Lectures on

Soil Organic Matter

by

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Foreword

To my friends and the friends of the subject.

In this manuscript are some unpublished results and therefore only for friends and not to use for publication.

I would enjoy having any comments on this material.

W. Flaig

Acknowledgments

This manuscript came about as a result of the kind invitation of Prof. Dr. W. H. Pierre, Head, Department of Agronomy, to give lectures about soil biochemistry. I am very thankful for this opportunity.

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W. Flaig

SOIL ORGANIC MATTER

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HISTORICAL SURVEY OF HUMUS RESEARCH

The humus problem is very complex. For the studies of this problem the cooperation of the different disciplines of natural science is necessary.

Generally agricultural science is mostly interested in the results. Substances in the soil influence their physical conditions. The composition of the different minerals are important for different factors of the plant growth. The alteration of soil organic matter are chemical reactions. Microorganisms and small animals prepare the raw material, the residues of plants and animals for the humification. The pedologist tries to find out the relation between the influence of the different soil components and the climate upon the formation of soil types. The Plant Physiologist is interested in the influence of certain components on the plant growth. Everybody who works on soil problems must consider the results of the disciplines in his neighborhood. This means that he must be careful with his conclusions. The study of soil organic matter must be and can only be done in teamwork.

The complexity of the humus problem, the lot of literature, the numberless contradictions of the mode of viewing of the different authors make it difficult to give a historical survey of humus research. But a critical inspection of the work of the different authors is necessary to clear up the essential errors and give an idea for the further work. It is not the task to give a complete survey, only the important facts shall be mentioned to be able to follow the main work of the different authors. For this reason the opinions of the authors can be understood easier.

The Beginning of Humus Research

The first handbook of agricultural chemistry was written by Wallerius (1761). He lived in Sweden. He referred to some facts of the formation of humus by the decomposition of plants and described some properties as the ability to absorb water and nutrients. Wallerius considered humus as a plant nutrient.

The ideas of the substances of the humus got more and more concrete, as these could be isolated from natural products. Probably Archard (1780) was the first who evaluated humus substances from peat with alkaline solutions. He precipitated dark-brown substances with acids and determined that in deeper layers of peat more humus substances can be isolated than in the upper layers.

Vauquelin (1797) isolated humus substances from wood of elm, which has been infected with fungus. Thomson (1807) called these substances later "Ulmin" or "ulmic acids." The Latin name for elm is "Ulmus".

The progress of chemistry, physics and plant physiology in the beginning of the 19th century stimulated the investigations. Even in this early time of humus research we can observe that the progress of the different branches of natural science influencesthe directions of work. At different times, results have been explained with methods of microbiology, at other times with colloid chemistry, and so on.

It is interesting to consider that at the beginning of the studies upon the influence of different components in the soil on plant growth, the scientist preferred the organic substances in the soil and not the inorganic. It seems to me that they had studied later on, therefore only the inorganic components because it has been much easier at first. The development of chemical methods, the apparatus for this purpose and the knowledge of the plant metabolism had not been sufficient. Therefore the inorganic nutrition of the plants and the inorganic fertilizing is now much better known than the effect of soil organic matter on plant growth. This tendency in the development of natural science is nearly similar in all directions. At first the crystallized dyestuffs have been elucidated and synthesized and then the high molecular substances; at first the nutrition of the animal organisms with proteins, fats, salts, had been investigated and then the influence of hormones, vitamins and trace elements on the metabolism. Newly recognized facts in science usually develop new branches of production, in our case, factories for inorganic fertilizers.

Now continuing the historical considerations of humus research, it is to mention that the progress in chemistry led to the first analysis of humic substances. Saussure (1804) found that the humified substances had a higher content of carbon and a lower one of hydrogen and oxygen than the plants as raw material. He extracted rotted plant materials and concluded from his experiments with plants that the humic substances are taken up directly by the plants and would be a part of the nutrition of these.

Albrecht Daniel von Thaer (1752-1828) developed the theory "humus for plant nutrition" in detail. He had been a physician and his love for nature led him to agriculture. His first demonstration-fields have been in 1802 in his home town Celle. This is a smaller town with 60,000 inhabitants, 30 km from Braunschweig. He wrote two books "Study for Thinking Farmers and Public Administrators" and "The Principles of Efficient Agriculture". Called to Berlin, the first Germany academy of agriculture was founded according to a plan developed by him. He is named the founder of agricultural science on account of his epoch-making principles of soil management. At that time, he was convinced by his experiments that soil productivity and plant nutrition depend upon the reserves of humus in the soil. This opinion was accepted in its most part till Sprengel (1837), Liebig (1840) and Boussignault (1847) published their results concerning the inorganic nutrition of plants.

The end of the 18th century and the beginning of the 19th century was the beginning of the isolation and identification of humus substances. These substances have been regarded as specific substances in the components of the soils. The first steps have been done to elucidate their chemical constitution and their effect on plant growth.

Systematic investigations have been made by Sprengel (1826, 1837). He analyzed humic acids and found a content of carbon of 58%. He described the important properties of the humic acids and these of their salts. He observed that the salts of monovalent cations are soluble, these of divalent or heavy metals are insoluble in water. Also he described the negative charge of the humic acids and the flocculation of silicic acid out of silicates, the reaction with bases such as calcium ions as an important factor for soil productivity.

The work of Sprengel was accepted not only in this earlier time but also now. The methods of isolation with alkali and those of purification are nearly the same. The fact remains that humic acids dried by heat or freezing get insoluble. He found also that humic acids recently flocculated disperse again in water.

Some Data of Sprengel

He was born at Schillerslage near Hannover (50 km. from Braunschweig) on March 29, 1787. In the year 1802 he was assistant of Thaer. Later he was agricultural advisor and made scientific voyages through Europe. In 1821, he began to study chemistry, mineralogy, botany, physics and mathematics at the University of Gottingen; 1824 Dr. degree; 1826 initiation of modern humus research; formulation of the "Law of Minimum" several years before Liebig (1840); establishment of a private control-station for soil and fertilizers at Göttingen; Winter-semester, 1827/28 lectures of agricultural chemistry, initiation of "mineral theory"; 1835 professorship at the Collegium Carolinum, now technical university in Braunschweig, first professorship in the world, especially for agricultural chemistry; establishment of an agricultural educational institution, first agricultural chemical laboratory for students. During this time and later he wrote several books, for instance, "Utility of an experimental field", "Soil Science", etc.

The Swedish scientist Berzelius (1806, 1833) investigated also the humus and described that, in addition to the dark decomposition products, there are also yellow substances, which he found in the mineral springs of Porla. Later on (1833, 1839) he referred that similar substances flocculate iron out of water which contains iron. Berzelius called these new compounds crenic- and apocrenic acid. He believed that the apocrenic acid is formed by oxidation of crenic acid. Berzelius summarized his results in a book, "Textbook of Chemistry", and divided ths humus substances into three groups:

1. Humic acid, soluble in alkali

2. Humins, comparable with the "Humuskohle" (humus-coal) of Sprengel

3. Crenic and apocrenic acid

The humic substances have been divided with chemical methods asfar as possible at this time. Elemental analyses, the different solubility of the salts have been used. Berzelius called attention to the different properties of humic acids and crenic acids and their role for the processes in the soils, for the migration of different components for the forming of soil types as podsol, which has first been described by Sibirzew (1900-1907).

Mulder (1840, 1841, 1847, 1861, 1862) a student of Berzelius and the Russian scientist German (1836, 1837, 1841, 1842, 1845) continued the investigations of humic substances. Both authors isolated humic substances out of peat or different soils, gave the elemental analyses and described the properties. The substances were more or less divided according to the scheme of Berzelius. They believed that the different types of humic substances as humic acids would be compounds of definite chemical structure.

At this time, the scientists had thought about which compounds known to exist in soil could be important in the formation of humic substances.

They compared synthetic products with those which had been isolated out of soils and peat. Not only Mulder and German, but other authors also before them as Braconnot (1807, 1819), Boullay (1830), Malaguti (1835), synthesized artificial humic substances especially by treating of carbohydrates or sugars with acids. They got dark brown products. Malaguti believed that he could give the following formula of the reaction:

$$C_{12}H_{22}O_{11} = C_{12}H_{12}O_3 + 5H_2O$$

All these different products had been analyzed, the content of C, H and O has been approximately the same as those of the isolated humic acids. (The similarity in elemental analysis shows a relation between the compounds which might be compared to the fact that ivory is found in both an elephant and a piano.) But even at this time the authors noticed that there were some differences in the properties. In modern sense these products are not model substances.

One paper must be mentioned in addition to the work of this time. Hoppe-Seyler (1889) called a special kind of substance hymatomelanic acids. These are soluble in alkaline solution, flocculate with acids and can be separated from humic acids by extraction with alcohol.

In the second half of the 19th century, colloid chemistry began to influence humus research. Tarchow (1881) and van Bemmelen (1888, 1910) mentioned that the reaction with alkali is much more complicated than it would be expected according to the laws of stoichiometry. They insisted that the acid properties should be explained by the properties of the humus colloids. The so-called salts of humic acids would be an adsorption effect.

The experiments to synthesize artificial humic acids were continued, but without any more success than before. The attempts to purify the humic acids could not separate all nitrogen out of the humic acids.

In this connection it may be interesting to hear the opinion of Liebig (1840). He opposed the theory that humus would be a plant nutrient. He presumed that humus would not be the cause of high soil productivity, but the result of a high level of yield. He suggested that humus would only be a source of CO_2, which increases the solubility of the mineral components for plant nutrition. The enrichment of CO_2 in the atmosphere near the soil would be a factor for promoting plant growth insofar as it could be partly absorbed by the plants.

In the last quarter of the 19th century microbiology and especially biochemistry of microorganisms began to arise. Many authors (Post (1862), Darwin (1882), Kostytschew (1886, 1889), Müller (1887), Ramann (1888)) studied humification as a biological process and not as a chemical or physical one. They investigated not only the influence of the microorganisms but also of the soil fauna on the decomposition of soil organic matter.

At this time and later humification has been studied with biological and biochemical methods which were available. The influence of temperature, humidity and aeration and other physical properties of the soil have been examined for the decomposition processes. In this connection the effect of humus substances of the soil structure and the questions which belong to this had been found. The authors of notable papers have been Schloesing (1876, 1902) Kostytschew (1890), Wollny (1886, 1897) Deherain (1888), Deherain and Demoussi (1896).

An observation of Dokutschajew and Kostytschew (1883) is interesting for our discussion later on. They showed that unbalanced culture of cereals also on chernozem increases the damages of dryness.

In the following years microbiology and soil science as new branches of natural science developed more and more. Therefore the decomposition of plant residues as well as definite compounds as sugars, proteins, fat and others have been intensively studied. Some authors doubted that the different isolated components out of the humus are definite compounds. They believed, in some cases, that humus would be a complicated and indefinite mixture of organic substances of unspecific nature.

Notable work has been done by Hoppe-Seyler (1889) who investigated the chemical decomposition of plant substances; Omeljanski (1899, 1902), anaerobic decomposition of cellulose; van Iterson (1904) aerobic decomposition of cellulose.

At the beginning of the 20th century, the chemical methods had again developed. The humus research proceeded in two directions: One group isolated well known substances out of the soil. These are non-specific substances of definite chemical composition. Consequently, they are not involved in humic substances. Another group was engaged in studying the specific humic substances as humic acids, etc.

In the years 1908-1930 Schreiner and Shore isolated very carefully a large number of chemical compounds as carbonic acids, aldehydes, heterocyclic compounds, carbohydrates, sterols, organic phosphorus compounds. Such work has never been done afterwards although it would be of great interest to look for different other compounds especially phenols or their ethers and glucosides in the soils.

Another group studied the specific humic substances. The most important has been Oden (1912, 1914, 1919, 1923). His work is also now of great interest. The classification of humic substances are based on his work.

	Color	Solubility			
		Water true/solution	Alcohol solution	Alkali soluble	
Fulvic acids	Yellow				Ca $\geq$ 55% C
Hymatomelanic acids	Brown	Suspension	Soluble	Soluble	Ca 62% C
Humic acids	Black	Dispersed	Dispersed	Soluble	Ca 58% C
Humin Humoskohle (according to Sprengel)	Brown Black	Insoluble	Insoluble	Insoluble	

Humus coal (Humuskohle) is according to the definition of Sprengel. Later Mulder and Berzelius gave this kind of substance the name "humin" or "ulmin". Humin is used now. Humus coal is insoluble in water, alcohol and alkali. It can be dissolved only in alkaline fusion.

Humic acids have a dark-brown up to black color. They are soluble in alkali but not in alcohol. The carbon content is 58%. The equivalent weight is approximately 340.

Hymatonelanic acids. The name of this group of substances was given by Hoppe-Seyler. According to the opinion of Odén, the acids are identical with the ulmic acids described before. Odén believed that these substances are formed by the decomposition of humic acids treated with alkali. The hymatomelanic acids are soluble in alcohol with a light-brown color. The carbon content is, according to the results of Odén, 68%; the equivalent weight is 250.

Fulvic acids. They can be extracted with water out of peat. If soil extracts made with alkaline solutions are acidified, the humic acids are flocculated. The fulvic acids remain in the solution. Their solution has a yellow to golden-yellow color. Odén combined the crenic-acid and the apocrenic acid, according to Berzelius, in one group. He believed that these two kinds of substances had not been investigated enough. Most of the salts of the fulvic acids are water soluble. Their carbon content is lower than 55%.

The colloid-chemical investigations of humic acids of Odén are also of interest today. The determination by potentiometric titration, that the concentration of hydrogen ions correspond to a pH value of 3.87. He believed, based on conductivity measurements that the humic acids would be a three-basic acid, although he described them later as a four-basic acid.

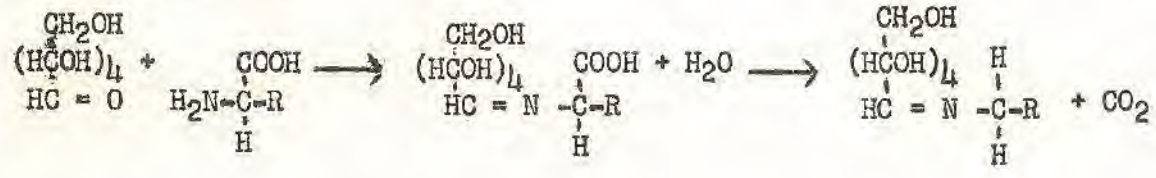
Different other authors have been more and more convinced in the following years that nitrogen is an essential compound of humic acids. The number of experiments with microorganisms has been enlarged. The results of Dojarenko (1901), Suzuki (1906-1908), Iodidi (1910-1913), Kelley (1924) and other authors at that time indicated that a part of the nitrogen of the humic acids belong to protein compounds.

Some time before, Hoppe-Seyler (1889) had succeeded in determining derivatives of phenols in alkali-fusion of humic acids. Sestini (1902) found the same results. The determination of the phenolic compounds on the one hand and the proteins on the other, led more and more to the idea that humic substances might be formed by reactions between phenolic compounds and proteins. But the experiments have been incomplete to prove the hypothesis.

At this time, the microbiologist made interesting investigations. They no longer studied the decomposition of organic materials only. They did not only observe the formation of brown-dark products produced by the microorganisms; they tried also to identify them. A basic work indeed in this direction was done by Beijerinck (1900). He found that actinomycetes (Streptothrix chromogenus) produce brown-dark colored substances on peptone as a culture medium and described them as quinones. An isolation and identification was possible. (In textbooks it is noted that he has identified these substances. But this opinion is written up one from the other. It is necessary to read the original paper.) Perrier (1913) got different important results. He observed that salts of phenolcarbonic acids such as benzoic acid and salicylic acid are altered into dark-brown products in cultures of fungi and bacteria (Bact. pyocyaneum). More than 10 years earlier, Bertrand (1898) had found that oxidizing enzymes transform polyphenols such as pyrogallol, guaiacol, gallic acid and also tyrosine in dark-colored substances. This fact developed the hypothesis that the oxidizing enzymes of the microorganisms are one of the basic factors for the alteration of parts of plant residues in humic substances.

The authors had not been sure whether phenols or generally aromatic compounds would be necessary for the formation of humic substances. Likewise, the different authors could observe that dark-brown products are formed in nutrient solutions without aromatic compounds. The solution of this problem has not been possible until 40 years later.

Humic acids contain more or less nitrogen. The observation had been made that microorganisms produce dark-colored products also in nutrient solution with sugars as the carbon source. In connection with these two facts, Maillard (1912-1917) tried to synthesize model substances by condensation of sugars with amino acids. He succeeded in getting humus-like substances of melanin type. He formulated the reactions as follows:



Maillard believed that the condensation is a chemical reaction. The microorganisms split up only the carbohydrates in sugars. This presumption may be right or wrong. The idea of Maillard has been important in that he said that the humic substances are newly synthesized products out of decomposition products of plants.

At nearly the same time Trusov (1916) studied the formation of humic substances from plant residues such as leaves of trees and grasses under conditions which are equal to those in nature. He divided the different plant substances into those which are easily available for the microorganisms, and those which are more or less resistant against the attack of microorganisms.

The easily available substances are cellulose, hemicellulose, saccacharides, glucosides, organic acids, and proteins and others. These are all indirect sources for the formation of humic substances. First they are taken up by the microorganisms for their metabolism and are afterwards components for the formation of humic substances.

The substances difficultly available for the microorganisms are lignin, tannins, other phenolic compounds, aromatic amino acids. These decompose also to a certain amount and are oxidized. Stimulated by general ideas about the oxidation and condensation of phenols, Trusov made the hypothesis that the difficultly available phenols are oxidized by the enzymes of the microorganisms and the oxidation products condense with the products of the decomposed proteins. But he never published the composition of his synthesized humic substances. He believed also that these are a mixture of different complexes.

Schmuck (1916-1930) was largely occupied with the chemical constitution of humic acids. He determined the nitrogen components in different soils and observed that the ratio of mono- and di-amino acids in the soils is near to that of the proteins of plants and animals. He prepared the ethylester of humic acids. He treated the humic acids with benzoylchloride. He proposed that the first reaction would be a measure for carboxylic groups and the latter a measure for the phenol groups. At this time, he could not know that these two reactions depend upon the acidity of the acid groups. It is not excluded that there are stronger acid phenol groups in the humic acids than carboxylic ones.

In alkali fusion of humic acids of chernozems he found decomposition products of proteins such as indoles, skatole, pyrrole, and also protocatechnic acid. These are the first experiments which were made in such a way that cyclic compounds can be regarded as involved in humic acids. In the following time the humic acids of peat, brown coal, and lignite have been studied more than those of soils.

Fischer and Schrader (1921-1923), Fuchs (1931-1936) and Stach (1933) tried to find the functional groups and the characteristic reactions of the humic acids. These have been oxidized with different chemicals as well as in alkaline fusion. The decomposition products have been isolated and identified. Phenolic and methoxyl groups have been determined. The first one esterified.

At this time there has also been different opinions about the formation of humic acids. Marcusson (1922, 1925, 1926, 1927) believed that cellulose was oxidized to hydroxy-cellulose and would be the raw material for humic substances. The uronides formed were supposed to be altered into furan derivatives and condensed into aromatic rings. But Fischer and Schrader showed that lignin oxidized in alkaline solutions in an autoclave formed humic substances, but cellulose did not. It seems to be that both are right. The humification is also a process which depends upon the assistance of microorganisms.

In the next ten years, the humus research made a great progress. The analysis of groups of components of which the plants consist has been introduced by Waksman (1927, 1929, 1930, 1931, 1933, summary 1939). He determined cellulose, pentosans, proteins and lignin. The alteration of these plant components had now been studied during the humification of different plant materials.

CHANGE OF CHEMICAL COMPOSITION OF RYE-STRAW DURING HUMIFICATION (Waksman, 1937)

Composition of straw	At the beginning	After 2 months under aerobic conditions
Total amount of organic substances	100	58.0
Organic fractions:		
Cellulose	41.5	18.3
Pentosans	26.0	10.3
Proteins	1.2	3.4
Lignin	22.5	20.0

Cellulose, pentosans and proteins decompose much more rapidly than lignin. Waksman considers modified lignin as one of the main substances for the formation of humic substances. At the same time, Springer (1934) used acetyl bromide to differentiate the humic substances.

The work of the latter authors and the time afterwards we will discuss in more detail in the appropriate sections.

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