Nature* 190, 4777, 703-704 (1961).
- ZENK, M.H.: Einbau von p-Hydroxybenzoesäure in die Hydrochinonkomponente des Arbutins in *Bergenia crassifolia*. - *Z. Naturforsch.* 19 b, 856-857 (1964).
- ZIECHMANN, W.: Spectroscopic investigations of lignin, humic substance and peat. *Geochim. Cosmochim. Acta* 88, 1555-1566 (1964).
- ZIECHMANN, W.: Infrared spectra of humic acids. *Brennstoff-Chem.* 39, 353 (1958).
- ZIECHMANN, W.: Die Darstellung von Huminsäuren im heterogenen System mit neutraler Reaktion. *Z. Pflanzenernähr., Düng., Bodenkunde* 84, 155-159 (1959).
- ZIECHMANN, W. and H. SCHOLZ: Spektroskopische Untersuchungen an Huminsäuren. *Naturwissenschaften* 47, 193-196 (1960).
- ZVJAGINCEV, D.G.: Some regularities of adsorption of microorganisms on ion exchange resins. *Mikrobiologiya.* 31, 399 (1962).
- ZVJAGINCEV, D.G. and L.L. VELIKANOV: Effect of adsorbents on the activity of bacteria growing on media containing amino acids. *Mikrobiologiya* 37, 1017-1023 (1968) (russ.).