

Astronomy
Research

HUMUS

ORIGIN, CHEMICAL COMPOSITION,
AND IMPORTANCE IN NATURE

HUMUS

ORIGIN, CHEMICAL COMPOSITION, AND IMPORTANCE IN NATURE

By

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*"Humus is the product of living
matter, and the source of it."*

—A. Thaer.



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PREFACE

Although the importance of humus in agriculture was recognized by the early Greek and Roman philosophers, it is only during the last century and a half that attempts have been made to disclose the nature of this group of organic complexes, their formation and decomposition, and their rôle in plant nutrition. Although a number of problems concerned with the study of humus still await solution, sufficient evidence has accumulated to warrant an attempt to summarize the available information in a monographic manner.

Several reviews have been published dealing with certain aspects of the origin, chemical nature, properties, and functions of humus. It is of particular importance to note here Wollny's book "Die Zersetzung der organischen Stoffe" published in 1897, Baumann's paper on the "History of the humic acids" in 1910, Oden's monograph on "Humic acids," several recent handbook summaries of chemical or agricultural aspects of humus, as well as the numerous books on coal, peat, forest soils, and composts. None of these, however, fully covered the subject of humus as a whole. The approach to the problem has usually been made either from a purely chemical, physico-chemical, agricultural, or technological point of view. Wollny is about the only one who has made an all-embracing study of humus as a natural body, of its formation, and transformation. Unfortunately, soil microbiology was still in its infancy at that time, and little was known concerning the rôle of microorganisms in the formation of humus.

No other phase of chemistry has been so much confused as that of humus, as a result of which it frequently becomes necessary to lay considerable emphasis upon the proper definition of the terms used. Vague generalizations, as "decay" and "putrefaction," have been used for specific processes of decomposition; the great complexity of the numerous humic acids, all of which designated not definite chemical compounds but mere preparations, and the unjustified comparisons between the natural humus compounds, formed in soils, composts, or bogs, with artificial preparations produced in the laboratory by the action of strong mineral acids on carbohydrates, served not to advance the subject of humus, but rather to confuse it.

Studies of the origin and chemical nature of humus have been carried out at the New Jersey Agricultural Experiment Station, during more than fifteen years. In this work, the author has been assisted by some twenty-five research workers, most of whom have obtained their advanced degrees from Rutgers University, using some phase of the study of humus as the thesis subject. To them, grateful acknowledgment should first of all be made. The author is particularly indebted to R. L. Starkey, of the New Jersey Agricultural Experiment Station, for reading and criticizing the manuscript as a whole; he is also grateful for criticism and assistance rendered by C. F. Marbut, of the United States Department of Agriculture, Washington, D. C.; by H. Jenny, Columbia, Missouri; by R. Bradfield, Columbus, Ohio; by W. Fuchs, of Rutgers University; and by C. E. Renn, who assisted in preparing the figures.

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INTRODUCTORY

THE RÔLE OF HUMUS IN THE ORGANIC CYCLE IN NATURE

With the exception of certain limited groups of organisms, known as autotrophic bacteria, only the green or chlorophyll-bearing plants, among all the living forms, are capable of synthesizing organic matter from simple elements and mineral compounds; these nutrient elements are derived partly from the atmosphere and partly from the soil, the sea, or other substrates where plants grow. The plant kingdom capable of bringing about this process is represented on this planet by forms which range in size from microscopic organisms to giant trees: the former require no fixed habitat, and comprise the various diatoms and other algae inhabiting seas, rivers, and lakes, their life being only of limited duration; the latter live for many centuries in fixed habitats. The common ability of these forms to synthesize organic matter is a highly important characteristic.

The animal kingdom uses the plants as the major source of food. The animals, however, do not utilize the plant substance as a whole. A part of the latter, frequently a major part, is either not consumed at all or is left in an undigested or partially digested form. This residual material is subjected to decomposition by microorganisms, including bacteria, fungi, and protozoa inhabiting the soil, the sea, and the compost, and represented there by numerous types possessing a great variety of activities.

The animals, as well, sooner or later die, and their bodies, in addition to the products of their metabolism, also become subjected to microbial decomposition. As a result of these microbiological processes, the elements which have originally been consumed by the plants for organic synthesis are returned to circulation, thus completing the cycle of the elements in the process of life.

However, the plant and animal residues do not become completely mineralized. A certain part of these residues is more or less resistant to microbial decomposition and remains for a period of time in an undecomposed or in a somewhat modified state, and may even accumulate under certain conditions. This resistant material is dark brown to black in color and possesses certain characteristic physical and chem-

ical properties; it is usually called HUMUS. As a result of the formation and accumulation of this humus, a part of the elements essential for organic life, especially carbon, nitrogen, phosphorus, sulfur, and potash, become locked up and removed from circulation. In view of the fact that the most important of these elements; namely, carbon, combined nitrogen, and available phosphorus, are present in nature in only limited concentrations, their transformation into an unavailable state, in the form of humus, tends to serve as a check upon plant life. On the other hand, since humus can undergo slow decomposition under certain favorable conditions, it tends to supply a slow but continuous stream of the elements essential for new plant synthesis.

Humus thus serves as a reserve and a stabilizer for organic life on this planet.

The actual concentration of organic matter in the form of humus in the soil and in the sea far exceeds that present in all the living forms of plants and animals. It is sufficient to call attention to the fact that the humus content of the soil is considerably greater than the total amount of organic matter present in all the crops harvested in a given year from all the fields, orchards, and gardens, or that available in the form of reserve foodstuffs. The large quantities of humus present in peat and in brown and hard coal, which far exceed the supplies of organic matter in our forests, represent organic accumulations during many thousands of years. The amount of organic matter found in seas, rivers, and lakes, whether in true solution, in colloidal suspension, or in the bottom material, also exceeds many times (593) the organic matter content of all plant and animal life in those waters.

The carbon content of the various forms of humus on this planet, as well as that present in all living forms and in the atmosphere, has recently (181, 1206a, 645) been calculated as follows:

	<i>metric tons</i>
Carbon content of atmosphere.....	600,000,000,000
Carbon content of hydrosphere.....	16,400,000,000,000
Carbon content of anthracite coal.....	422,000,000,000
Carbon content of bituminous coal.....	2,732,000,000,000
Carbon content of brown coals.....	1,499,000,000,000
Carbon content of all forms of peat.....	1,123,000,000,000
Carbon content of all soils, to a depth of 30 cm.....	400,000,000,000
Carbon content of all living matter.....	700,000,000,000

*No!!
2 x 10¹⁵ Kg
Handbook
Chem & Phys
assumes
4% C, G.*

Lundegårdh (656) calculated that the amount of CO₂ consumed annually by the green plants is about 59 billion tons; the total supply of

*metric
5
on 6 x 10¹³ Kg*

CO₂ in the atmosphere would thus last only about thirty-five years (989). *a.K. if atm. contain 2 x 10¹⁵ K.*

An understanding of the origin and chemical nature of humus, its formation and accumulation, and its transformation and decomposition represents a highly important phase of our knowledge of organic life. The microorganisms influence the cycle of humus in nature in more than one way: 1. They bring about its formation from plant and animal residues. 2. They continuously transform humus, under favorable conditions, and finally decompose it completely or "mineralize" it. 3. Their own cell substance contributes directly as a source of humus. The rôle of microorganisms in the cycle of organic matter in the soil, as well as in nature in general, is, therefore, indispensable. Without them, the continued existence of life upon this earth, as we know it, would have disappeared long ago, since most of the available elements essential for plant growth would have been stored away in the form of inanimate plant and animal residues.

This book is an attempt to tell the story of humus, its origin from plant and animal residues, its chemical composition, its physical properties, its importance in nature, especially in soil processes and in plant growth, and finally its decomposition. Humus is treated here as a natural body, produced universally in nature, wherever plant or animal residues are undergoing decomposition. Without denying the rôle of purely chemical reactions in the formation and transformation of humus, especially those of oxidation and reduction, hydrolysis and polymerization, it should be recognized that the primary agents in the formation and transformation of humus are the microorganisms; by overlooking their functions, the earlier chemists failed to understand the origin and significance of humus, in spite of the many years of effort, from the beginnings of organic chemistry until recent times. The soil, compost, peat bog, and ocean are living systems, where the organic constituents are continuously modified by numerous processes brought about by microorganisms which live in these systems and reproduce, utilize energy and give off heat, decompose organic substances, and construct new complexes. Humus and living microorganisms are connected by numerous, invisible ties, which must be appreciated in order to understand the origin and nature of humus.

PART A
HISTORICAL DEVELOPMENT OF OUR KNOWLEDGE OF THE
CHEMICAL NATURE OF HUMUS, ITS FORMATION, AND
ITS RÔLE IN PLANT NUTRITION

CHAPTER I

NATURE AND CHARACTERISTICS OF HUMUS. TYPES OF HUMUS

*. . . pinguis humus dulcique uligine laeta,
Quique frequens herbis et fertilis ubere campus . . .*
—GEORGICS OF VIRGIL.

The study of the origin, chemical nature, and transformation of humus has been limited chiefly to the rôle that humus plays in soil processes and plant nutrition. The importance of humus in the soil is manifold: it serves as a source of nutrients for plant growth; it modifies the physical and chemical nature of the soil in various ways; it regulates and determines the nature of the microbial population and its activities, by supplying sources of energy and various organic and inorganic nutrients essential for their growth, and by making the soil a more favorable substrate for their development. Humus gives to fertile soils some of their most important physical and chemical properties. Humus characterizes the soil, since differences in the origin, abundance, and chemical nature of humus result in the formation of distinct soil types.

Humus may be looked upon as a storehouse of important chemical elements essential for plant growth, especially of carbon and nitrogen, and to a less extent of phosphorus, calcium, iron, manganese, and others. The utilization of some of these elements held in the inorganic fraction of the soil is also influenced by humus, through its chemical interaction with the inorganic complexes. One should consider further the colloidal effects of humus on the soil; its buffering properties which modify the soil reaction; its combining power with bases; its influence upon the oxidation-reduction potential of the soil; its adsorption of certain toxic materials injurious to plant growth; its ability to supply certain catalytic agents and small quantities of certain rare elements essential for plant growth; its influence upon soil structure, upon the moisture-holding capacity of the soil, and upon soil temperature; as well as numerous other reactions which are of direct or indirect importance to plant growth. One will, therefore, not exaggerate in stating

that a knowledge of soil humus is most essential for a proper understanding of the origin and nature of the soil as well as of the processes that control plant growth.

The changing conceptions of humus. The term "humus" dates back to the time of the Romans, when it was frequently used to designate the soil as a whole. It was later applied to the organic matter of soils and composts or to different fractions of this organic matter, as well as to complexes formed by the action of chemical reagents upon a variety of organic substances. From Theophrastus (373–328 B.C.) to Wallerius (1709–1785), the conception of "oleum unctuosum," which stood for "the soil or fatness of the land," dominated the ideas of the naturalists. The great botanist Linnaeus (1707–1778) classified soils in a manner similar to his classification of plants. Among the various soil types thus recognized are found: *Humus daedalea* (garden soil), *Humus ruralis* (field soil), *Humus latum* (muck soil), *Humus damascena* (clay soil), *Humus chistosa* (red clay soil), etc. Wallerius (1245) first defined "humus," in 1761, in terms of decomposed organic matter. However, the prevailing ideas concerning the chemical nature of humus and the mechanism of its formation were very vague. Most often it was considered as a complex, formed in soils, in bogs, or in composts, from plant residues, by a special process of "humification."

De Saussure, in his famous work "Recherches chimiques sur la végétation" (942), devoted considerable attention to humus (*terreau*). He found that it is not a homogeneous substance, but that it consists of various complexes (extractives, oils, salts) which can be readily removed. Humus was found capable of absorbing oxygen, which combined with the carbon of the soil to give CO_2 . About that time humus was shown to contain a substance which was soluble in alkalies and precipitated on acidification of the alkaline solution. Thaer (1140) differentiated between "acid humus" or peat, formed with limited admission of oxygen, and "mild humus," formed in the presence of sufficient oxygen. Liebig (638) spoke of humus as "a brown substance, easily soluble in alkalies, but only slightly soluble in water, and produced during the decomposition of vegetable matters by the action of acids or alkalies."

The term "humus" came into general use at a time when organic chemistry was still in its infancy and when all organic and inorganic compounds were considered to be substances very simple in chemical composition. Unfortunately, it was not always used to designate the same organic substances or preparations. Some applied this term to

the total organic matter of the soil, while others designated by it that part of the organic matter which is readily oxidized by certain reagents, such as hydrogen peroxide or potassium permanganate (568, 345). Frequently "humus" meant only that fraction of the organic matter which is soluble in dilute alkali solutions (361, 1014); in many instances the complex formed on precipitation of the alkaline extract by acids was so designated (801, 79). More recently certain investigators (371, 1077) have referred to that part of the organic matter which is not acted upon by the acetyl bromide reagent as "humus." The use of the term to designate soil organic matter as a whole was probably the one most universally accepted, whereas the others, which included only a part of the soil organic matter, and frequently a very small part, were given less consideration.

Without going into a detailed review of the numerous conceptions of humus prevalent during the 19th century, it may be well to call attention to some recent ideas on this subject. Ollech (789) defined "humus," in 1890, as comprising "all those substances which are formed in the decomposition and fermentation of organic matter of plant and animal origin, or through the action of certain chemical agents upon this organic matter, in the form of amorphous, non-volatile, non-odorous, more or less dark colored organic compounds." Ramann (859) spoke of humus or "humus bodies" as "colloidal complexes of varying composition, consisting of unchanged colloids of the original plant substance mixed with carbon-rich decomposition products." In both of these definitions the rôle of microorganisms in the formation of humus is definitely recognized. According to Oden (781), however, humus represents "those yellow-brown to dark-brown colored bodies of unknown constitution which originate in nature through the decomposition of organic substances under the influence of atmospheric agencies or in the laboratory through chemical reagents (largely acids or alkalies); they possess a definite affinity for water and show, if not true solution or dispersion, a distinct swelling." In this definition no attention is paid to the importance of microorganisms which bring about the transformation of the plant and animal residues to give rise finally to humus (129).

Characteristics of humus. By taking into consideration the processes of humus formation, largely as a result of the activities of various microorganisms, one may suggest the following definitions: Humus is a complex aggregate of brown to dark colored amorphous substances, which have originated during the decomposition of plant and animal

residues by microorganisms, under aerobic and anaerobic conditions, usually in soils, composts, peat bogs, and water basins. Chemically, humus consists of certain constituents of the original plant material resistant to further decomposition; of substances undergoing decomposition; of complexes resulting from decomposition, either by processes of hydrolysis or by oxidation and reduction; and of various compounds synthesized by microorganisms (968). Humus is a natural body; it is a composite entity, just as are plant, animal, and microbial substances; it is even much more complex chemically, since all of these materials contribute to its formation. Humus possesses certain specific physical, chemical, and biological properties which make it distinct from other natural organic bodies. Humus, in itself or by interaction with certain inorganic constituents of the soil, forms a complex colloidal system, the different constituents of which are held together by surface forces; this system is adaptable to changing conditions of reaction, moisture, and action of electrolytes. The numerous activities of the soil microorganisms take place in this system to a large extent.

It is now definitely recognized that humus has resulted from the decomposition of plant and animal bodies, mainly through the agency of microorganisms although the possibility of certain chemical reactions taking place in the process is not excluded. Humus has, therefore, certain specific properties which distinguish it from other natural bodies. These properties can be briefly summarized as follows:

1. Humus possesses a dark brown to black color.
2. Humus is practically insoluble in water, although a part of it may go into colloidal solution in pure water. Humus dissolves to a large extent in dilute alkali solutions, especially on boiling, giving a dark colored extract; a large part of this extract precipitates when the alkali solution is neutralized by mineral acids. Certain constituents of humus may also dissolve in acid solutions and be precipitated at the isoelectric point, which is at a pH of about 4.8.
3. Humus contains a somewhat larger amount of carbon than do plant, animal, and microbial bodies; the carbon content of humus is usually about 55 to 56 per cent, and frequently reaches 58 per cent.
4. Humus contains considerable nitrogen, usually about 3 to 6 per cent. The nitrogen concentration may be frequently less than this figure; in the case of certain highmoor peats, for example, it may be only 0.5–0.8 per cent. It may also be higher, especially in subsoils, frequently reaching 10 to 12 per cent.
5. Humus contains the elements carbon and nitrogen in proportions

which are close to 10:1; this is true of many soils and of humus in sea bottoms. This ratio varies considerably with the nature of the humus, the stage of its decomposition, the nature and depth of soil from which it is obtained, and climatic and other environmental conditions under which it is formed.

6. Humus is not in a static, but rather in a dynamic, condition, since it is constantly formed from plant and animal residues and is continuously decomposed further by microorganisms.

7. Humus serves as a source of energy for the development of various groups of microorganisms, and, during decomposition, gives off a continuous stream of carbon dioxide and ammonia.

8. Humus is characterized by a high capacity of base-exchange, of combining with various other inorganic soil constituents, of absorbing water, and of swelling and by other physical and physico-chemical properties which make it a highly valuable constituent of substrates which support plant and animal life.

Importance of humus in soil processes: The functions of humus in the soil are largely threefold: 1. physical, thereby modifying the soil color, texture, structure, moisture-holding capacity, and aeration; 2. chemical, influencing the solubility of certain soil minerals, forming compounds with certain elements, such as iron, which renders them more readily available for plant growth, and increasing the buffering properties of the soil; 3. biological, by serving as a source of energy for the development of microorganisms, as well as by making the soil a better medium for the growth of higher plants; it also supplies a slow but continuous stream of nutrients for plant life.

Humus exerts various other important effects upon plant growth which are still awaiting explanation; although some of these effects are believed to be injurious in nature, most are definitely established to be highly beneficial. The various attempts to explain these effects by the formation of plant toxins, on the one hand, and of "plant stimulating substances" or "auximones" (135, 715, 933, 180, 1297), on the other, are still a matter of dispute. Of course, all reference to the "spirit of the soil" or the "reserve soil force" represents speculative generalizations not based upon sound experimental evidence.

Humus types. Although there is no doubt that because of their rôle in plant nutrition, the most important forms of humus are those found in field and garden soils, other forms of humus exist, which even if not utilized for agricultural purposes, have important industrial and other applications. The function of humus in plant and animal life

in the sea and in inland water basins is still a matter of conjecture, although its importance is well recognized. Humus in coal and in peat as a source of fuel has been one of the major agents in the development of modern industrial civilization. The function of humus in the origin of petroleum is still a matter of dispute (1173). Any attempt, however, to divide humus on the basis of its practical utilization would prove to be largely artificial.

Since the suggestion of Linnaeus to separate humus into several well recognized types, various classifications of humus have been proposed. An early student of humus (517) recognized four distinct types or varieties: 1. the brown variety, found in living vegetation, in recently fallen litter, in peat, in decomposing sea-weeds upon the shores and in fungi; 2. the black variety, usually found in an active state of decomposition in the deeper layers of soil, in decomposing leaves and wood of forests, in animal manures, in peat of swamps and in muds; 3. humus in a state of transference, namely in the waters of rivers, lakes, springs, and even in rain water; 4. humus in a fossil condition, in the form of lignite, brown-coal and other carbonaceous deposits, as well as in many minerals, such as hydrated ores of iron and manganese.

The accumulated knowledge concerning the origin and chemistry of humus permits a more logical system of classification based entirely upon the processes and conditions of humus formation.

A. Humus types formed by decomposition of plant and animal residues under aerobic, or only partly anaerobic, conditions, in composts and in soil:

I. Humus of composts:

1. composts of stable manures,
2. composts of plant residues, with or without addition of inorganic salts ("artificial manures").

✓ **II. Humus in soil:**

1. plant residues decomposed under conditions of high acidity or low temperature, or both:
 - a. raw humus in forest soils,
 - b. raw humus in heath soils,
 - c. alpine humus;
2. plant residues decomposed under less acid, neutral, or alkaline, conditions: typical soil humus (chernozems, humus in chestnut soils, serozems, forest mull humus, etc.).

B. Humus types formed by decomposition of plant and animal residues under anaerobic conditions:

I. Recent formations:

1. highmoor peats,
2. lowmoor peats,
3. sedimentary peats.

- II. Old formations:
 - 1. soft coals (brown coals, lignites),
 - 2. hard coals (anthracites).
- C. Humus types formed in water basins:
 - I. Recent formations:
 - 1. water-soluble humus,
 - 2. humus in marine bottoms.
 - II. Geologic formations:
 - 1. source beds of petroleum.

These different types of humus vary considerably in chemical composition, because of differences in the nature of the materials from which they originated, conditions of decomposition, and extent of decomposition. Some of these types are, therefore, frequently subdivided into several subtypes. This system of humus classification is not free from criticism: the sedimentary peats, for example, can readily be placed in group C; however, since they form humus accumulations similar to those of typical peats, they are classified with these. Frequently (258), soil humus is divided on the basis of its agricultural utilization into two general types; namely, "acid humus" and "mild humus"; the latter is rich in, if not saturated with, calcium, magnesium, and other bases, while the former contains largely hydrogen in its exchange complex and little, if any, calcium and magnesium. Under "acid humus" one usually understands humus of highmoor peats, raw humus forest soils, and sometimes humus of acid sandy soils. The "mild humus" represents the typical humus of chernozems, forest mull soils, and similar formations. These two types of humus are considered different, not because they were found to be markedly different in chemical nature or because they were produced under different climatic, soil, or vegetation conditions, but because they differ in the nature of the bases saturating the exchange complex. However, the mere addition of calcium to the "acid humus" does not change it into a "mild humus"; it would take many years of decomposition before the former could change into the latter, demonstrating even to superficial examination the marked chemical difference between the two types of humus. This will be brought out in detail in the following pages.

CHAPTER II

THE RÔLE OF HUMUS IN PLANT NUTRITION

“Nur an Humus fehlte es, so meinte man früher, nur an Ammoniak fehle es, so meint man jetzt.”—LIEBIG.

The earlier conceptions of the rôle of humus in plant nutrition. The nutrition of plants was considered by the Ancients, as well as during the Middle Ages, to involve processes similar to those in animals; the nutrients were believed to be absorbed in a preformed condition by the roots from the soil and to be subsequently modified in the plant tissues. “Earth” was believed to be one of the essential “elements” upon which plants feed, in addition to the other three elements; namely, water, air, and fire. Without knowing much about the existence of humus in the soil or its significance in soil processes, the Ancients attached considerable importance to its abundance. This can be recognized by the fact that the Romans judged the quality of the soil by its color, although Columella (185) emphasized the injurious effect of acid humus in peat.

Van Helmont (417) and other naturalists of the 17th century attempted to show that plants withdraw only water from the soil and that manures act favorably upon plant growth only by supplying heat and moisture. According to these naturalists, the *living power* of animals and plants enables them to construct all tissues, including even the mineral constituents, from the atmospheric air and the soil water. Toward the end of the century, Woodward (1303) concluded that earth, and not water, is the element essential for vegetable production.

The plant physiologists of the 17th century, including such prominent investigators as Malpighi, did not dispense with the idea that plants absorb their organic nutrients from the soil; the Aristotelian conception of this process was somewhat modified, to include the idea that the absorbed organic complexes undergo various chemical changes within the plant tissues, before they become a part of the living plant. The prevalent ideas concerning the nature of the materials absorbed from the soil were very vague and were usually veiled in various metaphysical speculations. Some investigators referred to the absorbed nutrients

as "the juices of the earth," while others spoke of "minute particles of soil." Some believed that plants, like animals, exert a selective action upon the food particles, which explained the favorable results obtained from plant rotations in practical crop production. Stahl, the founder of the phlogiston theory, expressed the idea that plant materials have the same chemical composition as inorganic substances; the former were believed to be produced from the latter, namely, from the inorganic salts and chiefly from water and "phlogiston" (125). In the course of time the importance in plant development of such an inorganic substance as nitrate was established (348); some appreciation of the true functions of leaves also developed.

The period between 1630 and 1750 was characterized by an industrious search for "the principle of vegetation"; during this period, saltpeter and water were individually proposed as the elements essential for plant growth. In 1730, Tull stated that "small earth-like particles serve as nutrients for plants, and air and water help to extract these particles from the soil." K ulbel (597), in his book on soil fertility, emphasized that *magma unguinosum*, supposed to be present in humus, was the principle of plant growth and the major source of soil fertility. Wallerius, soon afterward, in his famous book on "Principles of Agricultural Chemistry" (1245), concluded, from the chemical analysis of plants, that the humus of the soil is the essential nutritive element for plant growth (*nutritiva*), while the other soil constituents only assist in the process of nutrition by mixing the food or dissolving it, thus bringing it into a condition more suitable for entrance into the root systems of the plants (*instrumentalia*). The favorable action of lime on soil was believed to consist in dissolving the "fatness" of the humus, while the function of clay was considered as that of fixing and retaining this fatness. These ideas entered the agronomic literature, and the "fat of the land" became synonymous with soil humus and the supply of plant nutrients. Humus was considered to be of the greatest importance in plant nutrition.

The end of the 18th and the early part of the 19th centuries was a period of definite progress in knowledge of the processes involved in the growth of plants, largely as a result of the work of Ingen-Housz, Senebier, and de Saussure. Ingen-Housz (476) clearly recognized that leaves absorb from the air a gaseous constituent which they use in the presence of light to produce the combustible bodies in the plant. Senebier (995) suggested that the process of CO₂-assimilation involves reduction of this gas in the presence of light and results in the excretion

of oxygen; he believed, however, that the CO_2 necessary for the nutrition of the plants did not come chiefly from the air, but was absorbed by the roots from the soil and was brought to the leaves with the rising sap. The last conception was largely responsible for the fact that the humus of the soil was for a long time considered to be the true source of carbon for plant life. Only Th. de Saussure (942) succeeded in clearly establishing the importance of the gaseous exchange in the nutrition of plants. He definitely demonstrated that plants synthesize their organic matter from carbon dioxide and water, and give off oxygen; the CO_2 is obtained entirely from the air, while the nutrients derived from the soil are very insignificant in amounts, as compared with the total plant mass produced. He believed that the nitrogen was absorbed from the soil or the atmosphere, in the form of vegetable and animal extracts, as ammonia gas, or in other water-soluble forms. He emphasized that the inorganic substances are absorbed chiefly from the soil.

De Saussure was the first to develop the idea of modern plant nutrition, based upon careful chemical investigations. It was thus definitely shown that the plant obtains its oxygen and carbon dioxide from the air, while the nitrogen and various minerals, which make up a definite part of the plant constituents, are obtained from the soil through the root system of the plant. The fertility of the soil was believed to depend, to a certain extent and within certain limits, on the amount and nature of the water-soluble constituents that the soil contains. The plant, by absorbing these constituents from the soil, can exhaust the soil and render it infertile. A soil may, therefore, lose the greater part of its vegetative substance without showing any differences in its physical properties from those of a fertile soil.

In spite of these exact contributions to a better understanding of the nutrition of plants, the idea still prevailed during the early part of the 19th century that soil humus functions as a source of carbon. A special "vital force" in the plant cells was still believed to bring about the synthesis of mineral substances. Hassenfratz (see 457) definitely stated, about 1800, that the carbon necessary for plant growth is obtained directly by the roots from the dark colored soil constituents, which are found abundantly in fertile soils. Thus the prevailing idea that soil humus is the true nutrient of plants still remained. This conception of the rôle of humus was the more acceptable because it was generally recognized that the fertility of the soil depends upon this humus.

Thaer (1139) may be considered as the most outstanding exponent of the humus theory of plant nutrition during this period. The fact that stable manure consists largely of organic substances and that, on decomposition, manure gives rise to humus, led Thaer to suggest, in 1798, that plants thrive principally upon the humus in solution. He stated further, in 1808, that "humus comprises a more or less considerable portion of the soil; fertility of the soil depends largely upon it, since, besides water, humus is the only material which supplies the nutrients to plants." The favorable influence of certain inorganic substances upon plant growth was explained by the increase in humus formation in soil through the addition of these materials. However, even Thaer had to admit that the probable effect of humus upon vegetation was exerted through the influence of the carbonic acid gas which was produced.

These ideas concerning the function of humus in plant nutrition prevailed throughout the first half of the 19th century and were accepted by such prominent chemists as Berzelius, Mitscherlich, and Davy. This becomes evident from some of the conceptions of Davy (206), who stated that oils were good manures on account of the carbon and hydrogen that they contain; that the addition of lime to the soil has a favorable effect, because it dissolves the hard vegetable matter; that putrid urine is less useful as a manure than fresh urine; that farm-yard manure should not be allowed to ferment before it is applied to the land. He admitted, however, that the ash constituents of the soil are essential for plant nutrition and do not act merely as stimulants. Berzelius (113), as late as 1839, still considered that humus was a plant food, although a few years previously Sprengel (1075) had expressed ideas similar to those of de Saussure, that plants obtain the carbon dioxide from the air, while the nitrogen, which is also an important plant food, is derived from the soil.

With very few exceptions, the early agronomists, plant physiologists, and chemists considered that the organic matter of the soil, known as humus, was the chief nutrient for plants; the latter were believed to absorb the humus directly through their roots. The presence of humus in the soil was looked upon as the primary requirement for soil fertility. The carbon of the humus was considered to be an important source of carbon for plants, without necessity for its alteration previous to absorption. These ideas received support from experiments which indicated that plant growth increased with the humus content of the soil.

Early students of the chemical nature of soil-organic matter observed that humus and "humic acids" (a group of constituents of humus which were soon to become very popular) are insoluble in water, and are relatively soluble in alkali solutions. This led to the suggestion that the presence in the soil of alkalies and alkali earths, which are usually found in the ash constituents of the plant, contribute to the solubility and assimilation of humus. It was believed that a continuous stream of humus proceeds from the soil to the roots of the plants.

Some of the outstanding plant physiologists of the early 19th century, such as de Candolle, Treviranus, Meigen, and others, while carefully pursuing various problems of plant physiology, did not always pay sufficient attention to the chemical processes involved in the nutrition of plants. The humus theory of the chemists and agriculturists was accepted by them uncritically. These prevalent ideas concerning the rôle of humus in plant nutrition were well expressed by Liebig, in his typically sarcastic manner: "Vegetable physiologists consider the formation of woody fibre from humus as very simple; they say humus has only to enter into chemical combination with water in order to effect the formation of woody fibre, starch or sugar."

Liebig and his period. About 1840, there appeared two important contributions to the subject of plant nutrition, which dealt a severe blow to the humus theory, although they did not dispose of it entirely: Boussingault (141-2) demonstrated that plants can make normal growth with nutrient salts alone and without any humus whatsoever, and Liebig (638) published his famous book on "Chemistry in its Application to Agriculture and Physiology," in which he ridiculed the idea that plants derive their carbon from the soil and not from the carbonic acid of the air. Liebig considered the abundance of humus in the soil to be more a result than a cause of soil fertility. He concluded that only inorganic or mineralized substances are used as nutrients by all green plants. Plants live on carbon dioxide, ammonia, nitrate, water, phosphoric acid, sulfuric acid, silicic acid, lime, potassium, and iron, and some need, in addition, sodium chloride. Liebig thus brought home to agronomists, to agricultural chemists, and to plant physiologists the results of Ingen-Housz, de Saussure, and others, by emphasizing clearly and distinctly the importance of ash constituents in plant nutrition and the rôle of the carbon dioxide of the atmosphere in this process.

According to Liebig, humus, because of its insolubility, is not absorbed by plants and would never even suffice to supply the necessary

carbon to the total vegetation. The humus content of the soil is not diminished by plant growth but is actually increased. However, he came to recognize later that humus exerts a favorable effect on plant growth. This was believed to be due to the fact that it supplies a slow and lasting stream of carbonic acid, which serves as a solvent of soil constituents necessary for plant nutrition; a part of the carbon dioxide of the soil is diffused into the outer air; the plants covering the soil with their leaves assimilate more carbon dioxide through their leaves than do those that depend exclusively upon the carbon dioxide of the atmosphere.¹

Although Liebig's contribution was of inestimable importance in disposing of the humus theory of plant nutrition and in clearly emphasizing the fact that plants obtain their carbon from the carbon dioxide of the atmosphere and the minerals from the soil, his ideas on the nitrogen nutrition of plants were open to considerable criticism. He believed that ammonia was the specific source of nitrogen which the plants utilized and that the ammonia content of the soil atmosphere sufficed to supply the nitrogen needs of the plants, just as the carbon dioxide of the air provides sufficiently for the carbon requirements. Carbon dioxide, ammonia, and water were believed by Liebig to be the three essentials in plant nutrition. In his attempt to establish his theory that plants obtain only alkalies (potash) and phosphoric acid from the soil and the carbon from the atmosphere, Liebig committed a grave error in considering the atmosphere not only as the source of carbon but of nitrogen as well.

In spite of the investigations of de Saussure and Boussingault, supported by the brilliant arguments of Liebig; in spite of the work of Sachs, Knop, and others with water cultures, whereby it was demonstrated that plants can synthesize all their organic complexes from inorganic substances, in the complete absence of organic compounds, the idea still continued to prevail for some years that organic substances of the soil were intimately involved in plant nutrition. As late as 1872, Grandeau (361, 362, 1191) stated that humus furnishes carbon

¹ "Der Humus ernährt die Pflanze nicht dadurch, dass er im löslichen Zustande von derselben aufgenommen und als solcher assimiliert wird, sondern weil er eine langsame und andauernde Quelle von Kohlensäure darstellt, welche als das Lösungsmittel gewisser für die Pflanze unentbehrlicher Bodenbestandteile und auch als Nahrungsmittel, die Wurzeln der Pflanze, so lange sich im Boden die Bedingungen zur Verwesung (Feuchtigkeit und Zutritt der Luft) vereinigt finden, in vielfacher Weise mit Nahrung versieht."

to plants; according to him, the mineral nutrition of plants can take place only through the agency of the black matter. Humus rich soils, such as Russian chernozems, contain a peculiar organic substance which binds various inorganic compounds; these are capable of resisting the action of dilute hydrochloric acid. This substance is made soluble by ammonia water; it contains 3–6 per cent nitrogen and a large part of the phosphoric acid of the soil. The ammonia water was thus looked upon as the solvent of the food for plants.

Even de Saussure suggested, in 1842, that the function of ammonia or nitrates in plant growth consists in rendering the humus soluble and not acting directly as nutrients. He believed that his experiments definitely demonstrated the fact that "humic acid" and substances extracted by water from peat are absorbed by plants; he found that when humus enters the roots of the plant, as shown by the absorption of a deeply colored solution of potassium humate, it is changed there chemically and assimilated by the plant. Johnson (507) argued, in 1883, that although Liebig and his adherents were right in concluding that the final products of decomposition of organic substances in the soil, namely, carbonic acid, ammonia, nitric acid, water, and the ash ingredients, form the chief nutrients of agricultural plants, the fact remains that various forms of humus ("soluble humates, ulmates, crenates, and apocrenates, together with other soluble organic matter of the soil") are absorbed by the plants and assimilated. The superiority of stable manure over inorganic fertilizers for crop production was believed to be equally conclusive evidence that humus is directly utilized by plants (361, 152, 874, 464). Numerous other claims were made that plants grew well with their roots immersed in solutions of soil organic compounds, prepared by extraction with potassium or ammonium hydroxide. These claims were not sufficient, however, to establish definitely that humus is assimilated directly by plants, although they have demonstrated that it is not injurious and may actually be in some manner beneficial to plant growth, in contradistinction to the earlier ideas of Liebig.

The introduction of nutrient salt solutions for the cultivation of plants by Sachs and Knop in 1860 opened the way for exact experimentation in this direction. Acton (11) demonstrated, in 1889, that plants are able to assimilate directly glucose, sucrose, and glycerol in water cultures and utilize them for starch synthesis in the dark; glycogen, dextrin, and starch could not be assimilated. Similar observations were made by Laurent (614), who showed that corn and peas

assimilate glucose, not only in the dark, but also in the light, both in the presence and in the absence of carbon dioxide; sucrose, glycerol, and potassium humate were also utilized. Mazé (685) found that corn assimilates sugars, starch, and peptone. Cailletet (165) demonstrated that certain forest shrubs (*Adiantum*) are capable of growing in soil, at the expense of the organic compounds, by a process similar to that of the fungi of the soil. According to Knudson (554) when soluble carbohydrates are absorbed by plants, root growth is stimulated to a much greater extent than top growth. In the case of vetch, the ratio tops/roots was reduced from 4.6 to 2.0, in the presence of glucose, and to 1.2, in the presence of sucrose.

The ability of green plants to assimilate organic nitrogenous compounds was even more definite. Wiley (1281) reported in 1897 that oats grown in peat soils contained 25 per cent more nitrogen than oats grown in ordinary mineral soils; a large part of this nitrogen was found in the plant in the amide state and not as protein. He came to the conclusion that plants are able to assimilate the nitrogen present in peat largely as amide. Soon after, Lutz (661) showed that various lower amines can be assimilated and utilized by higher plants, without being first acted upon by microorganisms and transformed to ammonia or nitrate. Other substances, however, like phenylamines, naphthylamines, and alkaloids, exert a decided toxic effect upon plant growth, and do not offer available sources of nitrogen, unless they are first decomposed by microorganisms. Hutchinson and Miller (471) found that wheat and peas are able to assimilate urea, acetamide, glycerol, alloxan and peptone. The absorption by plants of nucleic acid, xanthine, guanine, creatinine, arginine, asparagine, and other nitrogenous compounds has been established by Schreiner and Skinner (986). These observations were confirmed by Brigham (155), who found, however, that better growth was obtained when the plant cultures were inoculated with *Bac. subtilis*.

In the presence of light, green plants synthesize practically all of their organic substances photosynthetically, and the presence of organic substances does not alter this process. Even in those instances where direct assimilation of organic complexes by plants has been studied, the rôle of microorganisms in the process has not always been excluded. The activities of these organisms in bringing about modifications of the organic matter depend upon a number of factors, such as nature of soil, nature of plant, environmental conditions and nature of organisms. In some cases, they may be of considerable importance

in the utilization of organic matter, as in the case of mycorrhiza fungi in the nutrition of forest trees and orchids.

In discussing the function of humus in plant nutrition, it may be well to consider the underlying factors responsible for the favorable effects of stable manures upon plant growth. Whether this effect is due to the organic complexes or to the mineral constituents of the manure is not a new question. Discussions of the problem appeared many years ago, even antedating those of Thaer and Liebig. None of the proponents on either side, however, claimed that the effect of manure is due solely to either the organic or the mineral constituents. Thaer and the representatives of the "humus" group believed that it is largely due to the humus content, whereas Liebig and the "mineral" group believed that it is the mineral constituents which are chiefly responsible for the favorable effect of the manure (772). According to a recent contribution (771), the favorable effect of stable manure is exerted through its colloidal substances, which stimulate the root system of the plant.

The results of the investigations cited here and of numerous others (124, 685, 722, 1021, 898, 875, 91, 179) on the absorption and assimilation of sugars, organic acids, and nitrogenous organic compounds by plants can be summarized as follows:

1. Various organic compounds, such as creatine, creatinine, arginine, histidine, guanine, xanthine, hypoxanthine, and nucleic acid, can be directly assimilated by plants and can replace nitrate in culture solutions (985-6).

2. Leguminous plants are able to obtain their nitrogen from root nodules in the form of organic compounds, probably amino acids (1212).

3. Under sterile conditions certain plants are able to assimilate various sugars (1021); lecithin can be assimilated as a source of phosphorus, and cystine, as a source of sulfur (1134).

4. Humus offers a very favorable source of available iron to plants and to microorganisms, at reactions which are optimum for the growth of plants (163, 790, 641).

5. Some plants lacking chlorophyll make use of organic substances from the soil humus as their exclusive sources of energy and material for synthesis. They are usually assisted in this process by mycorrhiza formations, whereby the organic matter is generally altered before assimilation. Other mycorrhiza associations appear to be involved in providing certain organic substances for chlorophyll bearing plants, as in the case of orchids.

The specific effects of certain organic substances upon plant growth cannot be interpreted as proving that organic complexes in general are directly assimilated by plants and that, therefore, the addition of such substances to the soil is highly desirable in plant production. There is no doubt that organic matter is of great importance in the soil, but this is not because some of the constituent complexes may be directly assimilated by the plants, but principally because humus exerts important effects upon the physical and chemical properties of the soil, because it contains a considerable quantity of plant nutrients, and because it offers a favorable medium for microbial activities. All attempts, therefore, to introduce into practical agriculture the use of organic fertilizers on a large scale, with claims based entirely upon the possible feeding capacity of the plants upon some of the organic constituents, or upon some other mysterious action of these complexes upon plant growth, have so far completely failed (218, 400, 401).

The presence in soil of specific plant stimulating substances is discussed in detail elsewhere (Chap. XV).

Modern ideas concerning the rôle of humus in soil processes and plant nutrition. Liebig had a purely chemical conception of the processes of decomposition of organic matter in soils and in composts. It was his belief that the organic bodies combine with oxygen of the air, by a process of "decay," giving very simple compounds; in the absence of oxygen, the organic substances interact, giving rise to reduction processes, namely, those of "putrefaction," as a result of which there is a greater amount of residual organic matter than by the aerobic process. The two processes were believed to exclude one another. With such primitive ideas concerning the decomposition of organic matter in nature and without the proper recognition of the activities of living organisms in these processes, it is not surprising that the importance of humus in the soil was not sufficiently appreciated. Liebig's influence upon the subsequent development of the science of plant nutrition was so great that even at the present time many chemists have not freed themselves from some of his opinions on this subject.

With the development of the new science of microbiology, when the numerous functions of the microscopic forms of life inhabiting the soil, composts, bogs, and the sea began to be more clearly understood, new light was thrown not only upon the origin and chemical nature of humus, but also upon its rôle in plant nutrition. Although various microbiologists, especially Mitscherlich in 1850 and Pasteur in 1852-1860, began to recognize the importance of microorganisms as chemical

CHAPTER III

THE CHANGING CONCEPTIONS CONCERNING THE CHEMICAL NATURE OF "HUMUS" AND "HUMIC ACIDS"

"Man befindet sich in Bezug der Würdigung organischer Stoffe im Boden noch in der Kindheit und dieses ersieht man daraus deutlich, dass man sie durchgehends kollektiv nimmt."—MULDER.

"*Humus*" and "*humic acids*." The term "humus" has had varied usage, principally because very little was known concerning the complicated processes which lead to the formation of the dark colored organic substances in soils, in composts, and in water basins. Some of the most outstanding chemists of the 19th, and even of the early 20th century, considered that these processes were rather simple in type and were effected chiefly, if not entirely, by atmospheric agencies. Chemically, humus was usually believed to be very simple in composition and made up entirely of one or more substances acidic in nature; these were generally classified as "*humic acids*." Some investigators (654) believed that humus was a compound of "*humic acid*" and lime; in the process of plant nutrition, the lime was absorbed by the plant, leaving the "*humus in the soil as humic acid*."

The term "*humic acid*" was also used by different investigators to designate different preparations. This term was most frequently applied to that part of the organic matter of soils, peats, and composts which is soluble in alkali solutions. In some cases, the term was applied to only that part of the alkali solution which is precipitated by mineral acids. In view of the fact that a number of "*humic acids*" have been described, Oden (781) suggested that "*humic acid*" or "*humus acid*" should be used to designate only that part of the acid precipitate which is not soluble in alcohol, while the alcohol-soluble part was given the name "*hymatomelanic acid*." In most instances the various "*humic acids*" were not definite chemical compounds but rather represented preparations possessing certain common physical, chemical, and biological properties. Beginning with one compound "*isolated*" nearly a century and a half ago, more and more names were introduced to designate new "*humic acids*"; this was apparently the

result of an attempt to explain the seeming discrepancies in the nature of compounds isolated from different sources of humus by different manipulations. Conditions became more complex with the growth of chemistry and the development of better techniques for the separation of organic compounds. The various chemical formulae suggested at different times for the "humic acids" were, for the most part, hypothetical in nature.

The progress of our knowledge of the organic chemistry of soils, peats, and composts, or the chemistry of humus, is closely related to the changing conceptions of the origin and chemical nature of the "humic acids" and their related compounds.

The early period (1786-1826). The first historical reference to the isolation of a compound similar to that which became later known as "humic acid" dates to Achard (8), who, in 1786, extracted a brown substance from soil and peat, by the use of alkali solutions. Upon adding sulfuric acid to the alkali extract, he obtained a dark brown to almost black precipitate. Achard also recorded the fact that different layers of peat are chemically different in nature, and seem to have undergone varying processes or degrees of decomposition; different quantities of material were extractable from them by alkali solution.

In 1797, Vauquelin (1206) obtained substances similar in appearance and behavior from the stem of an old elm tree infected with fungi and from the bark of other trees and from peat. The precipitate formed when the alkali extract was acidified was again dissolved by means of alkali solutions; it also produced salts with calcium and other bases. Vauquelin did not name the substance thus prepared; this was done later by Thomson (1158-9), who suggested the name "ulmin," from the latin name of the elm tree (*Ulmus*). Klaproth (548) found a similar black substance in the alkali extract of the gum secreted by an old elm tree. In course of time the term "ulmin" came to be applied to all preparations which could be obtained by means of alkali extraction from soils, peats, coals, and even from plants, and which were black in color.

De Saussure (942) applied the term *terreau* to the dark-colored matter formed from dead plants under the influence of air and moisture; he also used another synonymous term, "humus," the Latin equivalent of soil, to designate this material. De Saussure noted that this humus was richer in carbon and poorer in hydrogen and oxygen than the plant material from which it originated. Einhof (263) introduced the term "acid humus" ("sauere Dammerde") to designate the humus

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of peats and swamps, as distinguished from "mild humus," which is rich in bases (1139).

The ideas of de Saussure concerning the origin and chemical nature of soil organic matter or soil humus were too advanced for his period and were soon forgotten. In an attempt to discover new "humic acids" and to determine their chemical nature and origin, no clear distinction was made between complexes formed under the natural conditions prevailing in soils, composts, and peats, and the dark-colored complexes formed by the interaction of certain organic compounds with acids and alkalies, usually at high temperatures. When carbohydrates are treated with concentrated acids, a dark colored mass is formed which is similar in certain properties to the "humic acids" of decomposing plant residues. This led a number of investigators to assume that both are the same chemically and that the natural complexes formed by the little understood process of "humification" are similar to the products which result from the treatment of carbohydrates with acids.

In 1819, Braconnot (147) submitted starch and sucrose to the action of hydrochloric and sulfuric acids; as a result of this treatment a dark liquid was obtained, which gave a black precipitate on dilution with water. This precipitate, which was soluble in alkalies, Braconnot called "artificial ulmin," since he believed it was analogous to the "natural ulmin" found in the diseased elm tree. Later Braconnot obtained "ulmin" on warming glucose with an alkali solution. He also extracted a substance which he believed was identical with "ulmin" from the rotted material found in the root cavities of an old elm tree; this was soluble in alkalies and precipitated by acids in the form of brown-black flakes. "Ulmin" was found not only in the rotted organic matter of trees but also in peat and even in lignite. Braconnot suggested that "ulmin" must doubtless be an important constituent of "terre d'ombre," but it could not be obtained from coal. He prepared "artificial humus" or "artificial ulmin," not only by treating various organic substances with mineral acids, but also by treating lignous material with potassium hydroxide. Colin (182) and Proust (852) believed that they demonstrated the presence of a brown substance similar to "ulmin" in the products of dry distillation of wood.

In 1822, Döbereiner (225) designated the dark colored fraction of the soil organic matter as "humus acid" ("Humussäure"). Since then the terms "humic acid" and "humus acid" have been used quite indiscriminately, and seldom was any differentiation made between the two;

when distinguished, the first term was usually considered to be more inclusive, comprising all of the "humic acids," whereas the second was applied only to a specific preparation obtained as the precipitate from the alkali extract by treatment with an acid. Wiegmann (1279), in one of the earliest papers on the chemistry of peats, referred to the substance thus extracted as "ulmin" or "humic acid," thus opening the way for a confusion that was bound to arise from a lack of differentiation between the brown and dark colored complexes found in decomposing wood, in composts, in soil, in peat, and in brown coal, or produced on treatment of carbohydrates and proteins with mineral acids or alkalies.

Sprengel and Berzelius (1826-1839). In 1826, Sprengel (1074) undertook a detailed study of the origin and chemical nature of the "humic acids" and their salts. It is surprising to find that many of Sprengel's ideas are still current in the textbooks on soil science, without due recognition being given to the investigator who first conceived them. According to Sprengel, "humic acid" is formed during the decomposition of plants, whereby a large part of the carbon combines with atmospheric oxygen and with some water; this process was believed to be similar to that which takes place when "humic acid" is formed on treatment of plant residues with potassium hydroxide. The bases enable the plant substances to remove the oxygen from the air. The plant materials are transformed in the process into "humic acids," for which all bases have considerable attraction. If the soil is rich in bases, the resulting "humic acid" is immediately bound; the soil will then react neutral and contain "mild humus." Such soil shows a high degree of fertility. The "humic acid" may be decomposed further to carbon dioxide and water. If the soil is poor in bases, the "humic acids" remain free and the soil becomes acid, because of the "acid humus," as in the case of peat soils formed from highmoor peats.

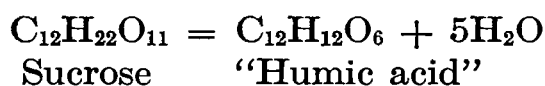
Sprengel treated dry peat with dilute acid to remove the bases still bound to the "humic acid." The residue was washed with water and digested for several days with ammonia, in a closed vessel. The dark brown solution was treated with hydrochloric acid, and a dark brown precipitate ("humic acid") was obtained. This was not a pure organic compound but contained some ferric hydroxide and clay. The precipitate was redissolved in sodium carbonate solution and reprecipitated in the cold with hydrochloric acid; heat was avoided so as to prevent the formation of a compound with iron oxide. The "humic acid" thus prepared had a high water-holding capacity, 100 parts of the moist

preparation leaving, on drying, only 5 parts of material which contained traces of ash. The dry residual substance had a shining black color and could easily be pulverized, breaking up into irregular pieces.

The freshly prepared, moist "humic acid" was insoluble in water as long as it contained some free mineral acid, but, as soon as the acid was completely washed out, the "humic acid" went into solution, coloring the wash water first yellow, then brown. It dissolved more readily in warm than in cold water, 6500 parts of ice cold water and only 150-160 parts of boiling water dissolving one part of "humic acid." When the water of hydration was removed by drying, freezing, or by means of an electric current, the "humic acid" again became insoluble in water. The "humic acid" which had been dissolved in water could be reprecipitated by all mineral acids, except phosphoric, and by all salts of alkali earths and heavy metals, except gold, giving rise to "humates." Precipitation could also be brought about by pulverized charcoal and partly by calcium and barium hydroxides. The "humic acid" thus obtained was negatively charged and acted as a stronger acid than carbonic, liberating silicic acid from silicates. It formed salts, giving soluble compounds with alkalies, whereas the salts of alkali earths and of heavy metals were insoluble. A solution of "humic acid" in potassium hydroxide treated with iron sulfate gave a precipitate of "iron humate"; compounds were also formed with aluminum hydroxide, from which the aluminum could be separated only with considerable difficulty. The various compounds thus produced were not constant in composition: some were acid, others basic or neutral in reaction. The methods developed by Sprengel for the preparation of "humic acid," for the study of its chemical composition and quantitative determination in soils, were generally adopted and used until recent years.

In 1830, Boullay (139) made a chemical analysis of the dark colored material obtained by treatment of sugar with mineral acids. He calculated that "artificial ulmic acid" (having thus changed the name of Braconnot's "artificial ulmin") had a chemical composition of $C_{30}H_{30}O_{15}$. Malaguti (669) suggested an explanation for the transformation of the carbohydrates by mineral acids into compounds similar to those produced under natural conditions in soils, peats, and composts. He stated that nitric acid changes sugar into oxalic acid, whereas hydrochloric and sulfuric acids give partly "humic acid," which is soluble in alkalies, and partly "ulmin," which is insoluble in alkalies. Concentrated acids act more energetically than weak acids.

Under the influence of the acid, the sugar loses water, giving first a compound of the structure $C_{12}H_{28}O_{14}$, which changes to "humic acid" and finally to formic acid. The mechanism of formation of the "humic acid" was illustrated as follows:



Stein (1092) proposed the formula $C_{24}H_{18}O_9$ for the "humic acid" obtained by the action of hydrochloric acid upon sugar. Berzelius (112) adopted later another formula, namely $C_{32}H_{32}O_{16}$, for this preparation.

Berzelius recognized the importance of the investigations of Sprengel but he was misled by the ideas of Boullay and Malaguti concerning the formation of "humic acids" from carbohydrates by acid and alkali treatments. He distinguished two dark brown bodies: 1. A substance soluble in alkalies, which gave a dark brown precipitate when the alkali was neutralized by an acid (the "humic acid" of Sprengel), was first called "mylla," then "geic acid," and finally "humic acid". 2. The other substance, which was insoluble in alkalies (the "humus coal" of Sprengel), he designated first as "mull coal" and later as "humine." Berzelius recognized that the term "ulmin" was being used for a variety of substances probably possessing marked chemical differences; the complexes extracted from the soil by the use of an alkali solution, for example, probably have no special relation to those which are extracted from an elm tree or from other plants. He called attention to the futility of designating by one name bodies only little investigated and possessing a certain superficial similarity.

In 1833, Berzelius isolated from mineral waters and later from slimy mud rich in iron oxide, two new compounds which he designated as "crenic acid" and "apocrenic acid." These complexes were believed to be present also in plants and in soil. They were prepared by extracting the material with hot potassium hydroxide solution; the alkali solution was then saturated with acetic acid, and copper acetate added; the brown colored precipitate was designated "copper apocrenate." When the free acetic acid was neutralized with ammonium carbonate, a grayish green precipitate, called "copper crenate," was formed. When the copper compounds were decomposed with hydrogen sulfide, the "free acids" were brought into solution. Under the action of air, the "crenic acid" in solution was believed to be oxidized to "apocrenic acid." The "crenic acid" preparation was soluble in water and in

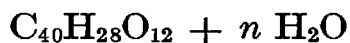
alcohol and formed insoluble compounds with silicic acid and with aluminum hydroxide. The "apocrenic acid" preparation was similar in its properties to "crenic acid" but was dark colored and was only partly soluble in water and in alcohol; it could be precipitated from its aqueous solution with inorganic acids and with ammonium chloride, and formed compounds with aluminum hydrate. The salts of these compounds with alkalis, with magnesium, with iron, and to some extent the salts with calcium were soluble in water. When Berzelius (113) investigated the "humic acid" of a rotting oak tree he could hardly distinguish it from "apocrenic acid." He suggested that "crenic" and "apocrenic acids" are formed in the decomposition of organic matter in general and in the rotting of wood in particular; fallowing of soil and cultivation give rise to "humic substances" which are assimilable by plants; when coal is acted upon by nitric acid, "crenic" and "apocrenic acid" are produced. Different formulae were suggested for these two preparations, namely $C_{24}H_{12}O_{16}$ and $C_{24}H_6O_{12}$.

Peligot (812) was the first to demonstrate that "artificial humic acid" varies chemically from "natural humic acid," the former containing 62 per cent carbon, and the latter, only 57 per cent. However, these analyses were not sufficiently conclusive to establish the difference between the two preparations, since, as will be shown later, the carbon content varies considerably in both artificial and natural complexes, depending upon the nature of the material used and the methods employed in their preparation.

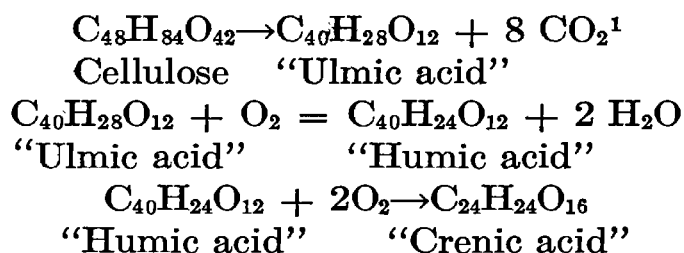
Mulder-Hermann (1839-1862). Beginning with 1839, there appeared a series of papers by Mulder (731-734), a pupil of Berzelius, concerning the formation of brown and black substances by the action of acids upon carbohydrates. The various preparations were separated into two groups on the basis of their color and solubility in alkalis: 1. brown bodies, or the alkali-soluble "ulmic acid" and alkali-insoluble "ulmin"; 2. black bodies, or the alkali-soluble "humic acid" and the corresponding alkali-insoluble "humin." The first group was believed to be somewhat richer in carbon.

According to Mulder, in the decomposition of plant substances, the organic matter is first changed to "ulmic acid" and to "ulmin," which are presumably found in dead leaves, rotting wood, and brown peat. On oxidation or on boiling with acid or with alkali solutions, oxygen is absorbed by the "ulmic acid" and the "ulmin"; this results in their transformation to "humic acid" and "humin"; on further oxidation, the "humic acid" is changed to "crenic acid" and finally to "apocrenic

acid," gradually giving rise to products continuously poorer in carbon. "Apocrenic acid" was reduced by nascent hydrogen to "crenic acid," and the latter was oxidized again by the oxygen of the air to "apocrenic acid." The "ulmin" and "ulmic acid" were believed to represent a group of bodies of the general formula,



n being 1, 2, 3, or higher. Mulder suggested that the following reactions are involved in the formation of "humic bodies" from plant constituents:



The humus preparations were dried at 140–195°C., a temperature sufficiently high to modify their chemical nature, hence the formulae suggested were practically meaningless. Mulder believed that "humic acids" are compounds of carbon, hydrogen, and oxygen, the latter two in a ratio of two to one as in water; nitrogen, which is always present in the "humic acid" preparations obtained from peat and soil, was looked upon as an impurity largely present in the form of ammonia. Mulder recognized later (735) that the nitrogen in "humic acid" is in the form of a protein, which remains in the soil for a long time as an impurity of the latter. Mulder described a number of new preparations called "glucic acid," "apoglucic acid," "chlor-humic acid," "humonitric acid," etc. These names were later abandoned, in preference to Berzelius' classification.

The complex terminology of the "humic acids" and the lack of understanding of the process of humus formation introduced considerable confusion during the middle of the last century. To summarize, it is sufficient to quote from Mulder himself: "rotting wood contains, at the beginning of the process of rotting, crenic, apocrenic and ulmic acids; if free air is admitted, the crenic acid disappears and is changed to apocrenic. The cellulose is changed to ulmin and ulmic acid, which, under the influence of air, are changed to humin and humic acid." These and similar ideas concerning the mechanism of decomposition

¹ No attempt is made to balance these reactions, since they are highly hypothetical.

of plant residues and their transformation into humus could not but exert an influence of extreme disorder upon the subsequent development of the subject.

These ideas influenced Liebig (638), who stated that humus is formed from plant residues by a process of "eremacausis," or slow combustion, whereby the plant bodies, especially substances which contain nitrogen, absorb oxygen and are slowly converted into humus. However, Liebig clearly recognized the limitations of the study of "humic acids" and their bearing upon our knowledge of the origin and chemistry of humus. He stated definitely in 1840 that "humic acid of chemists is a product of the decomposition of humus by alkalis; it does not exist in the humus of vegetable physiologists." Berzelius and Mulder, as well as Liebig, believed that "humic acids" are not present in a free state in the soil, but that they exist in the form of neutral bodies, largely as "ulmin" and "humin." When the insoluble bodies are washed with water and extracted with alkali solutions, they are partly dissolved, giving rise to the corresponding "ulmic acid" and "humic acid." Mulder emphasized that "natural humic acids" can be distinguished from "artificial humic acids" by the fact that the latter are totally insoluble in certain alkali salts, whereas the former are partly soluble in potassium nitrate and sulfate, and completely soluble in potassium acetate solution. Several years later, S. Johnson (507) found that if the soil is treated continuously with sodium carbonate solution, all the "humus" can be brought into solution. This led Johnson to express his doubts concerning the existence of "ulmin" and "humin," as distinct from "ulmic acid" and "humic acid."

A most extensive study of the dark colored compounds obtained from soil, peat, and coal, or prepared artificially in the laboratory, was made by Hermann (422-424). The humus bodies were divided into three main groups:

I. Substances soluble in alkalis and precipitated by mineral acids:

1. "Humic acids" of the type $C_{30}H_{30}O_{15}$, insoluble in sodium acetate solution and precipitated by all acids:
 - (a) "anitro-humic acid," $C_{30}H_{30}O_{15}$, free from nitrogen and prepared from sugar;
 - (b) "sugar-humic acid," $C_{30}H_{30}O_{12}N_3$, containing nitrogen and prepared from sugar;
 - (c) "ligno-humic acid," $C_{30}H_{60}O_{12}N_6$, prepared from rotten wood by extraction with alkalis and precipitation with acids;
 - (d) "meta-ligno-humic acid," $C_{50}H_{50}O_{12}N_5$, produced by boiling freshly prepared "ligno-humic acid" with water.

2. "Aprocronic acids" containing less water and more carbon. These are soluble in alkali acetate solutions, with the liberation of acetic acid, and are not precipitated from alkali solutions with acetic acid; the "apocronic acid" of Berzelius belongs to this group. These complexes were separated on the basis of their nitrogen and oxygen content:
- "torfic acid" and "apo-torfic acid," $C_{20}H_{34}O_6N_4$, found largely in peat, in soil, and in brown coal;
 - "arvic acid" and "apo-arvic acid," $C_{30}H_{48}O_6N_{12}$, with special reference to the "Tula-arvic acid" and "Siberia-arvic acid";
 - "Porla-apocronic acid," obtained by Berzelius from a Porla well (384).

II. Humus substances soluble in water:

- "Humous extract," $C_{16}H_{32}O_7N_2$. The "humous extract" was considered to be a body that remains in solution, when the alkali extract of a soil has been treated with acetic acid and with copper acetate, to remove the bodies belonging to Group I and the "cronic acid." When this extract was treated with lead nitrate and ammonia, a precipitate was formed giving a "chestnut-brown, shiny transparent substance, having a bitter taste." It was soluble in 80 per cent alcohol and in ether, and could be precipitated with various salts and acids as a brown mass of the nature of a waxy substance. With barium and calcium it gave brown compounds, soluble with difficulty. It was precipitated with basic lead oxide and copper acetate, even in the absence of ammonia, and was thus distinguished from "cronic acid."
- "Cronic acid" remained in solution when the alkali extract of a soil was acidified with acetic acid and when copper acetate was added; when this liquid was treated with an excess of ammonia, the "cronic acid" was precipitated. Hermann distinguished several cronic acids; namely, "ligno-cronic acid," $C_{18}H_{18}O_9N_2$, obtained from wood; "humo-cronic acid," $C_{18}H_{36}O_9N_4$, from a chernozem soil; "torfo-cronic acid," $C_{15}H_{48}O_{12}N_4$, from peat; "anitro-cronic acid," $C_{15}H_{24}O_{14}$, free from nitrogen. On further oxidation, these "acids" changed into the corresponding "oxycronic acids"; during this process of oxidation they were believed to be able to absorb nitrogen from the air; they were distinguished from the "cronic acids" by being precipitated with lead and copper salts, even in the presence of a slight excess of acetic acid. The formula for "torf-oxycronic acid" was given as $C_{12}H_{12}O_4N_4$.

III. Humus substances insoluble in water and in alkali solutions:

- "Anitrohummin."
- "Nitrohummin."
- "Nitrolin."

The first two complexes were those previously designated by Sprengel as "humus coal" and by Berzelius and Mulder as "humin." Hermann separated them on the basis of their nitrogen content. "Anitrohummin" was prepared from sugar and was, therefore, nitrogen-free. "Nitrohummin" contained nitrogen because it was obtained from soil. The third complex, "nitrolin," was discovered by Hermann in nitrogen-rich wood, the specific name originating from the words "nitrogenium" and "lignum," meaning nitrogen and wood respectively. The rotted wood was ground and washed with water; the material which settled in the water was boiled with potassium carbonate solution; the "nitrolin" did not go into solution; it was insoluble in water, alkalies, and acids and contained 12 per cent nitrogen.

On the basis of the aforementioned complexes, Hermann reported the following composition of peat in the vicinity of Moscow:

Peat-carbon, nitrolin and plant remains.....	77.5	per cent
"Humic acid".....	17	per cent
"Humic extract".....	4	per cent
Ammonia.....	0.25	per cent
"Crenic acid".....		trace
Ash.....	1.25	per cent

A chernozem soil yielded 89.58 per cent inorganic matter, 1.66 per cent nitrolin, etc., 1.77 per cent "humic acid," 3.1 per cent "humic extract," 1.77 per cent "torfic acid," 2.12 per cent "crenic acid."

All these designations which have been applied to preparations obtained from soil and peat, or from sugars by treatment with mineral acids, could have been multiplied *ad infinitum*, the limit being only the number of soils that one would care to extract. But even more fantastic than the names, were the ideas of Hermann concerning the origin of all these complexes. It is sufficient to call attention to the fact that he was firmly convinced that all plants obtain their nitrogen from the atmosphere, and that even the artificially prepared "humic acid" and "humin" can absorb nitrogen. When the "humic acids" are changed to "crenic" and "oxycrenic" acids, more nitrogen is absorbed. This conception was quite wrong, since most of the nitrogen found in these preparations originated from the nitric acid and ammonia which were used extensively in their extraction and precipitation. Senft (996) actually suggested that most of the nitrogen in the soil is present largely as ammonia, combined with the "humic acids."

These ideas were severely criticized by Mulder and, although Her-

mann (425) soon replied, Mulder disregarded his statements completely in his book on soil chemistry (735). In view of the fact, however, that Mulder also disregarded the very excellent work of Sprengel, Baumann (74) accused Mulder of overlooking the work of Sprengel and Hermann, in order to place in the foreground his own much inferior work. Baumann further emphasized the fact that in spite of certain repetitions and confusions in terminology (such as naming the "humic acid" of Berzelius, "torfic acid"; the "apo-crenic acid," "oxy-crenic acid"; and the "ulmic" and "humic acids" of Mulder, "anitra-humic" and "sugar-humic" acids) in Hermann's work, his manipulations and chemical analyses should deserve greater consideration than Mulder's ideas of separation of the humus complexes on the basis of brown and dark colors.

In addition to the "acids" of Mulder and Hermann, numerous others have been described, including: "mudesous acid," $C_{12}H_{10}O_8$, of Johnston (508); "carbo-ulmic acid," $C_{40}H_{36}O_{16}$, obtained by Herz (517) from lignite; "silico-azo-humic acids" which, according to Thénard (1148), are formed spontaneously in the soil from the "humic acid," from the ammonia in rainwater, from the nitrogen of the air, and from the silica in the soil (517).

The rapid increase in the number of preparations isolated from decomposing plant residues and from humus formations and described as "humic acids," as well as the growing confusion in the terminology of these various preparations, was largely due to the insufficient knowledge of the processes of decomposition of plant and animal residues in nature.

On the other hand, the use of words and symbols where ideas and facts were lacking has contributed further to the lack of understanding of the processes underlying humus formation, and, therefore, of the chemical nature of humus itself. It is sufficient to cite the following ideas of Souberian (1069) presented in 1850: "decomposed wood (*Dammerde*) consists of a mixture of pure 'humus,' some 'calcium humate,' and a substance which changes into humus, under the influence of alkalies, in the presence of air; the same is true for soil and peat, accompanied by a rapid absorption of oxygen by the organic matter kept in contact with ammonia. The favorable effect of bases upon acid peat is due to the transformation of the alkali-insoluble 'humus' into alkali-soluble 'humic acid.' "

The science of microbiology, which alone could elucidate those processes, was still non-existent. It is interesting to note that even at an

early stage of the development of our knowledge of the activities of microorganisms, suggestions were made concerning their contribution to the processes of humus formation. Braconnot, for example, reported in 1838 that the body of the fungus *Agaricus atramentarius* contains "humic substances." Similar suggestions were made for *Uredo segetum* by Lucas (655), who believed that the "humic" material in the spores of the fungus is formed from starch through the life activities of the organisms. A specific "acid" occurring in fungi upon decomposing wood has later (1088a) been described as "polyporic acid."

With an increasing understanding of the chemistry of plant products and their transformation by microorganisms, the chemistry of humus was bound to become better understood. A similarity was observed between tannins and a substance designated as lignoin, found in the old bark of trees; this lignoin was found to possess most of the properties characteristic of "humic acid" and was, therefore, believed to serve as a source of "humus" in nature. This idea was confirmed by Hesse (429), who found a parallelism between the transformation of the quinine and cinchonine in the bark of the quinine tree into lignoin and the formation of "ulmic acid" from sugar by the use of mineral acids. The presence of humus-like compounds in plants was demonstrated by Thénard (1149), who extracted "humus" from saw-dust by means of ammonium hydroxide; he further (1146) emphasized the rôle of these compounds in the composting of stable manure. Millon (790) isolated a similar preparation from wood carbonized at 330°C.

The synthesis of dark colored substances resembling humus from a variety of organic compounds continued. Berthelot (101) found that, when a mixture of alcoholic alkaline hydroxide is warmed with carbon tetrachloride in a closed vessel, substances similar to "humic acid" are obtained. According to Hardy (391), a mixture of chloroform and acetone, under the influence of sodium carbonate, gives a brown substance similar to "humic acid." This preparation was described as "acet-ulmic acid" of the composition $C_{14}H_{12}O_4$; it was easily converted to "dioxy-acet-ulmic acid," $C_{14}H_{10}O_8$. Liebig found (638) that an alkaline solution of lactose and tannin on standing in contact with air, gives rise to "humic compounds." Lefort prepared (616) from rotting wood a substance which he called "xylyl acid," of the formula $C_{24}H_{30}O_{17}$.

The relationship of nitrogen to the process of humus formation was especially confusing to a number of investigators, since nitrogen was found in some preparations and was either absent or present in small amounts in others. The common idea prevailed that nitrogen is pres-

ent in the humus in the form of ammonia, giving a salt with the non-nitrogenous "humic acid." Thénard (1145, 1150) emphasized the rôle of nitrogenous substances in the origin of humus. He suggested the name "funic acid" for the humus present in stable manure, in which nitrogen is known to play an important part; "funic acid" was also extracted from cultivated soil, but it was then found to contain only little nitrogen, much carbon, and certain amounts of hydrogen and oxygen. Mulder (735), however, believed that "funic acid" is merely an ammonium salt of "humic acid," in other words, "ammonium humate."

An insufficient knowledge of the chemical composition of plant and animal residues undergoing decomposition, a total lack of appreciation of the importance of microscopic forms of life in the processes of decomposition, and the failure to recognize the changes that take place in the various constituents of the plant and animal residues as a result of decomposition, were largely responsible for the failure to recognize the exact nature of humus. The introduction of the concept of the existence of specific "humic acids"; the description of an ever-increasing number of these acids; the use of formulae based merely on elementary analysis and on preconceived ideas concerning the simplicity of these compounds; the generalization that dark colored substances found in decomposing plant materials, in peat, and in soil are the same as those produced by heating carbohydrates with acids—all tended to further confuse the subject and introduce complications at a time when information on basic principles was still lacking.

Detmer-Hoppe-Seyler (1871–1889). In contradistinction to the ideas of the earlier workers concerning the multiplicity of humus substances soluble in alkalis and precipitated by acid, Detmer (219) came to the conclusion that all these preparations represent only one such substance. This can be obtained from soil or peat and can be prepared artificially from sugar; the formula $C_{60}H_{54}O_{27}$ was suggested for this compound, which was designated as "humic acid," while the name "humus acid" was reserved for those compounds which are soluble in water. The nitrogen present in the "humic acid" was still considered to be an impurity, and every possible effort was made to remove it. Peat was extracted with potassium carbonate solution for 48 hours; the extracted portion was precipitated with a mineral acid; this process was repeated by extracting the precipitate again with potassium carbonate solution and by reprecipitating and washing the precipitate with boiling dilute acid and with hot water. The preparation thus obtained was finally dissolved in ammonium hydroxide solution, and the calcium, mag-

chemical decomposition of a portion of the original precipitate, largely the nitrogen-free fraction. Eggertz considered nitrogen to be an essential constituent of the "humic acid molecule"; he also found that this "molecule" contains sulfur and iron. The iron could not be demonstrated with ordinary reagents in aqueous solutions of "humic acid," and sulfur was obtained only on complete oxidation of the organic complex. Phosphorus and other mineral constituents of the living cell were also believed to be present.

Eggertz doubted the existence in nature of "humic acids" and "ulmic acids," and considered them to be mere laboratory preparations; it was believed that they are formed, as previously suggested by Mulder, on treatment of the organic matter with alkalis. "Crenic acid" and "apocrenic acid" were looked upon as independent bodies, but they were not isolated. Eggertz distinguished between "mull" and "humus" complexes; the former embraced those bodies which originate in nature through the decomposition of organic residues, whereas the latter were said to include the artificial preparations obtained on treatment of sugar with acids. The natural bodies were shown to be distinctly different in chemical composition from the artificial preparations obtained in the laboratory from carbohydrates by treatment with acids and alkalis: the former were found to contain nitrogen and minerals; their salts were soluble in acetic acid, and the ammonium compounds were soluble in water; when obtained by extraction with cold alkalis, they gave preparations poorer in carbon than the artificial complexes (708); their carbon content increased on boiling with acids.

Dehérain (208) suggested that the potassium hydroxide extract of "humus" from old wood can absorb nitrogen from the air. Similar claims for "natural humic acids" were made by other investigators (1150, 1032, 803, 850, 1180). The hypothesis was thus advanced that "humic acid" provides available nitrogen in the soil. Simon (1033) suggested the following reaction for this process:



These claims were denied by Schloesing (947), who definitely established that the organic substances of the soil are not responsible for the direct fixation of nitrogen; the increase in nitrogen reported in such cases was believed to be due to the absorption of ammonia from the air by the organic substances.

Eichorn (261) isolated "humic acid" from peat by extraction with sodium carbonate and precipitation with hydrochloric acid. This

preparation, when washed and dried, contained 0.16 per cent ash and 4 per cent water. When 4 gm. was treated with 50 cc. of a 2 per cent ammonium chloride solution for 4 days in the cold, 0.025 gm. of free hydrochloric acid was liberated. However, when peat, previously washed with dilute hydrochloric acid and water to remove the bases, was used even more free acid was liberated from the NH_4Cl . The liberation of free acids from such salts, as phosphates, by "humic acids" was first demonstrated by Sprengel in 1826. Eichorn found that 100 gm. of "humic acid" decomposed 11.4 gm. of calcium phosphate in guano, making all the phosphate soluble.

These results were confirmed and further extended by Fleischer (301), Kissling (546), Hess (428), and others. It was usually assumed that the liberation of phosphoric acid on treatment of phosphate with peat is due to free "humic acid," of the sort believed to be present in highmoor peats in the absence of bases. Fleischer observed that the upper layers of the peat bog possess the greatest ability to liberate phosphoric acid. Different soils, however, exerted different effects on treatment with salts, which led to the conclusion that the acid-replacing complex is not the same in all soils. This led to a revival of the age-old questions concerning the chemical identity of the various "humic acids" (75).

There were also new speculations concerning the "artificial humic acids" and their unqualified comparison with natural bodies. Grote and Tollens (374) found that on boiling sucrose with sulfuric acid, levulinic acid is produced from the levulose part of the sugar. Sestini observed (997-999) that in this process substances are formed which appear under the microscope as small spherical bodies, 2 to 8μ in diameter; these particles may conglomerate to give rise to irregular clumps. He designated these formations as "sacculmin," which was not considered to be a chemical compound, but rather a mixture of various substances. After being boiled with acid, it was soluble in alkalis and gave rise to "sacculmic acid." "Sacculmin" was considered to be the anhydride of "sacculmic acid" $(\text{C}_{11}\text{H}_{10}\text{O}_4)_n$. The latter contained 63.72 per cent carbon and 4.64 per cent hydrogen, whereas the former $(\text{C}_{44}\text{H}_{38}\text{O}_{15})$ contained 65.5 per cent carbon and 4.8 per cent hydrogen. Natural "humic acids" yielded much more furfural than did the artificial preparations.

The observations of Sestini were confirmed by Früh (321), who found, however, that the particles of "sacculmin" measured only about 1μ in diameter and approached the natural humus compounds

hydroxide solution; on acidification with hydrochloric acid, a precipitate was obtained which was purified by redissolving in an alkali solution and reprecipitating with an acid. The final preparation was partly soluble in 85 per cent alcohol; the soluble part contained 62.2 to 63.7 per cent carbon, whereas the insoluble part contained only 57.5 to 57.8

TABLE 1
Formation of artificial "humic substances" from carbohydrates

MATERIAL	ACID	CON- CEN- TRA- TION OF ACID	TEM- PERA- TURE	TIME	YIELD	AUTHOR
		<i>per cent</i>	<i>°C.</i>	<i>hours</i>	<i>per cent</i>	
Cane sugar	HCl	9-10	100	17	20	Conrad and Gutzeit (187)
Glucose	HCl	9-10	100	17	9.5	Conrad and Gutzeit
Fructose	HCl	9-10	100	17	20	Conrad and Gutzeit
Galactose	HCl	9-10	100	17	16	Conrad and Gutzeit
Arabinose	HCl	9-10	100	17	41	Conrad and Gutzeit
Lactose	HCl	9-10	100	17	18	Conrad and Gutzeit
Cane sugar	HCl	conc.	100	..	15.6	Berthelot (101)
Glucose	HCl	6.2	100	28	2.6	Berthelot
Glucose	HCl	12.3	100	28	8.5	Berthelot
Glucose	HCl	conc.	100	24	54.3	Berthelot
Glucose	HCl	conc.	100	55	89.0	Berthelot
Glucose	H ₂ SO ₄	8.5	100	28	1.4	Berthelot
Glucose	H ₃ PO ₄	50	100	115	16.9	Berthelot
Glucose	H ₃ PO ₄	50	100	168	23.1	Berthelot
Glucose	H ₃ PO ₄	50	100	644	23.6	Berthelot
Fructose	HCl	conc.	100	24	56.4	Berthelot
Maltose	HCl	12.5	100	24	7.1	Berthelot
Maltose	HCl	conc.	100	24	54.7	Berthelot
Cane sugar	H ₂ SO ₄	40	65	3	3	Eller (264, 265)
Glucose	H ₂ SO ₄	50	70	5	2	Eller
Lactose	H ₂ SO ₄	40	65	3	10.5	Eller
Cellulose	H ₂ SO ₄	conc.	70	1	20	Eller
Starch	HCl	10	100	62	10	Fuchs (331)

per cent carbon. The two preparations differed chemically from "artificial humic acid" obtained from sugars.

On the basis of his study of the colloidal properties of the organic matter of the soil, Van Bemmelen (86) concluded that all attempts to separate the humus substances into various chemical complexes were so far unsuccessful. "Humin" and "ulmin," "humic acids" and "ulmic acids," as well as all the other so-called "acids" were not true

hydroxide solution; on acidification with hydrochloric acid, a precipitate was obtained which was purified by redissolving in an alkali solution and reprecipitating with an acid. The final preparation was partly soluble in 85 per cent alcohol; the soluble part contained 62.2 to 63.7 per cent carbon, whereas the insoluble part contained only 57.5 to 57.8

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Galactose	HCl	9-10	100	17	16	Conrad and Gutzeit
Arabinose	HCl	9-10	100	17	41	Conrad and Gutzeit
Lactose	HCl	9-10	100	17	18	Conrad and Gutzeit
Cane sugar	HCl	conc.	100	..	15.6	Berthelot (101)
Glucose	HCl	6.2	100	28	2.6	Berthelot
Glucose	HCl	12.3	100	28	8.5	Berthelot
Glucose	HCl	conc.	100	24	54.3	Berthelot
Glucose	HCl	conc.	100	55	89.0	Berthelot
Glucose	H ₂ SO ₄	8.5	100	28	1.4	Berthelot
Glucose	H ₃ PO ₄	50	100	115	16.9	Berthelot
Glucose	H ₃ PO ₄	50	100	168	23.1	Berthelot
Glucose	H ₃ PO ₄	50	100	644	23.6	Berthelot
Fructose	HCl	conc.	100	24	56.4	Berthelot
Maltose	HCl	12.5	100	24	7.1	Berthelot
Maltose	HCl	conc.	100	24	54.7	Berthelot
Cane sugar	H ₂ SO ₄	40	65	3	3	Eller (264, 265)
Glucose	H ₂ SO ₄	50	70	5	2	Eller
Lactose	H ₂ SO ₄	40	65	3	10.5	Eller
Cellulose	H ₂ SO ₄	conc.	70	1	20	Eller
Starch	HCl	10	100	62	10	Fuchs (331)

per cent carbon. The two preparations differed chemically from "artificial humic acid" obtained from sugars.

On the basis of his study of the colloidal properties of the organic matter of the soil, Van Bemmelen (86) concluded that all attempts to separate the humus substances into various chemical complexes were so far unsuccessful. "Humin" and "ulmin," "humic acids" and "ulmic acids," as well as all the other so-called "acids" were not true

chemical substances, the various chemical formulae attached to them being absolutely valueless. He believed that these complexes, possessing an amorphous and colloidal nature, originated from the colloidal substances in the plants, through chemical changes and molecular modifications, the nature of which was not yet understood.

Hoppe-Seyler (459) distinguished three groups of humus substances on the basis of their solubility in alkalies and in alcohol: 1. Complexes insoluble in alkalies and in alcohol; here belong Mulder's "ulmin" and "humin." 2. Substances soluble in dilute alkalies and precipitated by acids, in the form of a voluminous mass with a high water content, and insoluble in alcohol; here belong "humic acid," "ulmic acid," and certain tannins. 3. Substances soluble in alkalies, becoming soluble in alcohol on precipitation and washing with water; when the alcohol is distilled off, they form a brittle mass which can be melted on warming with water, but they are no longer soluble in alcohol; here belong certain tannins and the alcohol-soluble part of "humic" and "ulmic acids," namely, "hymatomelanic acid." The preparations belonging to groups 1 and 2 became alcohol-soluble on melting with an alkali, such as caustic potash.

Hoppe-Seyler studied both artificial and natural products and found that on treatment of organic bodies with alkalies, dark colored substances are produced only in the presence of air, whereas on treatment with acids, dark colored complexes result even in a hydrogen atmosphere. Pyrogallol, pyrocatechuic acid, pyrocatechin, quinone, and other aromatic compounds also give dark colored substances as a result of oxidation. In the natural decomposition of plant residues, lignin complexes were found to take an active part in the production of "humic acid." Wood gum or xylan was also found in an unchanged state in soils high in organic matter, and was therefore considered as an important constituent of the group of alkali-soluble and acid-precipitated substances. Hoppe-Seyler thus established the fact that a great variety of plant constituents can give rise to "humic matter"; he also pointed a new way of approach to the study of the origin and chemical nature of the dark colored substances of the soil.

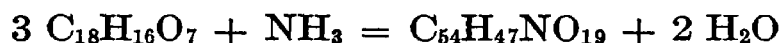
The ideas of van Bemmelen concerning the colloidal nature of the humus complexes, the contributions of Hoppe-Seyler concerning the chemical composition of the plant residues and the rôle of the various chemical constituents in the formation of the humus complexes, and the results obtained by Hébert (408) and Dehérain (209), discussed in detail later, concerning the rôle of microorganisms in decomposition

processes and in humus formation are by far the three most outstanding contributions to our knowledge of the origin and chemistry of humus made during the last half of the 19th century. It was essential, however, to combine these ideas in order to establish the true nature of humus. This was left for the 20th century. Before this was done, however, numerous contributions were made to the "humic acid" conception of humus.

Berthelot and André-Baumann and Gully (1891-1912). Berthelot and André (104-107) made another attempt to characterize artificial and natural dark colored substances as definite "humic acids." They believed that the practically insoluble dark brown material, which is formed on boiling sugar with hydrochloric acid, is an anhydride of "humic acid" and not a mixture of substances. When this anhydride is treated with a dilute alkali solution, a part is made soluble, with the formation of soluble basic salts, while the larger part gives rise to an insoluble acid salt; on treatment with dilute hydrochloric acid, both the insoluble and the soluble "salts" are decomposed with the formation of a mixture of an anhydride and a hydrate. This "anhydride of humic acid" contained 66.41 per cent carbon and 4.57 per cent hydrogen and was given the formula $C_{18}H_{14}O_6$; it was exactly the same preparation which was previously considered as "humin." Under the influence of water, the anhydride was believed to change partly to the hydrated form of "humic acid," namely, $C_{18}H_{16}O_7$. This preparation could also be obtained by dissolving the anhydride in alkalis and by precipitating it with hydrochloric or sulfuric acid. Since the hydrate lost water even at ordinary temperature, all preparations which were not dried quickly at low temperatures were believed to represent mixtures of the anhydride and hydrate.

Three series of salts were recognized as being formed by reactions between "humic acid" and alkalis: 1. monobasic salts, insoluble in cold water even after prolonged action; 2. tribasic salts, also insoluble in, but gradually decomposed by, cold water; 3. salts with an excess of base, soluble in water. The monobasic or acid salt, when dried at $100^{\circ}C.$, gave a black, horny, shining mass, corresponding in composition to $C_{18}H_{15}O_7K + H_2O$. The water could be removed on drying. The salt was insoluble in water and absorbed base from an alkali solution; it was only slightly soluble in hot water. Under the action of strong mineral acids, it was completely decomposed with the formation of "humic acid." The tribasic acid was given the formula $C_{18}H_{13}O_7K_3 + nH_2O$. Its formation took place on treatment of "humic

acid anhydride" with cold, dilute alkali solution for several days, followed by filtration; the insoluble tribasic salt remained on the filter. Only the salts of sodium and potassium could be thus obtained. When ammonia was used to form the salt, and the complex was washed with water, most of the ammonia went into solution, but a part was still left in the precipitate and could not be removed even by treatment with magnesium oxide. This was believed to be due to the formation of an acid amide, according to the following reaction:



When the anhydride was heated with ammonia in closed vessels, at 100°C. for two hours, preparations were obtained containing a greater concentration of amide nitrogen, in a stable form. Berthelot and André suggested that these reactions indicate that "humic acids" are acid- and alcohol-anhydrides corresponding to lactones.

Berthelot and André (40) definitely disproved the earlier ideas of Mulder, Hermann, and others concerning the absorption of nitrogen from the air by "humic acids." However, all their attempts to apply the results obtained from the study of artificial "humic acids" to natural materials found in soils or in composts failed completely. The fact that they also overlooked the contributions of previous investigators to this subject did not tend to add more weight to their unjustified generalizations.

In 1896, Benni (92) stated that he could "humify" soluble carbohydrates by the use of oxidizing agents, such as permanganate (867). However, v. Feilitzen and Tollens (286) demonstrated that Benni's conclusions were completely wrong, since the brown precipitate which he obtained and which he designated as "humic acid" was nothing more than precipitated manganic oxide. Wollny (1300) considered that all humus substances are dehydrated carbohydrates, because they are richer in carbon.

Adolf Mayer (684) reported that "humic acid" prepared from sandy soil contains considerably more nitrogen and carbon than does a similar preparation from an ortstein soil. Baumann suggested that these differences appeared because the two soils were not extracted at the same temperature. Miklausz (708) found that when peat is treated first with alcohol to remove the resins, then with hydrochloric acid to remove the bases, and finally with alkalis, certain organic complexes of the nature of "humic acids," which would otherwise have remained insoluble, go into solution. When the alcohol-insoluble "humic acid"

is dissolved in an alkali solution and precipitated by mineral acid, it becomes partly alcohol-soluble, the degree of solubility depending on the concentration of the alkali and on the time of action. The carbon content of alcohol-soluble preparations is higher than that of the initial material. The alcohol-insoluble portion is also changed by the alkali treatment, since a larger part becomes soluble in pyridine than previous to treatment. The chemical composition of "humic acids" from peat is changed considerably if the peat is previously boiled with hydrochloric acid, as shown by an increase in the carbon and a decrease in the hydrogen content. Such results as these raised further doubt as to the definite chemical composition of the "humic acids."

Malkomesius and Albert (670) used lithium carbonate in the extraction of "humic acids" from Cassel brown. Preparations were obtained which, even after treatment with concentrated nitric acid, still contained 0.82 per cent ash; this consisted of iron, aluminum, calcium, magnesium, potassium, sodium, and sulfur. The carbon and hydrogen content of these preparations was about the same as that reported by Detmer (220) for the "humic acid" from peat. According to Schermbeck (946), these preparations consisted largely of waxes and resins.

Robertson and his associates (896) demonstrated that, although considerable uniformity existed in the composition of different specimens of artificial "humic acid" obtained from cane sugar, the carbon content (64.72 per cent) was considerably greater than that of preparations obtained by alkali extraction of peat (54.48 per cent carbon). The natural substances also had a higher hydrogen content and a considerable amount of combined nitrogen. On the other hand, the methoxyl content of the natural preparations was much lower than that of the artificial ones: 1.71 to 2.47 per cent for the former, and 6.47 per cent for the latter. Robertson concluded that little reliance can be placed on the superficial similarity of the natural and artificial preparations. The former also varied in composition, within the group, depending on the method used in its isolation.

In spite of the fact that evidence, which was continuously gathering, indicated that the older opinions concerning the "humic acids" were irrational, advancement was very slow. Even in 1908, Boudouard (138) still retained the idea that there existed four groups of "humus bodies," which he designated by the formulae, $C_{18}H_{14}O_6$, $C_{18}H_{14}O_9$, $C_{18}H_{18}O_9$, $C_{18}H_{14}O_{11}$. Euler (277, 359, 1308) also divided the "humus substances" into four groups, on the basis of the prevalent ideas:

1. "Humins" insoluble in alkalies and in alcohol. It was believed

that these could also be obtained from carbohydrates, by heating with dilute alkalis at 200°, and from tannins and phlobaphenes even in the absence of oxygen. These complexes were considered to be intermediary substances produced in the process of formation of "humic acids." The carbon content of the "humins" was reported to be 62.66 per cent, and the hydrogen content, 3.7–4.6 per cent.

2. "Humic acids," insoluble in alcohol, easily soluble in dilute alkalis, and precipitated in the form of abundant flakes from the dark brown solution by acids (242).

3. "Hymatomelanic acid," soluble in alkalis and precipitated by acids; the precipitate is soluble in alcohol and becomes insoluble on drying. This body was considered to be an acid anhydride, of the formula $C_{26}H_{22}O_9$.

4. Water-soluble substances, of a low carbon content and present in the waters of peat bogs (50).

As opposed to this idea of the specific acid nature of the "humus complexes," there grew up, during this period, a new conception of humus which can be designated as colloid-chemical. According to this theory, the acidity of humus is not due to free humic acids, but is associated with the reactions of humus with mineral salts; the bases are adsorbed from the salts, liberating the mineral acids. The foundation of this idea was laid by Van Bemmelen (89) and further extended by Baumann and Gully (75). In 1909, Baumann (74) published a critical summary of the status of our knowledge of the "humic acids," in which he came to certain very important and definite conclusions. The chemical composition of the natural preparations was believed to vary considerably; the available information pointed to the non-existence of definite chemical compounds that could be designated as "humic acids." These ideas were substantiated by the work of Hermann, Eggertz, Sostegni, A. Mayer, and Miklausz. Most of the "humic acids" so far investigated were considered to be mixtures of plant (and sometimes also animal) products, partly decomposed, partly conserved because of their resistance to decomposition, and mostly combined in a colloidal state. The chemical constituents of these complexes could be separated from one another only with difficulty; they included fats, waxes, pentosans and other hemicelluloses, amino bodies, and resins, in various combinations, since the composition of the plant residues from which they originated varied. The possibility was not excluded that organic acids (propionic, butyric, etc.) were present in the colloidal complex. However, such a substance as "humic acid" was believed to be entirely ab-

acid, into two isomeric bodies. Ehrenberg and Bahr (260), after studying the dissociation isotherm of the compound formed between ammonia and "humic acid," came to the conclusion that the latter is, by comparison with other weak acids, a real acid. The alkali "humates" behaved as salts of a true acid with a basicity of three to four (see also 1106, 18, 20, 200, 379, 380, 769).

In 1907-1913, there appeared the results of the investigations at the Bureau of Soils in Washington, particularly those of Schreiner and Shorey, which invalidated most of the ideas of the "humic acid" theory. These investigators succeeded in isolating from the "humic," "ulmic," "crenic," and "apocrenic" acids, a series of organic compounds of definite chemical composition; they thus established beyond any doubt the non-existence of "humic acids" as definite chemical entities. The soil humus proved to be not a single compound or a small group of chemical compounds, but a mixture of a large number of substances. The idea that the numerous plant constituents are in some mysterious way transformed into a single group of closely related bodies, called "humic acids," was shown to be entirely wrong. Cameron (167) wrote in 1911 that "the existence of humic acid is purely hypothetical and without experimental or scientific verification." The chemical nature of the compounds comprising the soil humus is quite as varied as that of the plant or animal substances from which humus originates, as will be shown later.

The chemistry of various "humic acids" depends largely upon the method used in their separation, especially upon the nature and concentration of the alkali and acid, upon the temperature of extraction and precipitation, and upon the length of treatment. It is not surprising, therefore, that no exact comparison could be made between the results obtained by different investigators. The chemical formulae suggested on the basis of elementary analysis could lay no claim to accuracy, since no chemically pure substance was obtained by the use of alkalis as solvents. In summarizing the previous investigations on the "humus" bodies of the soil, Schreiner and Shorey (975, 979) noted that "the most conspicuous feature of this work is the discordant results obtained for bodies bearing the same name and often obtained from the same source."

Neither the contributions of Baumann and Gully nor those of Schreiner and Shorey, however, definitely settled the "humic acid" problem. This was evident from the statement made by Ehrenberg and Bahr that the compounds isolated by Schreiner and Shorey make up only a small

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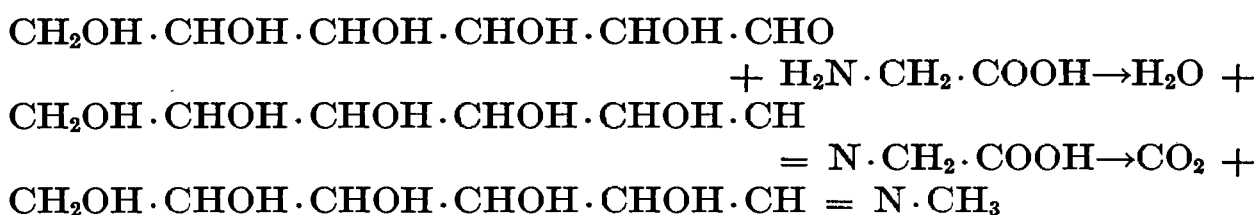
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part of the total humus; further, the fact that these compounds did not include any black colloidal material was considered as sufficient evidence for considering them as impurities of the humus.

Maillard-Oden (1912-1921). The following decade saw a renewed interest in the "humic acids" as definite chemical compounds. New methods of approach were developed in an attempt to synthesize compounds resembling the natural "humic acids" in their general properties. In some of these methods, the presence of nitrogen was given serious consideration. More attention was also paid to the origin of the humus complexes in the process of decomposition of plant and animal residues.

Earlier investigators (736, 955, 404, 807, 396) showed that when proteins are boiled with concentrated mineral acids, a brown to dark colored residue is formed. On boiling a mixture of glucose and urea in strong hydrochloric acid solution, dark colored substances containing 6.73 per cent nitrogen were produced (1192). Samuelly (938, 555, 792), suggested that the formation of these complexes, designated as "artificial melanins" or "melanoidins," is due to a secondary reaction between amino acids and carbohydrates. Maillard (664-6) carried out a number of experiments which tended to prove that "humic acids" are formed as a result of interaction of various amino acids with sugars. When a mixture consisting of one part of glycocoll and four parts of glucose, in aqueous solution, was placed on a water bath, at 75°C., a brown color developed in a few minutes. Maillard (665) suggested that as a result of an interaction of the aldehyde and ketone groups in the sugar molecule with the $-\text{NH}_2$ and $-\text{COOH}$ groups in the amino acid molecule, a CO_2 group is removed from the latter and a molecule of water from the former, and a "humic acid" complex containing 4-6 per cent of nitrogen is produced:



The formation of humic materials in nature was thus believed to be a result of purely chemical reactions, in which microorganisms play no part except in the formation of sugars from complex carbohydrates and of amino acids from proteins. Gortner (356) found that on boiling tryptophane with sugar in a 22.9 per cent hydrochloric acid solution,

86 per cent of the nitrogen is converted into a "humin" complex. Other amino acids were also found (356, 369, 458, 640, 921) to behave in a manner similar to tryptophane, especially the α -amino groups of arginine and histidine.

The high concentration of amino acids and sugar, as well as the high temperature employed by Maillard, left room for doubt as to whether or not the above reactions can be considered to be similar to those which take place in the process of formation of humus complexes in nature. According to Trussov (1183), dark brown substances are produced, as a result of the interaction of sugars with amino acids, only in the presence of definite concentrations of both, and not in all proportions and relative concentrations. Trussov has further shown that by the action of ammonia and other alkalies upon glucose and other carbohydrates, dark colored substances are also formed. However, he concluded that this process is probably only of secondary importance and can at best account for only a limited amount of the dark substances produced during the decomposition of plant and animal residues in nature.

Neuberg and Kobel (758) could not demonstrate the formation of any dark colored substances or CO_2 as a result of the interaction of fructose and alanine at low temperatures, even after treatment for several weeks. One may conclude, therefore, that although such substances are produced at high temperatures as a result of the interaction of amino acids with sugars, it is very unlikely that this process takes place more than to a very limited extent in soils and in peats, where no free sugars or amino acids are present beyond mere traces and where the needed high temperatures are seldom attained.

The production of dark colored substances on boiling furfural with hydrochloric acid was also used as a basis for a theory presented to explain the formation of "humic compounds" (356, 674). It was suggested that "humin" and "humic acid" complexes are formed when carbohydrates are boiled with acids, through the furfural stage; according to Beckley (80), the first product is hydroxy-methyl furfural, which is later changed to "humus" (197, 311).

An attempt was finally made to rejuvenate the theory of the existence of several definite "humic acids" in peats and in soils, by applying modern physicochemical methods of investigation. This was primarily a result of the work of Oden (778-781). In differentiating between "humic compounds" and "humic acids," Oden defined the first as "the light-brown to dark-brown substances of unknown constitution which are formed in nature by the decomposition of organic matter

through the action of atmospheric agencies or in the laboratory by chemical reagents," and the second as "those humic substances which are capable of giving hydrogen ions and form typical salts with strong bases." The nitrogen was considered as an impurity.

Oden isolated "humic acids" from peat and from soil, by treating these first with an acid, washing with water, and extracting overnight, at 30–80°C., with 4 *N* ammoniacal or NaOH solution; the extraction was repeated 15 to 20 times until all of the alkali-soluble material was removed. Sufficient NaCl was then added to the alkali solution to make it 2 *N*. A coagulum was produced; this was removed by centrifuging. The dark colored filtrate was now concentrated, acidified with hydrochloric acid, again centrifuged, and washed. The last precipitate contained both "humus acid" and "hymatomelanic acid," which were separated by alcohol treatment.

Oden demonstrated, by means of potentiometric measurements, the presence of organic acid ions in soils and in peats; the hydrogen ion concentration of "humic acid" prepared from peat was equivalent to pH 3.87. Oden suggested that the acid nature of soil humus is due to hydrogen ions formed by the "humic acids." The action of NH₄OH on "humic acid" was considered to give rise to a true salt. The neutralization of the "acid" with an alkali (NaOH) was followed by means of conductivity measurements, whereby an approximate equivalent weight of 339 was found; the conductivity of "sodium humate," during the process of dilution, made it seem probable that this is a tribasic acid (778).

Later (781), however, Oden described "humus acid" as a tetrabasic acid of medium strength, soluble in water with difficulty, but readily giving colloidal solutions. The formula C₆₀H₅₂O₂₄·(COOH)₄ was not in disagreement with the analytical results obtained by different investigators; however, the formula (R-hum) H₄ seemed to be preferable, with R-hum corresponding to the radical C₆₄H₅₂O₃₂ = 1332. The alcohol-soluble "hymatomelanic acid" was believed to be formed by hydrolysis of the "humus acid," in the process of treatment with the alkali. According to Oden, the alcohol-soluble "acid" has a deeper brown color, a lower equivalent weight (about 250), a somewhat higher carbon content (about 62 per cent against 58 per cent of the "humus acid"), and a greater degree of dispersion, whereby colloidal solutions of greater constancy than those of "humus acid" are formed. On repeated solution and reprecipitation of "humus acid" preparations, their nitrogen content was reduced from 2.5 to 0.7 per cent. However,

even the lower nitrogen content could not correspond to the four replaceable hydrogens; this led Oden to conclude that the nitrogen was probably present as an impurity, and not as a constituent of the molecule, a conclusion reached previously by Detmer and others.

Oden finally came to distinguish four organic complexes in the humus of soils and peats. "Humus acid" and "hymatomelanic acid" were believed to be definite chemical entities, while "humus coal" and "fulvic acid" were looked upon as groups of complexes (table 2). Kreulen (589) separated a phenol-soluble part of "humic acid," which he called "pyrohymatomelanic acid." It was believed that the formation

TABLE 2
A summary of the properties of the "humic acids" of Oden (781)

NAME OF PREPARATION	SOLUBILITY IN			SALTS	COLOR	EQUIVALENT WEIGHT	CARBON CONTENT
	Water	Alcohol	Alkali				
"Humus acid"	Soluble with difficulty, but dispersible	Insoluble, but dispersible	Soluble	Alkali salts soluble in water, dispersed in alcohol	Dark brown with red tinge	340	per cent 58
"Hymatomelanic acid"	Difficultly soluble, easily dispersible	Soluble	Soluble	Salts of other bases difficultly soluble in water but dispersible	Brown with yellow tinge	250	62
"Fulvic acid"	True solutions	Soluble	Soluble	Most water soluble	Golden yellow to pale yellow	...	55

of this complex takes place as a result of interaction between "hymatomelanic acid" and the "residual humus acid." According to this idea, the "humic acids" form a series of polymers of increasing complexity, in accordance with their solubility in alcohol, in phenol, and in alkali solutions.

To the ever-growing list of "acids," Popp (835) added, in 1920, "humal acid," a substance soluble in water and closely related to the sugars, with 43 per cent carbon and 6 per cent hydrogen. This "acid" was found to be partly fermentable; it could be obtained from all types of peat, but not from brown coal. Popp considered it to be a decomposition product of "humus acid"; the fact that it could be readily decomposed to CO₂ led Popp to the conclusion that this compound was

intermediary between humus and carbon dioxide. "Humal acid" was studied further by Marcusson (677) and was found to be closely related, in its general properties, to the "fulvic acid" of Oden and to the earlier "crenic acid" and "apocrenic acid" of Berzelius. When the alkaline extract of peat was acidified, the "humic acids" were precipitated. The filtrate was neutralized by means of an alkali solution and concentrated. The "humal acid" was extracted from the concentrate by means of alcohol, yielding quantitatively 20–30 per cent of the total original peat. It had an equivalent weight of 350 and was believed to form an important step in the formation of coal from cellulose:

Cellulose→"oxycellulose"→"humal acid"→"humic acid"→coal.

The recent advances in our knowledge of the chemistry of hemi-celluloses and especially of the uronic acid complexes, as well as the fact that more than 50 per cent of the constituents of sphagnum plants (1236, 1242) consist of such complexes, would lead one to consider this so-called "humal acid" not as a decomposition product, but as a constituent of the original plant residues. If it is formed at all during the decomposition processes taking place in peat, it is probably due to the synthesizing activities of microorganisms, as in the case of the formation of bacterial slimes and gums, which contain glucuronic acid groups; the last mentioned compound was actually found by Marcusson in the water-soluble fraction of decomposed oak wood.

Modern Period (1922–1935). The modern period of humus investigation has been characterized by two important tendencies: 1. the recognition of the benzol structure of some of the important constituents of humus and the study of the chemical nature of humus as related to that of the plant constituents from which it originated, notably lignins; 2. the recognition of the rôle of microorganisms in the decomposition processes and in humus formation. According to Eller (264), the "humic acids" obtained by treatment of carbohydrates with mineral acids have nothing in common with the natural products, in spite of the superficial similarity. By determining the carbonyl-oxygen in the "humic acid" complexes, Leopold (629) has also demonstrated that a marked difference exists between the natural and artificial preparations. However, on oxidation of phenols and their derivatives, products were obtained which were very similar in their chemical and physical properties to the natural "humic acids" (265). The chlorine derivatives of "humic acids" from phenols and from natural materials contained 42–44 per cent chlorine, were easily soluble in alcohol, ether,

Eller's ideas did not receive immediate recognition, however. Ehlandt (255) obtained three "humic acid" preparations from brown coal. This coal contained 63.7 per cent carbon, 4.3 per cent hydrogen, 1.58 per cent nitrogen, 0.95 per cent sulfur and 29.5 per cent oxygen on a dry ash-free basis, and 9.4 per cent ash. These preparations were classified on the basis of their solubility in alcohol: 1. insoluble in alcohol, 2. soluble in alcohol, and 3. soluble in alcohol and ether and precipitated with water. Bitumen-free coal was considered to consist of Ca, Mg, and Fe salts of these "acids." The coal was first treated with benzol or alcohol, to remove the bitumens, then with 5–6 per cent hydrochloric acid to liberate the "acids"; these were extracted, at 60°C., with 4 per cent NaOH solution and then precipitated with HCl. Their relative concentration in coal was 40, 28, and 12 per cent respectively, which, together with 10 per cent ash and 10 per cent bitumen, made up the coal. Eller's ideas concerning the identity of "phenolic humic acids" and "natural humic acids" were criticized because, on nitration, 4.92 per cent nitrogen was taken up by the artificial preparation and only 3.4 per cent by the natural product, which originally contained 2 per cent nitrogen; the formation of chlorine derivatives took place more energetically in the natural than in the artificial preparations.

Bottomley (136), Marcusson (675), Jones and Wheeler (511), and others (543) still believed that the humus compounds, namely, the "humic acids" originated from carbohydrates. They ascribed the furan structure, not only to the preparations obtained by treatment of carbohydrates with acids, but also to natural compounds. Eller, on the other hand, emphasized the aromatic nature of these compounds. According to Orlov (791), the structure of a humic substance is independent of the structure of the original material. Humic bodies produced from paraffin by oxidation at 120–140°C. were found to be closely related to natural "humic acids."

The probable rôle of incrusting substances in the formation of humus in soils and composts began to attract the attention of a number of investigators. Lange (607) expressed the idea that "humic acids" are closely related to the "lignic acids." According to Hoffmeister (456), dark colored substances are formed by the extraction of lignin with an alkali solution, finally yielding "humic acids." Fischer and his associates (292–295) were particularly emphatic in calling attention to the important rôle of lignins in the formation of humus. Cellulose has an aliphatic or furan-like structure, whereas lignin has an

Eller's ideas did not receive immediate recognition, however. Ehlandt (255) obtained three "humic acid" preparations from brown coal. This coal contained 63.7 per cent carbon, 4.3 per cent hydrogen, 1.58 per cent nitrogen, 0.95 per cent sulfur and 29.5 per cent oxygen on a dry ash-free basis, and 9.4 per cent ash. These preparations were classified on the basis of their solubility in alcohol: 1. insoluble in alcohol, 2. soluble in alcohol, and 3. soluble in alcohol and ether and precipitated with water. Bitumen-free coal was considered to consist of Ca, Mg, and Fe salts of these "acids." The coal was first treated with benzol or alcohol, to remove the bitumens, then with 5–6 per cent hydrochloric acid to liberate the "acids"; these were extracted, at 60°C., with 4 per cent NaOH solution and then precipitated with HCl. Their relative concentration in coal was 40, 28, and 12 per cent respectively, which, together with 10 per cent ash and 10 per cent bitumen, made up the coal. Eller's ideas concerning the identity of "phenolic humic acids" and "natural humic acids" were criticized because, on nitration, 4.92 per cent nitrogen was taken up by the artificial preparation and only 3.4 per cent by the natural product, which originally contained 2 per cent nitrogen; the formation of chlorine derivatives took place more energetically in the natural than in the artificial preparations.

Bottomley (136), Marcusson (675), Jones and Wheeler (511), and others (543) still believed that the humus compounds, namely, the "humic acids" originated from carbohydrates. They ascribed the furan structure, not only to the preparations obtained by treatment of carbohydrates with acids, but also to natural compounds. Eller, on the other hand, emphasized the aromatic nature of these compounds. According to Orlov (791), the structure of a humic substance is independent of the structure of the original material. Humic bodies produced from paraffin by oxidation at 120–140°C. were found to be closely related to natural "humic acids."

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aromatic structure containing the benzol ring, with acetyl and methoxyl groups. Fischer demonstrated that in the formation of peat the celluloses of plant residues change to carbon dioxide and water, whereas the lignins remain and accumulate. The lignin molecule does not remain unchanged, however, but loses certain acetyl groups, with the result that the phenol-containing, alkali-soluble body of the molecule is changed to "humic acid." By an increase in the size of the molecule, either by oxidation or by dehydration, the "humic acid" is later transformed into insoluble "humin," and then into coal (509, 1031).

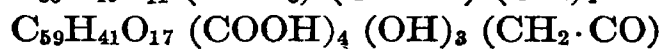
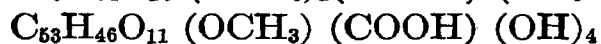
Fischer and Schrader (294) divided the natural humus compounds into the following groups:

- I. Neutral components:
 1. "Humus," completely insoluble in alkalies,
 2. "Humins," soluble in alkalies only on prolonged boiling.
- II. Acid components:
 1. "Proto-humic acid," soluble in alkalies on long standing in the cold or on heating,
 2. "Humic acid," soluble in alkali carbonates even in the cold (958).

According to Fuchs and Leopold (331, 629), "humic acids" obtained from peat contain both COOH and phenolic OH groups, as demonstrated by the process of methylation. The carboxyl groups allow salt formation; the hydroxyl groups are also capable of combining with bases. Salts can be prepared by treating the "humic acids" with salts of mineral acids (413). On shaking "humic acids" with an alcoholic solution of potassium acetate or by saponifying the methylated "humic acids" with alcoholic potassium hydroxide, salts were prepared (331). The base content of the salt corresponded quantitatively to the methoxyl content of saturated methylated compounds. In the case of natural "humic acids," the methoxyl content was found to vary with the source of the material (295). In one instance, the presence of 6.9 per cent methoxyl (OCH_3) and of three methylated OH groups was demonstrated (325, 326), thus corresponding to a molecular weight of 1300-1400. The carbonyl (CO) content of "humic acid" was reported (453) to vary from 0.4 to 2.2 per cent. Fuchs concluded that the "humic acid" molecule contains three to four carboxyl groups, three to four hydroxyl groups which are subject to methylation, one methoxyl group, and one carbonyl group.

"Humic acid" was, therefore, considered to be a group of natural oxy-carbonic acids originating in the decomposition of dead organic

material as dark amorphous substances capable of giving off H-ions and of forming salts and possessing base-exchange capacity (327). The following formulae were suggested for the complexes isolated from peat:



When "humic acid" is treated with ammonia, the latter is bound in two different ways, one in which it is removable by an alkali and the

TABLE 3

Comparative chemical properties of cellulose, lignin and humic acids (325)

PROPERTY	CELLULOSE	LIGNIN	"HUMIC ACIDS"
General nature	High molecular aliphatic alcohol	Mixture of cyclic phenol ethers	Mixture of cyclic oxy-carbonic acids
Stoichiometric molecule	$\text{C}_6\text{H}_{10}\text{O}_5$ (162)	$\text{C}_{40}\text{H}_{44}\text{O}_{15}$, etc. (ab. 800)	$\text{C}_{66}\text{H}_{52}\text{O}_{30}$, etc. (ab. 1400)
Special characteristics	3 alcohol groups, 1 oxygen bridge, 1 glucoside oxygen	Methoxyl groups, secondary alcohol groups, little phenolic-hydroxyl, cyclic oxygen	Little methoxyl, phenol groups, carboxyl groups, cyclic oxygen
Hydrolysis by acids	100% glucose	Hardly acted upon	Hardly acted upon
Oxidation	Few characteristic products, not autooxidizable	Give oxycarbonic acids of similar chemical nature, autooxidizable in presence of alkali, give benzol carbonic acids	acids of similar
Heat	All give amorphous, carbon rich bodies of partly aromatic structure		

other in which it is not; the ammonia in the latter form made up 3 per cent of the preparation and was considered to be cyclically bound, replacing oxygen. The presence of nitrogen in various "humic acid" preparations was explained by Fuchs as due, either to the presence of a protein molecule bound to a nitrogen-free compound, or to the replacement of oxygen by ammonia in the cyclic compound.

A summary of the chemical characteristics of "humic acids" as com-

"humin" fractions of brown coal: different coals show differences in the degree of methylation.

The equivalent weight of "humic acid" has been reported to be 147 (1087). Erdtmann (276) obtained Ba-"humate" with 24 per cent Ba and Ba-"hymatomelanate" with 30 per cent Ba, thus corresponding to equivalent weights of 218 and 153. According to Samec and Pirksmaier (937), the molecular weights of the alcohol-insoluble and alcohol-soluble preparations differ with the material from which they are isolated, as shown by the following summary:

Source	Lignite	Peat	Brown coal
"Humic acid".....	1,445	1,235	1,345
"Hymatomelanic acid".....	855	761	739

Among the natural products which were considered as almost "pure humic acids," dopplerite and more recently Cassel brown received particular attention. Dopplerite is considered to be a naturally occurring calcium salt of "humic acid" and is completely soluble in sodium hydroxide solution (956); it was also looked upon as a mixture of acid anhydrides (1162). According to Miklausz (708), dopplerite is formed when the colloidal solution of "humic acid" in water is brought into contact with calcium. Cassel brown, because of its practical insolubility in acetyl bromide, is considered to be "pure humus"; this will be treated in detail later.

A detailed chemical study (832a) of "natural humic acid" obtained from lignite and of "artificial humic acid" obtained from coal definitely established the fact that the two types of dark colored material are distinctly different in chemical nature. The first was shown to have an empirical formula of $(C_{82}H_{69}O_{28})_x$ or $[C_{77}H_{54}O_{11}(OCH_3)(OH)_8(COOH)_4]_x$. Two of the hydroxyl groups were associated with keto-enol isomerism, and the remaining six hydroxyls were characterized by high acidity. The second had the empirical formula of $(C_{59}H_{49}O_{23})_x$ or $[C_{55}H_{41}O_{11}(OH)_4(COOH)_4]_x$. Of the four hydroxyls, three were aliphatic and one of a much more acidic type.

Recent tendencies. Several recent contributions to the subject of "humic acids" modify the earlier conceptions of these compounds. Oden's conception of "humic acids" portrayed a group of organic substances which are capable of liberating hydrogen-ions and which react with bases to form typical salts and water. Page (801) proposed that use of the term "humus" be discontinued altogether because of the widely different meanings attached to this word by various investigators. The term "humic matter" was suggested, to describe the

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"dark-colored high-molecular colloidal organic matter" which is a characteristic constituent of the soil; the term "non-humic matter" was applied to the colorless organic substances, largely soluble, which result from the chemical and biological decomposition of the plant and animal residues, such as celluloses, lignins, waxes, and from the further decomposition of the "humic matter" itself. That part of the "humic matter" which is soluble in cold, weak alkali and is reprecipitated by acids was referred to as "humic acid"; the part insoluble in cold alkali but soluble in hot alkali solution was referred to as "humin." The "fulvic acids" of Oden were included in the "non-humic matter." A similar distinction was made (667) between "humus" and "humus-accompanying substances".

Page (247, 248) was convinced, however, that no satisfactory evidence had been shown so far to prove that any of the preparations obtained from the colored "humic matter" of soils and composts might be regarded as chemical individuals. This "humic matter" could be readily fractionated by various physical and chemical methods into groups of substances with characteristic physical and chemical properties. The isolation of such groups as the "humin" and "humic acid" preparations was considered as preliminary to the isolation of well-defined chemical compounds from the soil; their characterization was believed to throw light upon the origin, nature, and function of the "humic matter" of the soil.

In an attempt to correlate the recent progress made in the study of the decomposition of organic matter with the older conceptions of the chemical identity of the "humic acids," Strache and Lant (1104) suggested that the different "humic acids" consist of the same chemical compound, accompanied by various impurities. They proposed that the natural compounds should be classified separately from the "artificial humic acids." The natural compounds formed during the decomposition of organic materials were called "natural humic acid," soluble in alkali carbonate and precipitated by acids; "humin," insoluble in alkali carbonate but soluble on continued boiling with hot alkalies; and "humus-coal," insoluble even on continued boiling with strong alkalies. From the artificial compounds obtained by treatment of organic substances with chemical reagents they named those soluble in alkali carbonate and precipitated by mineral acids, "artificial humic acid" or "huminoïd acid"; and those similar to "natural humins," "artificial humin" or "huminoïd substances." Fischer and Fuchs (328) applied the term "humic acids" to that part of the brown coal which is freed from ash and bitumen, including the alkali-insoluble substances.

The early conception of "humus" was thus transferred to that of the "humic acids." Springer (1078) came to the conclusion that "humic acids" include compounds which are easily decomposed and resistant to decomposition; alkalis not only dissolve but also decompose the "humic acid" preparations, the degree of decomposition depending on the nature and concentration of the alkali. By means of acetyl bromide he obtained, from a neutral peat, a "humic acid" residue which had 4 per cent N and a C:N ratio of 14.2:1. This led him to conclude that "soil humic acid" consists of a mixture of nitrogen-free and nitrogen-containing "humic acids."

Some investigators recognized, however, that soil humus, including the "humic acids," is much more complex than can be expressed by a single formula or even by a limited group of formulae. This was well expressed in a summary presented by Shmook (1005): (a) "humic acid" is a nitrogenous body of an acid nature, the acidity being due both to its power of adsorption, as a result of the colloidal condition of the humic acid, and to the presence of COOH groups; (b) "humic acid" contains a tri-valent benzol ring; (c) a large part of the nitrogen in the "humic acid" is in the form of a protein combined in a physicochemical manner with the other part of the complex; a small part of this protein is less firmly combined and can be extracted by neutral salts; the protein of the humic acid is characterized by a high content of amide nitrogen; (d) the elementary composition of "humic acid" is C-61.84 per cent, H-4.21 per cent, N-3.28 per cent, O-30.67 per cent.

A summary of the nomenclature and classification of the various "humic acids" is given in table 4. Although during the discussion up to this point the conception of the "humic acids" has been mostly emphasized, other terms have also received much consideration. The term "humins," for example, also had an extensive historical development. It was usually applied to neutral bodies insoluble in alkali or soluble with difficulty; it came to be used later by coal chemists for designating the more highly condensed, carboxyl-free compounds; the term "humus coal" was either synonymous with "humins" (781) or was used to designate those bodies which are insoluble in hot concentrated alkali (1079).

The "hymatomelanic acid" complex has frequently been included with "humic acid" or, more specifically, with "humus acid." It is soluble in acetyl bromide as well as in aqueous sulfurous acid under pressure (1079, 784). Springer, therefore, suggested that this complex is nearer to lignin than to "true humic acid". Simon (1037) divided the humus compounds into three groups: 1. "true humic acids," in-

soluble in acetyl bromide and soluble in suitable neutral or slightly acid reagents, such as fluorides and oxalates; 2. "humolignic acids" or "humocelluloses," made soluble by alkali reagents; 3. "fulvic acids" soluble in water or boiling sodium acetate.

Siedlitzki (1023a) has recently shown, by means of spectographic analysis, that "humic acid" preparations from various peats and soils have a similar atomic arrangement; the central nucleus of these preparations resembles that of lignin, although the connections at the peripheries are different.

SUMMARY

After a century and a half of intensive study, our knowledge of the chemical nature of humus and its constituent groups, including the "humic acids," is still in a highly confused state. The conception that humus is comparatively simple in chemical composition and that purely chemical processes are responsible for its formation still persist in some quarters. "Humic acids" are even now considered to be the most important constituents of humus in soil, peat, and composts. Some chemists are still convinced that the "humic acids" obtained by treatment of carbohydrates with mineral acids are identical with those present in decomposing plant residues and in soil. It is still believed that humus consists of a few chemical complexes, which can be obtained from the organic matter of soils and peats by the use of alkali solutions.

This simple system of classification of the complex forms of organic matter present in soils, bogs, and composts does not take into consideration the numerous processes involved in the decomposition of the plant and animal residues by numerous microorganisms, the chemical complexity of these residues, and the variety of products resulting from their decomposition. The chemical and atmospheric agencies should no longer be held responsible for processes that are not understood. One of the most important elemental constituents of humus is nitrogen. This frequently makes up 3 to 6 per cent of the total organic material, thus accounting for a third of the total humus in the form of protein, but it is still generally omitted from the various chemical formulae of "humus" and "humic acids," since it does not fit well into any of these postulated compounds.

The various "humic acids" commonly isolated from humus account at most for only 50 per cent of the total organic matter. Before the exact chemical nature of these "acids" has been definitely established, before their function in humus is known, one is hardly justified in developing a system of classification of the chemical properties of various

types of humus based upon these preparations. A system of this nature merely founded upon the isolation of a few substances by arbitrary chemical procedures fails to give a picture of the true nature of humus, its origin, and its dynamic condition in the soil. The complexes which have been isolated from decomposed tree stumps, from sphagnum peat bogs, from soils, from manure composts, from coal, and even from filter paper treated with mineral acids, are far from being identical; their comparison based upon elementary analysis tells very little concerning their origin or their true chemical nature.

A number of factors have contributed to the existing confusion concerning the chemical nature of humus. These can be briefly summarized as follows:

1. The introduction of numerous terms for designating the dark colored constituents of humus, without due recognition of the fact that these represented only preparations and not specific chemical compounds.

2. The persistent designation of various preparations of humus obtained by alkali treatment of soils, peats, coals, and composts, by terms which were introduced when organic chemistry was still in its infancy and when all organic compounds were considered as comparatively simple in nature.

3. The confusion introduced by non-critical comparison of artificial preparations obtained by treatment of sugars with inorganic acids with natural preparations obtained from soils, composts, peat, or coal.

4. A lack of knowledge concerning the rôle of microorganisms in the processes of decomposition of plant and animal residues leading to the formation of humus.

One may, therefore, feel justified in abandoning without reservation the whole nomenclature of "humic acids," beginning with the "humins" and "ulmins," through the whole series of "humus," "hymatomelanic," "crenic," "apocrenic," and numerous other acids, and ending with the "fulvic acid" and "humal acids," the last additions to the list. These labels designate, not definite chemical compounds, but merely certain preparations which have been obtained by specific procedures. The only name warranting preservation is HUMUS, because of its historical importance; it should be used to designate the organic matter of the soil as a whole. "Humus substances" or "humic matter" can be used to describe humus complexes as a whole; the general implication would thereby be made that they are comparable to plant, animal, and microbial substances.

CHAPTER IV

“HUMIFICATION” OF ORGANIC MATTER IN SOILS AND IN COMPOSTS, AND METHODS OF “HUMUS” DETERMINATION

“The determination of that part of the soil humus, which is soluble in dilute alkalies . . . can teach us very little. Such simple procedures are entirely unsatisfactory in order to judge the value of the humus.”—VAN BEMMELEN.

“Humification” as a specific process of humus formation. The earlier investigators believed that humus formation takes place in nature by a specific process of “humification,” whereby the plant residues are bodily transformed into dark colored substances, or humus.

The first definite suggestion concerning the nature of this process is traced to Wallerius (1245), who stated that humus is formed from decomposing vegetation. As long as the plant residues underwent continued decomposition, the product was called “humus”; when they were saturated with water, the product gave rise to peat. This idea was expended by de Saussure in 1804, who emphasized that humus originates from vegetable matter through the combined action of air and water. These simple conceptions prevailed among many chemists and, as late as recent years, one finds definite statements to the effect that the decomposition of organic residues in nature and the formation of humus are largely processes which involve simple oxidation and condensation. In many instances, even when the rôle of microorganisms in the decomposition of plant and animal substances in soils and in composts was taken into consideration, the processes were designated by such vague generalized terms as “decay,” “fermentation,” and “putrefaction.”

Liebig, in 1840, spoke of the production of humus in the decomposition of vegetable matters by the action of acids and alkalies; he further stated that “woody fibre in a state of decay is the substance called humus.” Rosenberg-Lipinsky (915) defined humus as “a mass of brown, partly soluble, partly insoluble, partly acid and partly neutral products of decomposition, which, in the presence of air, water and heat, undergo further decomposition, giving carbon dioxide, water and am-

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monia." According to Hilgard (442), plant material added to the soil has first to be "humified" before the nutrient elements contained therein become available for plant growth. Humus was thus considered to be a substance produced as an intermediary product during the decomposition of organic residues; it was also looked upon as that portion of soil organic matter which can readily become available for plant nutrition (601).

Oden (781), among the more recent investigators, also believed that the process of humus formation in nature is purely chemical, similar to the formation of "artificial humic acids." Maillard (665) proposed a purely chemical theory of humus formation, namely, the interaction of the sugars produced in the hydrolysis of polysaccharides with the amino acids formed from the proteins to give rise to humus; this process was believed to be one of "dehydration and humification." As late as 1930, humus formation, beginning with the first stages of browning, was considered (1310) to be physicochemical and non-biological in nature: during this process of "humification," oxygenated water and benzol-ring compounds which act as antiseptics are formed; the rays of the sun and temperature were believed to be the chief agents in this process; a definite relation was said to exist between plant pigmentation and humification, since the maternal substance (aromatic bodies) are the same and the energy of formation is the same. These ideas and others of a similar nature are largely speculative and not based upon sufficient experimental evidence.

Wieler (1280) stated that all plants contain "humic acids." Fraps and Hamner (314) and Gortner (353), using ammonium hydroxide solution, obtained from fresh plant materials an extract similar to "humus"; after the plant residues were added to the soil, the concentration of this "humus" complex was found to diminish; they suggested, therefore, that no specific "humification" process takes place in the soil but that "humus" is actually added to the soil in the plant remains. These results seem to be quite contrary to the prevalent theories concerning the formation of humus and its resistance to decomposition, a phenomenon responsible for its persistence in soil and its accumulation in peat bogs.

The current ideas of "humification" considered as a specific process of humus formation were thus found to be, in most instances, as vague as, if not more so than, those concerning the chemical nature of humus itself. No attention was usually paid to the fact that the chemical constituents of the plant and animal residues may be decomposed at

different rates, by various organisms, giving a variety of products. Decomposition of the plant material was frequently looked upon as a single process. The complex chemical nature of the materials was not fully recognized, nor was the fact that in the microbial transformation of different organic complexes many reactions are involved which lead to the formation of numerous new compounds. In many instances, one finds only broad generalizations as to the rôle played by microorganisms in the formation and accumulation of the dark colored organic matter, namely, humus (173).

An enumeration of the terms used at various times to designate the process of decomposition of plant and animal residues is sufficient to illustrate the confusion current in the literature of the last century and even during the first three decades of this century concerning this important natural process. The following terms have been most commonly employed:

Decay (Verwesung, Eremacausis)
 Moder formation (Vermoderung)
 Fermentation (Gärung, Vergärung)
 Mineralization
 Putrefaction (Fäulnis and Verfäulnis)
 Humification (Humifikation, Huminifikation)
 Ulmification (Ulmifikation)
 Peat formation (Vertorfung)
 Rotting (Verrotung)
 Combustion
 Bituminization (Bituminierung)
 Coal formation (Inkohlung)

Some of these terms were defined in detail by Wollny (1301). Only a few of these need be discussed further here.

Decay was defined as “the process of decomposition, whereby some organic constituents are volatilized and the non-volatile are left behind and are changed into assimilable minerals.” The process takes place in the presence of oxygen and is accompanied by the liberation of ammonia and carbon dioxide. According to Potonié (842), decay brings about the complete destruction of the organic constituents, with only the mineral complexes left behind.

Moder formation was considered to be a process of decomposition less extreme than that of decay, the term “moder” designating a complex between the original plant material and the resultants of complete decay.

Fermentation was originally used by Pasteur to designate anaerobic

processes or life without oxygen; this term has come to mean, however, the decomposition of carbohydrates with the evolution of gas or the formation of acid or both.

Putrefaction was applied to the processes of decomposition that take place under reduced oxygen pressure or under completely anaerobic conditions. A limited amount of gaseous products, consisting, according to conditions, of CO_2 , CH_4 , H_2 , H_2S , N_2 , N_2O are formed, and there is left behind a more or less dark-colored mass of organic matter resistant to further decomposition and containing non-nitrogenous and nitrogenous compounds, volatile acids, and minerals, largely in unassimilable forms. This term was frequently applied to such processes of decomposition of proteins which lead to the formation of foul smelling substances.

Peat formation also takes place in the absence of air. The process is carried out under water without any oxidation; the changes are intramolecular, with some molecules condensing and liberating CO_2 , H_2O , and CH_4 . Although more recent investigators believed that living organisms take an active part in the first four processes listed in the foregoing, the function of such organisms in the formation of peat was considered questionable, even as late as 1922 (539). Blacher (119) stated in 1925 that the process of "peat formation" stands midway between "moder formation," with partial admission of oxygen, and "putrefaction," which takes place in the total absence of oxygen. Potonié defined this process as follows: "Peat formation is one of self-decomposition, which represents the last phase of combustion, decay and putrefaction processes, following one another." Ost (794) defined peat as "a product of moder formation of recent bog plants."

Von Post (838) suggested the use of a graded scale of ten units for measuring the degree of "humification" or "huminosity" of peat. The color and turbidity of the water liberated from the peat when squeezed by hand, as well as the change in plant structure as recognized by the naked eye, were used as criteria of transformation. This system seems to be a modification of an earlier, less complicated one proposed by Wallgren in 1910 (119). Needless to say, this system is arbitrary and unfounded upon knowledge of the chemical processes involved in the decomposition of peat. In speaking of the products formed as a result of various decomposition processes, von Post distinguishes the formation of several substances: (a) "gyttja," or "sapropel"-like material, resulting from "putrefaction" or "fermentation"; (b) formation of "dy," or colloidal humus material, in environments supplying amounts of air

that are limited as a result of water cover; (c) production of "raw humus" under conditions of limited aeration and drainage; (d) "moder" formation, occurring when a plentiful supply of oxygen is admitted. "Sapropel" and "dy" are further distinguished by the color of the alkali extract, the former being greenish and the latter brown. No consideration was given to the microorganisms active in the decomposition or to the chemical transformations involved, which alone could explain the formation and physical characters of the products. Such systems are at best only descriptive in nature.

Methods of "humus" determination. Because of the significance attached to the formation, in the process of decomposition of plant and animal residues, of specific complexes possessing characteristic properties and known as "humus," it was quite natural that various methods should be devised for its quantitative determination in soils and in composts. The need for such methods was based upon the recognition of a distinct difference between "humus" and the decomposing residues. As far back as 1861, Fremy (317) stated that peat consists of structural material of undecomposed plant residues and of varying proportions of brown compounds, neutral or acid, nitrogenous or nitrogen-free, which "we designate in our ignorance by the general name ulmic compounds."

Similar ideas are found in the work of numerous investigators in very recent times. It is sufficient to cite Springer (1077), who divided humus into two groups of constituents: (a) one consisting of undecomposed plant residues, which can be identified with cellulose, pectins, tannins, lignins; (b) the other consisting of true "humic substances," under which "one understands those yellow-brown to dark-black-brown colored substances of unknown constitution, called by Grandeau *matière noire*, which are formed as a result of chemical decomposition in nature of the above organic substances under the influence of atmospheric agencies."

It is reasonable to assume *a priori* that, with the prevalent confusion concerning the nature and origin of the humus substances of the soil, the methods for their quantitative estimation should give varying results, since, by the use of different methods, different complexes are frequently measured. A detailed review of the numerous methods proposed at different times for determination of "humus" is given here because of the historical significance attached to the results obtained by these methods. Very few of these methods are valuable in interpreting the abundance of soil organic matter or its specific nature (see also 114, 188, 270, 584, 643, 707, 738, 864, 809, 831, 884, 885, 1048).

ALKALI EXTRACTION METHODS

Grandeau's method and its modifications. Achard (8) was the first to extract peat with alkali solutions and to neutralize the extract with sulfuric acid. The yield of dark brown to almost black precipitate was taken as an index of the "degree of humification" of different peats. Since that first investigation, numerous measurements have been made of the content of "humus" in soil and in peat, by extracting the dark colored material with alkali solutions. The procedure most commonly employed was that recommended by Grandeau, who extracted the dark colored organic substances with ammonium hydroxide solution, after preliminary treatment of the soil with dilute hydrochloric acid. He believed that these materials are the most important nutrients for plants. This method was modified later by Hilgard (439, 484). He treated the soil first with dilute hydrochloric acid solution (1 to 10 per cent) to break down the "calcium humate," filtered and washed the soil with water, and then extracted it with 4 per cent ammonium hydroxide solution; the extract was removed by filtration, evaporated, dried at 105°C., and then weighed and ignited; the loss in weight was taken as the "humus" content (*matière noire*) of the soil.

This method of "humus" determination was found to be open to considerable criticism. In the first place, not all of the dark colored constituents of the organic matter go into solution by this procedure, while some of the colorless constituents are dissolved. Secondly, the amount of "humus" found in a soil depends upon the concentration of the ammonia, the volume used, length of time of extraction, and the manner of extraction, as shown in table 5. Huston and McBride (469) suggested the use of a 4 per cent solution of ammonium hydroxide and a 12-hour period of extraction. Ammonia was found to deflocculate the clay fraction, which is not removed by filtration. Various modifications were introduced for the purpose of removing clay from the alkali extract (724), such as filtration through a clay filter (168, 169, 535), coagulation in the process of evaporation of the extract on a water bath, the use of ammonium sulfate or potassium chloride (314), and separation of the clay by electrolysis (862) or by centrifuging (1266).

None of these modifications proved to be entirely satisfactory and still left the method open to criticism. If the clay is not removed, its high content of constitutional water will invalidate the results obtained on ignition of the residue; if an ultra-filter is employed to remove the colloidal clay, some of the colloidal "humus" is also removed; when the

clay is coagulated with an electrolyte, some of the organic complexes are also coagulated. These difficulties tended to discourage further use of this method. Alway and his associates (27) and Fraps (309) recognized that a large number of past determinations of “humus” were unreliable and ascribed this to the high ash content. Peter and Avritt (815) suggested that 10 per cent be subtracted from the determination to allow for the error involved. However, this also was shown to be unreliable and inaccurate (1077).

Springer carried out the determination of “humus” as follows: A 5- to 50-gm. portion of soil, according to the “humus” content, was treated first with 100–200 cc. of 1 per cent HCl solution, followed by warming, decanting, and washing. The soil was then shaken for at

TABLE 5

Influence of concentration of ammonia upon the removal of “humus” from soil (1282)
Per cent of “humus” in soil

NATURE OF SOIL	AMMONIA CONCENTRATION							
	2 per cent		4 per cent		7 per cent		8 per cent	
	Method of extraction							
	Gran- deau	Huston	Gran- deau	Huston	Gran- deau	Gran- deau	Huston	Huston
Peat soil.....	9.61	15.74	15.03	20.72	19.81	21.80	15.73	21.61
Black soil.....	3.99	6.95	3.05	7.20
Clay loam.....	1.81	4.28	2.44	3.76	2.14	4.25	1.88	4.26

least 2 days with 400 to 900 cc. of a 4–5 per cent ammonium hydroxide solution. The extract was placed in tall graduate cylinders and allowed to remain undisturbed for several weeks, until the clay settles. An aliquot portion of the supernatant liquid was then removed and shaken with a little ammonium carbonate solution. After coagulation, part of the liquid was evaporated, dried at 105°C., weighed, ashed, and weighed again.

In spite of the numerous criticisms directed against this method of humus determination in soil and in spite of the limited information concerning the nature of the humus complex thus determined, thousands of determinations were made throughout the world (1051, 703). However, sooner or later, this method was found to give results highly disappointing, and it was finally dropped from the official methods of the American Association of Agricultural Chemists.

Precipitation of humus extracts with acids. Another procedure for the determination of the alkali-soluble portion of the organic matter of the soil involves extraction with a dilute solution of sodium or potassium hydroxide and subsequent precipitation of the filtered alkali extract with an acid. This method has been used since the time of Sprengel, and the precipitate thus obtained was referred to either as "humus" or "humic acid," as pointed out previously. If a sufficient excess of acid is employed for precipitation, the mineral substances, largely the aluminum silicates which are also partly soluble in alkali solutions and are precipitated on neutralization with an acid, will be redissolved (1222), thus giving a "humus" preparation containing a low amount of ash. This method can be conducted as follows: A 50-gm. portion of mineral soil is treated with two consecutive 100-cc. portions of 2.5 per cent sodium hydroxide solution, heated in an autoclave, at 15 lbs. pressure, for 30 minutes or left standing in the cold for 48 hours, with frequent shaking. After each extraction, the liquid is removed by filtration through paper, and the residual soil is thoroughly washed with some fresh alkali solution and finally with water. The filtrates and washings are combined and treated with a 10 per cent warm hydrochloric acid solution until a precipitate is formed; half as much more of the acid solution than was required to bring about the precipitation is then added. The precipitate is filtered through dried and weighed filter paper and washed several times with 2 per cent HCl solution and with water until free from acid. The paper containing the precipitate is dried at about 70°C. and weighed, and the contents are analyzed for total ash and nitrogen. The preparation thus obtained contains only about 1 to 2 per cent ash and about 3 per cent nitrogen. It was suggested that this preparation, which might be called "humus" or "humic acid," should be designated as the α -fraction of the soil humus.

When the filtrate from the α -fraction is carefully treated with an alkali solution, another precipitate is formed. An excess of alkali should be avoided, and the reaction adjusted to about pH 4.8. This precipitate is filtered off, washed with water, dried, weighed, and analyzed for ash, total carbon, and total nitrogen; it was designated as the β -fraction of humus ("neutralization" fraction of Hobson and Page) and consists largely of aluminum hydroxide combined with about 10 to 30 per cent organic matter. Appreciable amounts of humus constituents will be found in this fraction when mineral soils and especially the B-horizon of the podsol soil profile are treated. The influence of organic manures and inorganic fertilizers upon the content of humus in

soil, as measured by the α - and β -fractions and by their nitrogen content, is shown in table 6. This method as well cannot be recommended as a routine procedure for quantitative determination of soil humus. Although it has been found that distinct differences in the yield of these fractions are obtained from different soils or even from the same soil but differently treated, the two fractions represent only a part of the soil humus; the data obtained throw little light upon the origin of the humus and its rôle in soil processes [see (799)].

TABLE 6
Influence of manurial soil treatment upon its “humus” content (1222)
 On basis of 100 gm. of dry soil*

TREATMENT OF SOIL FOR A PERIOD OF 20 YEARS	NITROGEN CONTENT OF SOIL	α -FRACTION		β -FRACTION			NITROGEN IN SOLUTION FROM β -FRACTION
		Yield	Nitrogen content	Yield	Organic matter content	Nitrogen content	
	per cent	mgm.	mgm.	mgm.	mgm.	mgm.	mgm.
Stable manure.....	0.134	766	26.0	1,894	598	22.9	36.1
Untreated.....	0.074	248	8.2	1,468	478	16.2	19.4
NaNO ₃ and minerals.....	0.097	438	15.6	1,688	526	17.5	31.8
(NH ₄) ₂ SO ₄	0.095	434	14.2	1,833	585	18.2	33.4
Stable manure, nitrate and minerals. . .	0.132	792	21.8	1,831	579	19.0	37.8
Lime and manure.....	0.128	674	23.0	1,702	556	19.8	41.8
Lime alone.....	0.080	293	9.9	1,863	554	14.6	31.6
Lime, (NH ₄) ₂ SO ₄ and minerals.....	0.078	456	14.0	1,785	539	18.0	37.8
Lime and minerals.....	0.082	281	9.6	1,812	548	15.1	24.4

* 5 per cent NaOH solution used for extraction.

† The ash content of this fraction was only 1.3 per cent.

According to Page (48), hot alkali solutions extract about 70 per cent of the organic matter of the soil in 5 hours, as measured by the amount of total carbon in the extracts; cold alkali solutions remove only about one half as much of the carbon. The nature of the alkali and the length of the extraction period are of great importance in this connection, as shown in figure 1. In accordance with Oden’s nomenclature, Page suggested that the organic matter of the soil insoluble in cold alkali solution consists largely of “humin”; on treatment with a hot alkali solution, the “humin” undergoes hydration and is changed to “humic acid.” The fact that the subsoil contains a type of humus which is more

readily soluble in cold alkali than is the organic matter of the surface soil led to the conclusion that the organic matter in the subsoil was not formed *in situ* as a result of decomposition but had been washed down from the surface soil.

Simon (1034-5) employed neutral salt solutions, especially sodium fluoride or sodium oxalate, for the extraction of the "humus" fraction from the soil. A given quantity of soil is treated with 10 volumes of a 1 per cent salt solution; the extract is filtered and the filtrate concentrated by evaporation; the "humus" is then precipitated with hydrochloric acid, removed by filtration, washed, and dried. This procedure

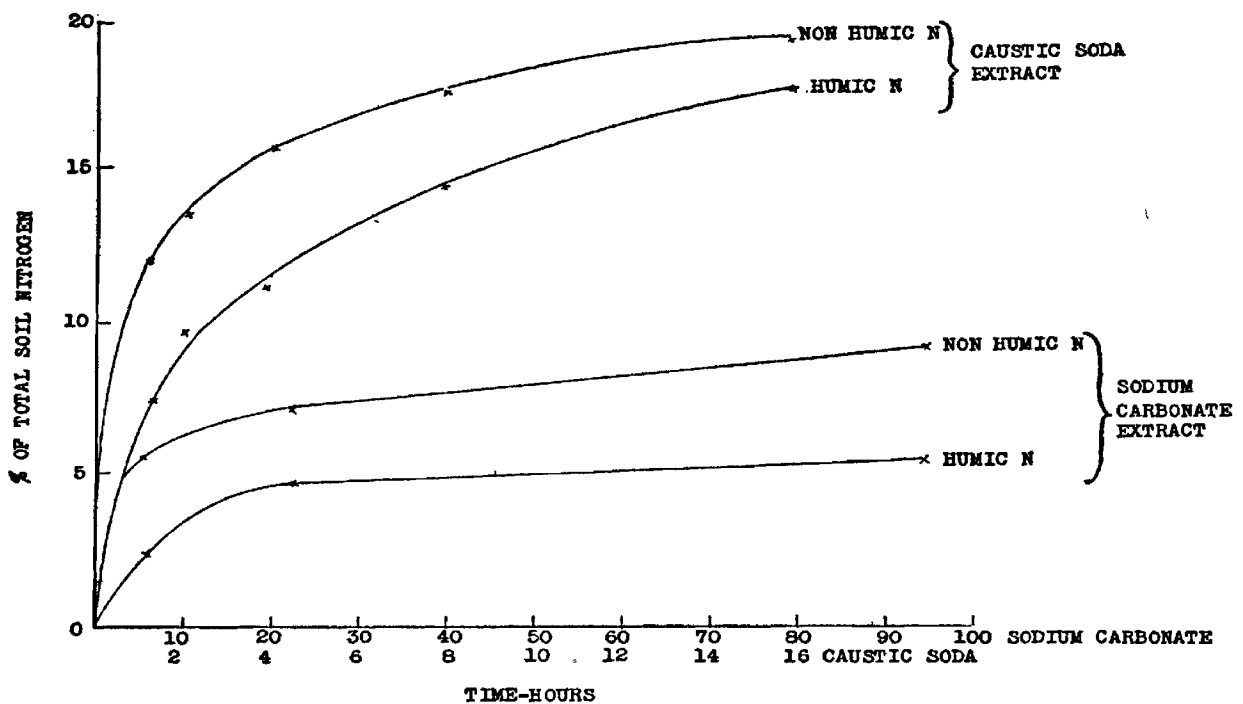


FIG. 1. Extraction of soil humus with sodium carbonate and sodium hydroxide solutions, for different periods of time (Hobson and Page).

as well, whatever its value for preparing a certain dark colored fraction of the soil organic matter, has nothing to recommend itself for quantitative determinations of the soil humus or of a definite portion of it.

Colorimetric procedure for "humus" determination. In view of the fact that the dark color of humus has been taken as its most characteristic property, it is quite natural that colorimetric tests should have been suggested. Beam (76) was the first to employ such a method for humus determination; a dilute sodium carbonate solution was used for preparing the extract but it was not stated whether the extract was left overnight to settle or was centrifuged; the two procedures do not always give the same results.

Alway (27) reported that, in the case of surface soils of the same locality, the intensity of color of the ammoniacal extract is in close agreement with the amount of "humus" present, as determined by other procedures. However, on comparing humid and semi-arid subsoils, a marked difference was found in color intensity, although in both instances the same amount of "humus" was found, as determined gravimetrically. Blacher and Douglas (120) extracted various peats with 2 per cent NaOH solution and compared the color of the extract with that of a standard solution; the results obtained were found to be far from satisfactory.

Melin and Oden (699) defined "humus" as the dark brown to black substance of unknown constitution which originates through the decomposition of organic residues in nature or in the laboratory through the action of acids and alkalis upon sugars. Assuming that humus is characterized by the dark pigment and assuming further that alkalis extract these "humified" substances from soils and peats, Melin and Oden felt justified in using the color intensity of the alkali extract as a proper index of the "humified" portion of the organic matter.

Oden (781) has further shown that the course of light absorption by various "humus" preparations and by Merck's "humic acid" is a uniform one, within the limits of colorimetry, in spite of slight differences in the color nuance; therefore, it appeared possible to compare the color of various "humus" preparations with one another. With the advance in the decomposition of the organic matter an increase in the color intensity was recorded. Oden designated the colorimetric values obtained for peat as the "humification values," whereby the term "humification" was applied to the process of transformation of the plant residues into the dark colored "humus." Stadnikoff and Mehl (1088) also obtained satisfactory results by using the colorimetric method for determining "the degree of peat formation."

The question of a standard for color comparison has attracted considerable attention. In many cases (76, 27), especially for determining the "humus" content of mineral soils, satisfactory results were obtained from the use of a soil with a known humus content, as determined by Grandeau's method. For the determination of the degree of "humification" of peat, the "acidum humicum" of Merck was frequently employed (119, 781); this is prepared by extracting highmoor peat with sodium hydroxide solution and precipitating the extract with acid. This preparation, however, contains, not only "humic acids," but also pentosan and other hemicelluloses. Stadnikoff and Mehl used as a standard a

moist paste of "humic acid" prepared from peat. Joseph (514) treated a soil with dilute hydrochloric acid to remove the bases, washed it free from acid, and extracted it for 24 hours in the cold with 50 cc. of 4 per cent NaOH solution. The suspension was centrifuged, and the color of the solution was compared with that of a solution of a known "humus" preparation. In some cases, the alkali extract was filtered through a membrane filter, before the color comparison was made (455).

Standard preparations were shown (252), however, to present certain disadvantages, because the humus found in different soils varies in color as a result of differences in chemical composition. The color intensity of equal quantities of water-free and ash-free humus preparations in the form of Cassel brown, "acidum humicum," and "hymatomelanic acid," all dissolved in a 5 per cent NaOH solution, gave (1080) respective ratios of 7.5:5.0:4.3. The color intensity of alkali solutions of "humus" weakens on standing, even within a few hours. Springer found that a concentrated solution of iron chloride was preferable and could be used conveniently for this purpose. The rapidity of change in color of the alkali solution depends upon the concentration of the alkali and the length of action (118). One-tenth per cent "acidum humicum" in a 0.4 per cent ammoniacal solution lost 15 per cent of the color intensity in 24 hours and 20 per cent in 48 hours; the same amount of the "humus" preparation in 2 per cent NaOH solution lost 18 and 26 per cent of its color intensity in 24 and 48 hours, respectively. Higher alkali concentrations brought about an even greater reduction in color intensity, because the more concentrated solutions exert a destructive, as well as a coagulating, effect upon the dark colored organic substances.

For carrying out the determination of "humus" by the colorimetric procedure, Springer recommended the treatment of 1 to 20 gm. of soil, or 0.5 to 1 gm. of peat, with 100–200 cc. of 5 per cent HCl solution for 30 minutes at 50°C., after which the material is filtered and the residue is washed. This is followed by extraction with 100 cc. of 5 per cent sodium carbonate solution, at 100°C., for 30 minutes; the suspension is cooled, placed in a 250-cc. graduated cylinder, and made up to volume; after this has stood for 1 to 2 days, an aliquot portion is carefully removed, diluted, and immediately compared with the color standard. An iron chloride solution equivalent in color to 100 mgm. "acidum humicum" free from water and ash was used as a standard (1036).

The colorimetric method for determining the "humus" content in soil and peat met with considerable criticism. Blacher (118, 119), who was one of the first to use this procedure, as well as Gorbenko (352),

stated emphatically that, although it can give useful information because of its rapidity, the results must be applied with great care, because of the chemical instability of the humus bodies. Gortner (354) called attention to the fact that the soil pigment does not necessarily represent the same substance as the soil organic matter; a number of factors were found to influence the color of the solution containing a given amount of "humus," namely, the amount of the black pigment, the amount of the red-brown coloring materials found in the plant residues, the amount and nature of the vegetable indicators, and the proportion of colorless compounds. Soils containing the same amount of humus may vary as much as 500 per cent by the colorimetric procedure (26).

Page (48) determined the ratio between the tint of color and the carbon content of the extract prepared by treating the soil for 5 hours with a hot alkali solution. The results were found to vary between different soils, between soils and subsoils, and between soils differently treated. The conclusion was reached that the organic matter of surface soils is more deeply colored than that of subsoils; the organic matter of soils receiving applications of manure is more deeply colored than that of soils receiving no manure at all or receiving artificial fertilizers; the organic matter of mineral soils is less colored than that of peat. However, for want of another method, they recommended that this procedure be used for determining the degree of "humification" of the soil organic matter.

Shorey (1014) severely criticized this method, 1. because it is impossible to prepare a color standard which represents a definite quantity of organic matter; 2. because there are present in the soil colorless organic compounds that do not yield colored solutions with an alkali; 3. because the "humus" extract represents only a part, and usually an unknown part, of the total organic matter of the soil, making the method inapplicable for measuring the total soil organic matter; 4. because the color of the extracts varies with the nature of the soil; different soils cannot, therefore, be compared by means of this method, since they give different shades of color. To these criticisms, it might be further added that the humus complexes vary considerably in chemical composition, especially when those of inorganic soils are compared with those of peat and composts. These facts indicate that the colorimetric method is at best very limited in application.

Oxidation of humus extracts. When soil or peat is treated with an alkali solution and the extract precipitated with acid, the resulting precipitate, by whatever name it may be designated, contains only a part

of the humus made soluble by the alkali treatment. The amount of organic matter calculated from oxidation of the whole extract is much greater than that contained in the precipitate. Borotraeger (130) proposed treatment of the alkali extract with calcium hypochlorite solution or Javelle water; however, no sharp end point was obtained by this method. Aschmann and Faber (55) extracted the soil with 5 per cent sodium hydroxide solution on a water bath, then diluted the extract with water and titrated it with $N/100$ $KMnO_4$ solution, until no discoloration took place on prolonged boiling. The brown precipitate was brought into solution with an excess of oxalic acid and again titrated with $N/100$ $KMnO_4$. The "humus" content of the soil was calculated by comparing the titration value with that of an alkali solution of 0.25 gm. "acidum humicum" in 1 liter of solution. The end point, however, was found to depend on the concentration of the permanganate and the length of time of boiling (1078).

Fallot (283) modified this procedure as follows: A 5-gm. portion of soil was first treated with 10 per cent nitric acid solution to remove the bases; the residue was filtered, washed, and extracted with 100 cc. of 10 per cent KOH solution, for 1 hour, at $100^\circ C$.; the solution was cooled, made up to 250 cc., and filtered. An aliquot portion of the extract was then diluted to 100 cc. with water and heated to boiling; $KMnO_4$ solution (10 cc. of $N/10$) was added, boiled for 10 minutes and acidified with H_2SO_4 ; a measured excess of $N/5$ oxalic acid was now added and the excess titrated back with $N/10$ $KMnO_4$. One cubic centimeter of the $KMnO_4$ solution is equal to 8 mgm. of oxygen or 6 mgm. of "humic matter." Similar methods were proposed by Springer (1078) and by Kreulen (590) although the method of calculation was somewhat different.

Vincent (1211) divided the alkali-soluble organic matter of the soil, which was spoken of as "total humic matter," into "humus" or the fraction precipitated by acid, and "soluble humic matter" comprising those organic substances which remained in solution. The "humic" fractions were oxidized with $N/10$ $KMnO_4$ solution, and the amount of the latter required was used as a basis for expressing the concentration of these fractions. A 4 per cent NaOH solution was found to extract in the cold less "humus" than did ammonium hydroxide, as shown by the two corresponding ratios ("humus" extract: $N/10$ $KMnO_4$ solution) of 2.03 and 1.65. These results prove that the nature of the alkali used for the extraction of the "humus" influences the amount of permanganate required for oxidation. The oxidation per cubic centimeter

of permanganate was found to vary with different soils, the oxidation of the "total humic matter," "humus," and "soluble humic matter" fractions for three different soils being 1.55, 0.97, 2.19 mgm. for one soil, 1.36, 0.95, 3.58 for another, and 1.62, 0.97, 1.10 for a third soil.

Carbon and nitrogen content of humus extracts. In some instances the alkali extract of soil has been analyzed for total carbon (353), total nitrogen (500), methoxyl groups (706), or amino nitrogen (37, 227, 576, 1119). Marked differences were obtained when the carbon content of the ammonium hydroxide extract of soil was compared with the weight of the residue left on evaporation of the same extract; a lower yield was found in the residue. This was explained by a loss of easily oxidizable carbonaceous materials during evaporation of the extract on a steam bath (34).

The carbon-nitrogen ratio of the "humus" in the alkali extract was found (1274) to be the same as in the soil itself. By extracting a soil with 3 per cent sodium hydroxide solution for 3 hours, 30.5 per cent of the humus was removed; after 88 hours' extraction, 56.8 per cent of the humus was dissolved or dispersed. A comparison of the amount of "humus" found in soil with the crop yield from the same soil, using a series of differently treated plots, showed that the total soil humus, estimated by multiplying the carbon content by the factor 1.724, is a more reliable index of soil fertility than is the "humus fraction" determined by alkali extraction.

EXTRACTION OF HUMUS WITH PYRIDINE

Piettre (826, 829) suggested that the "free humus" of the soil be determined by treating 20–30 gm. of soil with pyridine diluted with an equal volume of water. The extract was removed and the solvent carefully distilled off; the concentrated residue was transferred to a tared dish, evaporated on a water bath, and dried 12 hours at 105–110°C. To determine the "combined humus," the residue from the first extraction was treated for several hours with 5–10 per cent hydrochloric acid, filtered, washed, and again extracted with pyridine. The powdered pyridine extract was now washed with a 1:1 mixture of ether and ethyl alcohol, whereby fatty acids and resins were removed. The pyridine reagent was found to dissolve 10–25 per cent of the humus contained in a rich virgin soil and 40–55 per cent in a fatigued coffee soil.

This method as well has several distinct disadvantages: (a) "humic substances" absorb the reagent which then cannot be removed easily on drying at 105–110°, as a result of which too high yields may be

obtained (64); (b) pyridine dissolves only a part of the humus; the so-called "humins" are left behind and the remaining soil organic matter still gives brown colored extracts with sodium hydroxide solution (1077).

DETERMINATION OF HUMUS BY DIRECT OXIDATION

Oxidation with potassium permanganate. This method is based upon the degree of oxidation of humus, when treated directly with a standard potassium permanganate solution; the amount of reagent consumed in the process of oxidation is used as a measure of the humus content (681, 479). A given quantity of soil (0.25–0.50 gm. in the case of a soil with a low organic matter content and 0.1–0.2 gm. of soil with a high organic matter content) is treated with an excess of 0.1 *N* or 0.2 *N* permanganate solution, in order to bring about complete oxidation; an equal amount of water and 2–4 cc. of 1:5 sulfuric acid solution are then added. The contents of the flask are boiled for 40–50 minutes, the solution is decolorized by the addition of standard oxalic acid, and the excess of the latter is titrated back with the standard permanganate. If *v* is the number of cubic centimeters of the permanganate solution consumed and *m* its concentration, the "humus" content of the soil taken for the analysis can be expressed as,

$$11 \times m \times \frac{v}{100} \times 0.471 \text{ gm.}$$

The "humus" concentration can be calculated by multiplying the number of cubic centimeters of *N*/5 permanganate solution consumed by the factor 0.0010362.

In order to avoid the errors that this method involves, it was suggested (480) that the procedure be standardized: high concentrations of permanganate and sulfuric acid were to be avoided so as to prevent losses of oxygen into the atmosphere; excessive quantities of soil were not to be used; to make certain that the precipitated manganic oxide was redissolved, the solutions were to be boiled with oxalic acid; an excess of water was to be added and boiling continued for about 1½ hours. Further modifications were introduced later (909, 367).

Both the original method and its modifications (1064), however, give variable results. This is primarily because the humus of the soil is not completely oxidized. Furthermore, neither the humus itself nor a definite fraction of it is measured as such, since the determination is based on the amount of oxygen consumed in the oxidation process. Moreover, the evidence is indirect and, in view of the fact that the

chemical nature of the humus varies in different soils, the results also vary. Largely because of these limitations, this procedure has yielded results which are either lower than the organic matter content of the soil, as calculated from total organic carbon, or sometimes even higher (342).

Oxidation with silver chromate. The use of silver chromate for the oxidation of humus has also been proposed (1038). A small quantity of soil is treated with 25–30 cc. concentrated sulfuric acid and 8–10 gm. silver chromate. The container is placed on a water bath and heated for 4 minutes, and the CO₂ liberated is measured. The results obtained by this method were found to agree well with those of the combustion method (13) and were even higher than the results obtained by the chromic acid procedure. Balks (64) used 50 cc. of 72 per cent sulfuric acid and came to similar conclusions (345). Mercury chromate does not give as good results as the silver salt.

By oxidizing the soil with potassium chromate, in the presence of concentrated sulfuric acid, and calculating the humus from the amount of oxygen consumed, results have been obtained which were used for the rapid estimation of humus, as shown in the appendix.

Oxidation with hydrogen peroxide. König (567) was the first to demonstrate that on continued treatment of soil with concentrated hydrogen peroxide solution, a certain amount of the humus is oxidized. It was suggested that the amount of CO₂ produced as a result of this reaction could serve to distinguish the amount of “easily decomposable humus,” from the “difficultly decomposable humus,” which is not readily oxidized by hydrogen peroxide. However, carbon dioxide is not always the sole product of oxidation, since König himself found acetic and formic acids in solution. Certain aliphatic di-carboxy acids, especially oxalic and succinic, as well as aromatic poly-carboxy acids, may also be formed during this reaction (1272).

Robinson and Jones (902, 903) treated composts and soils with 6 per cent hydrogen peroxide solution, at boiling temperature, and measured the amount of organic matter destroyed; they suggested that by means of this procedure one is able to distinguish the “humified” from the “non-humified” portion of the organic matter. They believed that the amorphous, structureless, decomposed (“humified”) organic matter is brought into solution by this treatment, while the structural material is not attacked. By using this method as a measure of the “degree of humification” of the organic matter, they were able to show that the “highest degree of humification” has been attained in peats and uncultivated soils, which are kept under anaerobic conditions. The fact that

the residue left after prolonged treatment with the hydrogen peroxide solution no longer gave any brown color upon addition of hot sodium hydroxide solution was considered as proof that the "humus" of the soil was destroyed by the former reagent. Jones (512) used this method for determining the degree of decomposition of farmyard manure. The term "humification" was applied to those processes which are involved in the transformation of the organic matter in plant and animal residues into structureless material; some distinction was implied between this process and "humification" of organic matter in the soil. In the absence of litter, about one-half of the organic matter in stable manure was found to be in a "humified" state at the very beginning of the process of composting. The "humification value" of the manures examined varied from 35.0 to 75.0 per cent. It was further suggested that the determination of the "degree of humification" be utilized as a criterion of the physical condition of farmyard manure.

Springer (1077) preferred to use König's original procedure, in order to avoid the action of hydrogen peroxide at boiling temperature. About 10 gm. of soil were placed in a flask, moistened with water, and 2-cc. portions of 30 per cent hydrogen peroxide solution added daily. The measured amount of CO_2 liberated was multiplied by 0.471 to give the amount of "easily decomposable humus" in soil. It was believed that only the "humified" organic matter was thus determined, whereas on heating the extract the "non-humified" substances were also oxidized.

Waksman and Stevens (1241) found that although with the advance of decomposition there is a marked increase in the amount of material oxidized by hot 6 per cent hydrogen peroxide solution, undecomposed plant residues also show a considerable degree of oxidation under these conditions. This was in line with the results of König (571) who demonstrated that lignin can be removed from wood by oxidation with H_2O_2 ; the water-soluble substances, certain hemicelluloses, and a definite amount of the lignin are oxidized by this reagent. To classify as "humified" materials such substances as the products of decomposition, including the synthesized microbial cell substance, was to overlook completely the nature of the decomposition processes in soils and in composts. The action of hydrogen peroxide upon undecomposed plant materials was thus shown to be far from negligible, especially in the presence of soil; this action varies with the nature of the material (882). The destruction of the organic matter in soil by means of H_2O_2 was found to be (463) a function of the H-ion concentration of the soil, as

tically all of the organic constituents will be brought into solution, forming acetylated and methylated products; however, the dark colored complexes which are produced in the process of decomposition of plant residues, namely the "humus" of soils and composts, are not attacked by this reagent. Karrer, therefore, proposed the use of this method for the separation of the undecomposed plant residues from the "humified" substances. Groszkopf (371) found that Cassel brown, after the removal of the bitumen, was not acted upon by acetyl bromide, while a "hymatomelanic acid" preparation was dissolved; hence, he concluded

TABLE 7

The yield of "humified" material, as determined by different procedures (1078)
Per cent of total organic matter ($C \times 1.724$)

	SOIL TYPE							
	Clay loam	Sandy loam	Sandy soil	Clay soil	Dolomitic sandy loam	Peat soil	Alpine pasture soil	High-moor peat
	Carbon content							
	0.50	1.10	2.8	3.31	7.83	8.59	8.69	51.2
Acetyl bromide.....	57	55	53	50	65	50	60	..
Sodium hypochlorite.....	93	81	92	84	97	80	72	77
Hydrogen peroxide.....	48	50	63	54	66	..	15	25
Grandeau method.....	40	58	39	36	51	47	54	..
Pyridine extraction.....	47	47	44	56	46	66	47	45
Extraction with 5 per cent NaOH and oxidizing.....	64	67	71	67	77	71	59	83
Extraction with 5 per cent Na ₂ CO ₃ and oxidizing.....	45	43	47	43	51	55	41	59
Colorimetric estimation of the 5 per cent Na ₂ CO ₃ extract.....	13	21	25	18	35	32	53	51

that the latter is lignin-like in nature. This alone would be sufficient grounds on which to question the value of acetyl bromide as a reagent for distinguishing two groups of constituents of humus, one consisting primarily of residual undecomposed plant constituents and the other of modified and synthesized complexes.

Springer (1078) spoke of that part of the humus insoluble in acetyl bromide as "pure humus." The material is first extracted with ether and alcohol and then dried at 105°C. An aliquot portion of the residue is treated with 50 cc. acetyl bromide in Soxhlets, at 40–50°C., for 3

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days with frequent shaking; the filtered residue is dried at 90° for 30 minutes, washed with ether, dried at 105° to constant weight, weighed, ignited, and weighed again. The difference between the last two weights is a measure of the "pure humus." In the case of mineral soils, the total carbon of the organic matter left after the treatment is determined and multiplied by 1.72. The "humus" soluble in ammonium hydroxide was found to have no quantitative relation to the "pure humus." When a soil was extracted with 5 per cent NaOH solution, and the extract oxidized with permanganate, higher values were obtained than those found by the acetyl bromide method; this was believed to be due to the fact that the NaOH also extracts certain plant constituents (table 7). The ratio between the carbon of "pure humus" and of the total humus was designated as the "degree of decomposition." Springer later distinguished two types of organic compounds insoluble in acetyl bromide: (a) "Cassel brown" type of material found in acid soils or in neutral and slightly alkaline soils, where there is little decomposition ("humification"), giving brown-colored alkaline extracts; (b) "Chernozem" or "black earth" type, a humo-silicate complex, found in soils characterized by "strong humification," giving gray or black alkaline extracts (1080).

HYDROLYSIS OF HUMUS BY CONCENTRATED MINERAL ACIDS

It has been definitely established that when plant residues undergo decomposition in soils or composts, the carbohydrates disappear rapidly, while other constituents, especially the lignins and the proteins tend to accumulate, as will be shown in detail later. In view of the fact that carbohydrates give reducing sugars on hydrolysis with acids (72 per cent sulfuric acid for cellulose, and weaker acids for other carbohydrates), Keppeler (537) proposed that the degree of decomposition of peat be measured by determining the amounts of hydrolyzable and non-hydrolyzable portions. He proposed a definite formula for making such calculations. This procedure is commendable since it is based on the actual processes of transformation of the plant constituents. However, it can be applied only to materials which have originated from specific plants of known composition, as in the case of highmoor peats; further, insufficient consideration is given to the synthetic processes of microorganisms, which may become very prominent under aerobic conditions of decomposition. More detailed reference will be made to this method in the subsequent discussion of the chemistry of peat.

OTHER METHODS FOR DETERMINING THE "HUMIFIED" PORTION OF HUMUS

A number of other methods have been suggested at various times for the purpose of distinguishing the "humified" from the "unhumified" portions of organic matter in plant residues which have undergone decomposition in soils, peats, and composts. Several of these methods are mentioned here:

1. The liberation of iodine from iodates, in the presence of potassium iodide. Baumann and Gully (75) suggested the use of a solution of 2 gm. of potassium iodide and 0.1 gm. potassium iodate in 100 cc. water; a given amount of soil or peat is added and shaken for 15 minutes. The solution is then filtered and the filtrate added to 100 cc. of dilute starch solution. The intensity of the blue coloration, due to the liberation of the iodine by the free "humic acid," was taken as a measure of the concentration of the latter.

2. The color of an aqueous solution of lithium humate formed by the action of a portion of the humus upon lithium phosphate. Lithium humate was found to go into solution, the phosphoric acid being liberated (17).

3. Borntraeger and later Tacke suggested the treatment of peat with freshly precipitated CaCO_3 in a stream of hydrogen gas, at ordinary temperature; the CO_2 liberated was absorbed in a standard alkali solution (130, 1114, 1123).

4. The titration of a hot alcoholic extract of humus with alcoholic potassium hydroxide solution (946).

These and other methods were based upon the determination of only certain fractions of the humus complex, because of their specific reactivity with various reagents. The results obtained by the use of these methods contributed little information concerning the chemical nature of the humus as a whole and frequently even of the particular fraction measured. The most important of all the methods was the simplest, namely, the determination of the total humus. By measuring the amount of organic carbon and multiplying by a factor (1.724), a fair estimation of the amount of humus is obtained (87, 648). However, where it becomes necessary to determine the extent of decomposition of plant residues, as in composts and peats, certain other procedures can be readily utilized. The most logical of these is that of Keppeler or one of its modifications (p. 83).

The chemical nature of the "humified" portion in the humus of soils, peats, and composts. In order to demonstrate the complete lack of justification for overemphasizing a specific group of humus constituents,

to be designated as "humified" organic matter, "pure humus," or "humic acid," the following experiments are cited (1235). Lowmoor peat and a straw compost, prepared by allowing cereal straw to decompose under favorable conditions and in the presence of available nitrogen, for 12 months, were used as sources of humus. These two materials were extracted in the cold, for several days, with 4 per cent NaOH solution; the extract was removed by filtration through paper. The residue was treated again with fresh 4 per cent NaOH solution, at 120°C., for several hours; the second extract was filtered hot through paper. The extracts were acidified with hydrochloric acid, and the precipitates filtered, washed with water, and dried; the hot extract was boiled for a few minutes after acidification. The residues left after the hot alkali extraction were neutralized with dilute acetic acid, washed with water and alcohol, and dried. The two filtrates left, after the acid precipitates were removed, were combined and analyzed for total nitrogen, ammonia nitrogen, and reducing substances.

The peat and the straw compost were thus divided, by treatment with alkali solutions, into four groups of complexes: 1 and 2. the acid precipitates of the cold and hot extracts, equivalent to preparations of the classical "humic acid"; 3. the residue left after the hot alkali extraction, equivalent to the "humins" and "ulmins"; 4. complexes dissolved by the alkalies but not precipitated by the acid, more or less equivalent to "crenic acid" and Oden's "fulvic acid." A chemical analysis of the first three groups of complexes, as compared with that of the original materials, is given in table 8.

The original peat contained 54.14 per cent carbon and 3.55 per cent nitrogen. Nearly two-thirds of its chemical constituents comprised lignin-like complexes and proteins; the remaining third included cellulose, hemicelluloses consisting largely of pentosans and uronic acid complexes, mineral substances, and a small admixture of a variety of organic compounds. The two acid precipitates of the alkali extracts varied considerably in composition; the cold precipitate contained about as much carbon and nitrogen as the original peat, whereas the hot precipitate was richer in carbon and poorer in nitrogen. This is a result of the relative increase in the concentration of lignin-like complexes, caused by the greater hydrolysis of the protein by the hot alkali and acid treatments. Both preparations were low in ash and high in alcohol-soluble substances or the "hymatomelanic acid" fraction, which is probably formed from lignins and lignin derivatives as a result of the alkali treatment.

Similar and even more striking results were obtained on analysis of the "humic acid" fractions from the straw compost. These results emphasize the fact that the composition of "humic acid" preparations is not constant, but is determined by a number of factors, which can be briefly summarized as follows: 1. the nature of the plant residues from which they were derived, 2. the processes of decomposition brought about by microorganisms, 3. the degree of their decomposition,

TABLE 8

Chemical composition of lowmoor peat and composted straw and of the "humus" fractions isolated from these (1235)

Per cent of dry material

CHEMICAL CONSTITUENTS	LOWMOOR PEAT				COMPOSTED STRAW			
	Original peat	Cold alkali extract, precipitated by cold acid ("humic acid")	Hot alkali extract, precipitated by hot acid ("humic acid")	Residue after hot alkali extraction ("humic")	Original material	Cold alkali extract, precipitated by cold acid ("humic acid")	Hot alkali extract, precipitated by hot acid ("humic acid")	Residue after hot alkali extraction ("humic")
Total carbon.....	54.14	52.73	54.36	47.95	48.98	58.18	63.98	43.00
Total nitrogen.....	3.55	3.26	1.79	2.21	2.48	2.68	1.39	0.34
Ether-soluble fraction....	0.12	0.26	0.39	2.68	0.92	5.42	1.50	1.12
Alcohol-soluble fraction...	0.99	14.06	21.92	3.59	2.87	12.66	18.19	0.81
Hot water soluble organic matter.....	2.26	8.86	3.29	4.47	5.16	1.96	1.06	1.04
Total hemicelluloses.....	8.84	1.05	4.54	4.46	14.49	0.74	1.00	12.02
Pentosan.....	5.02	4.30	15.16	12.88
Cellulose.....	1.73	0	0	2.36	14.38	0	0	54.68
Lignins and lignin-like complexes.....	43.18	48.95	52.55	47.65	25.62	56.41	62.57	14.13
Protein.....	19.31	19.75	10.94	11.81	12.75	16.69	8.62	1.40
Ash.....	12.80	2.90	1.90	14.40	17.70	0.50	0.90	2.00

4. the nature of the alkali used for their extraction, 5. the concentration of the alkali used, as well as the temperature and length of time of extraction, 6. the nature of the acid used for precipitation and the temperature at which precipitation takes place.

The foregoing conclusions also apply to the "humic" fractions. These were found to contain smaller amounts of carbon and nitrogen than the original materials, since a large proportion of the lignin-like complexes and proteins was removed by the alkali treatments. They were characterized by a lower hemicellulose and a higher cellulose

content, because the former are soluble in alkalies and the latter are not. An analysis of the filtrates brought out the fact that, because of hydrolysis of the organic nitrogenous compounds, about half of the nitrogen dissolved by the alkali treatments was not recovered in the acid precipitates. From 18 to 40 per cent of the nitrogen in the cold filtrate was present in the form of ammonia, because of the high amide content of the humus proteins. Both filtrates were rich in sugars, since a large part of the hemicelluloses in the humus was brought into solution by the alkali treatments and was subsequently hydrolyzed by the acid.

The literature on humus contains statements that "humins" are highly resistant to decomposition. The aforementioned preparations were added to soil and the rate of their decomposition was measured by the evolution of carbon dioxide and the accumulation of nitrate. The results obtained pointed to a complete lack of justification of the assumption. The "humin" preparations of both the peat and the compost decomposed readily, even more so than the "humic acid" preparations. The "humin" residues were rich in cellulose, especially in the case of the compost, and low in nitrogenous compounds; hence considerable evolution of CO_2 took place, not accompanied by the liberation of nitrogen; considerable consumption of this element in an available form by the microorganisms took place in the case of the compost preparation. These results tend to explain the findings of Hilgard (441) that "unhumified" organic matter does not nitrify. The terms "humified" and "unhumified" have been applied to phenomena which were not fully understood, and the explanation offered, as is frequently the case, was not the correct one.

Summary. Practically all the methods suggested at various times for determining the amounts of "humus" or of the "humified" portions of the organic matter in soils, peats, and composts are unsuitable for this purpose, primarily because they were developed with little or no regard to the processes that take place when fresh organic matter undergoes decomposition.

Failure to characterize the numerous interrelated processes would make practically valueless almost any definition of the "humified" part of plant and animal residues undergoing decomposition. One could conceive of such a complex only as long as the belief prevailed that decomposition is relatively simple in nature and gives rise to a specific group of dark colored substances. Now that the complexity of the process is established and the instability of humus recognized, the justification for applying the terms "humification" and "humified"

to decomposed organic matter may be questioned; these terms fail to convey any idea of the exact nature of the reactions involved or of the chemical nature of the humus produced.

Among the numerous gravimetric, volumetric, and colorimetric methods (944) proposed at different times for measuring the "humified" part of organic matter undergoing decomposition, the following have received favorable consideration: 1. the method of extraction with ammonium hydroxide solution (*matière noire* of Grandeau); 2. the extraction of humus with sodium hydroxide solution, then precipitation of the "humic acid" with a mineral acid; 3. the extraction of humus with sodium hydroxide solution and the determination of the depth of color of the solution by a comparison with a certain standard, or oxidation of the organic matter in the extract by means of a suitable reagent; 4. oxidation of humus with a dilute solution of H_2O_2 , or of H_2O_2 and ammonium hydroxide solution, with potassium permanganate solution, or with some other oxidizing agent; 5. treatment of humus in soils, peats, and composts with acetyl bromide. In most instances, these methods for the determination of the "humified" portion of the organic matter in soils, peats, and composts accounted for only a fraction which was indefinite in composition, in origin, and in relation to the humus as a whole.

One is justified in speaking of humus only in regard to the sum total of the organic matter in soils, peats, or composts. A study of the nature of this humus involves an investigation of the chemical nature of the plant and animal residues from which it originated, of the chemical processes of decomposition involved in its formation, of the nature and activities of the microorganisms bringing about the decomposition, as well as of the environmental conditions under which the decomposition took place.

Humus is not an intermediate product of decomposition, as was suggested by some agronomists and chemists, who believed that plant residues are first changed to "humus," this in turn being further broken down into its elementary constituents; "humus nitrogen" was supposed to be the most readily available form of nitrogen in the soil. These ideas were totally unjustified and were not borne out by studies of the processes of decomposition of organic matter in soils, peats, and composts. Neither is humus a final product of decomposition, as was believed by some chemists, who attempted to establish the chemical nature of this final product by its extraction with alkalies and precipitation with acids.

PART B
ORIGIN AND NATURE OF HUMUS

CHAPTER V

ORIGIN OF HUMUS

“L’acid fumique ne dérive pas de la matière animale, mais d’une réaction de la matière animale sur le ligneux ou sur les parties extractibles de la paille, des feuilles ou de la sciure de bois. . . . Les éléments complémentaires se brûlent ou s’évaporent.”—THÉNARD.

The existing confusion concerning the chemical nature of humus is due largely to an insufficient understanding of its origin. With the advance of our knowledge of the chemical composition of plant materials, with a better understanding of the rôle of microorganisms in their decomposition, and with a greater appreciation of the complexity of humus substances, there has also been rapid progress in the development of a more sound theory accounting for its formation in soil, peat, and composts. The fact began to be recognized (586) that, instead of confining all attention to humus which has already been formed, it would be more logical to begin with fresh plant residues and follow the course of change which takes place during the process of their transformation into humus. It was found that the humus thus produced is not a chemical individual but a mixture of substances varying under different conditions of formation, depending on such factors as the nature of the vegetation, nature and intensity of its decomposition, climatic conditions, and physico-mechanical and chemical soil properties.

The first prerequisite to a knowledge of the origin and chemical nature of humus is an understanding of the chemical composition of the plants which largely contribute to its formation. Further, consideration of the digestive processes brought about in the animal system and of the chemical composition of animal residues, especially of stable manures and other waste products, as well as consideration of the physiological activities of microorganisms and the composition of the microbial cells, would also reveal facts which would contribute to a better understanding of the chemistry of humus.

CHEMICAL COMPOSITION OF PLANTS

Plants synthesize numerous chemical compounds, most of which play limited rôles as sources of material for humus formation. Plant

residues are returned to the soil in the form of roots, stubble, green manures, stable manures, and composts, in cultivated field and garden soils; as leaves, pollen, twigs, and roots, in forest soils; and in the form of the whole plant or its major parts, as well as various plant products, in peats. These plant products are, for the most part, cell wall constituents. Of these, cellulose (a condensation product of glucose) is the most important representative. Next to cellulose come the hemicelluloses which are polymers of various sugars (hexoses and pentoses) and of sugars with uronic acids; here belong also the pectic substances which are made up of condensation products of galactose, galacturonic acid, and pentose; some of the hemicelluloses are present

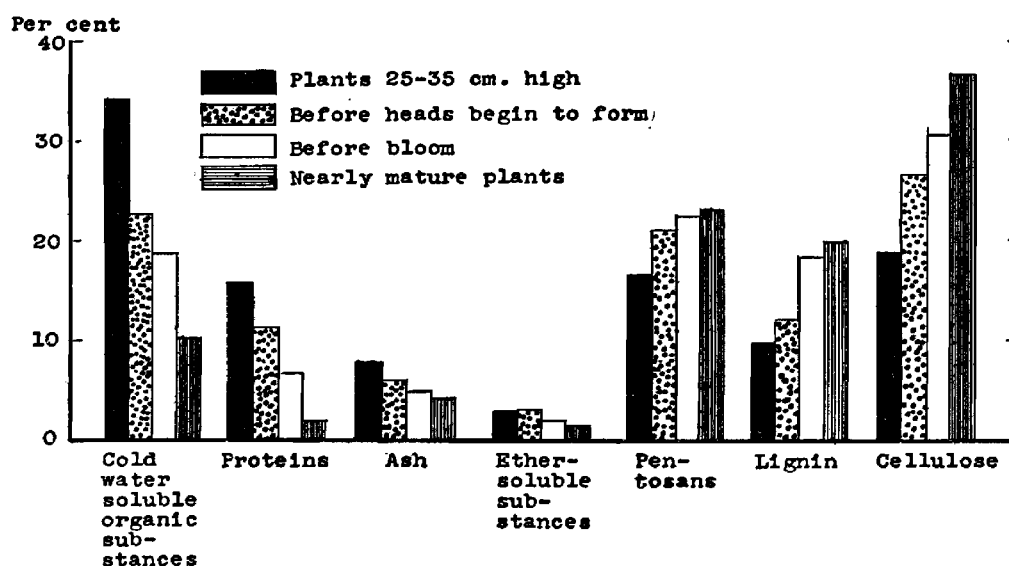


FIG. 2. Influence of age upon the chemical composition of rye plants (Waksman and Tenney).

in the cell wall in the form of salts of Ca, K, Mg, and Fe. The primary cell wall, which is made up of cellulose and hemicellulose, becomes incorporated with lignin, in the case of lignified tissues, or with cutin, in the case of cuticularized tissues; the lignins have a ring structure, while the cutins consist of oxidized and condensed fatty acids. On the other hand, the protoplasm of the plant consists chiefly of proteins and their derivatives together with sugars, starches, and other compounds in smaller concentrations (fig. 2).

It is not necessary to make a complete chemical analysis of the plant residues in order to follow the decomposition processes which lead to the formation of humus. A knowledge of their proximate composition, especially of the major constituents, is sufficient. The composi-

tion of a series of typical plant materials is shown in table 9. Information concerning these constituents is sufficient in the case of most of the plants, which may become sources of humus. In some instances, however, more complete data are needed concerning certain specific substances. This is the case of sphagnum plants, marine algae, pollen, and other plant products, which contain a considerable concentration of uronic acid complexes and other substances not adequately considered among the constituents listed in table 9.

The chemical structure of the various important components of the cell wall and their constituent groups is indicated in chart 1. The nature of the combination existing between these complexes in the plant has aroused considerable discussion. This is especially true of

TABLE 9
Comparative chemical composition of various plant materials (1923)
Per cent of dry material

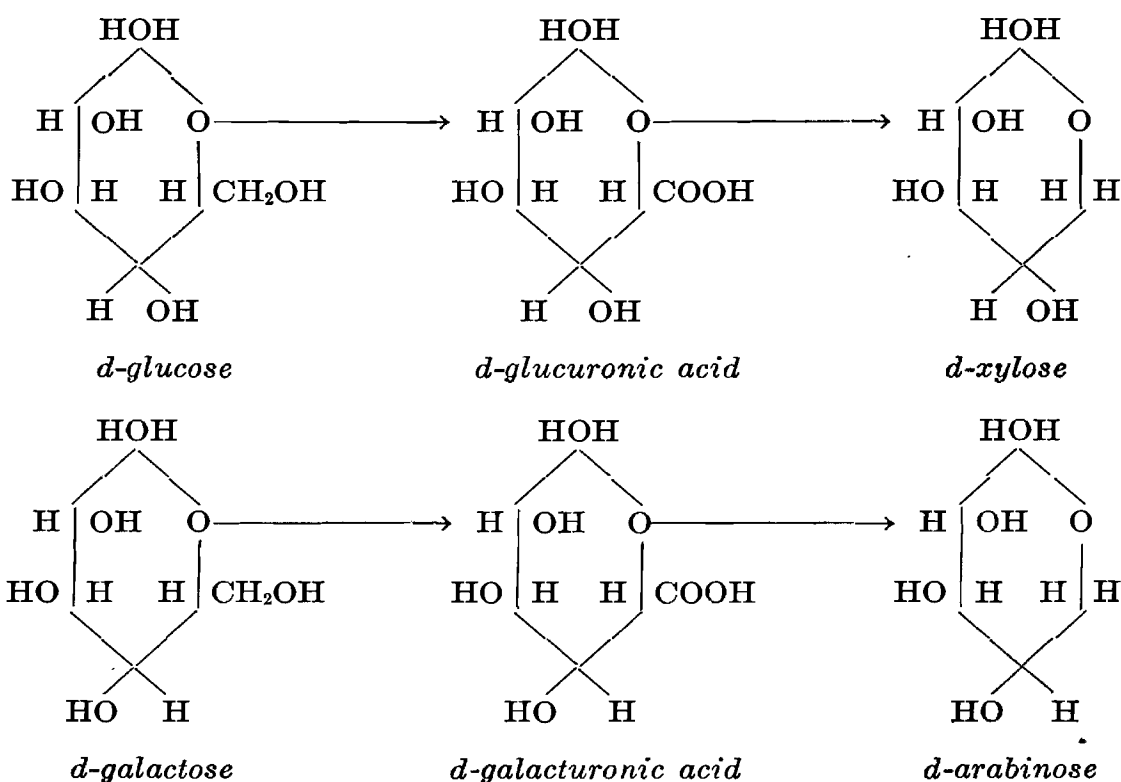
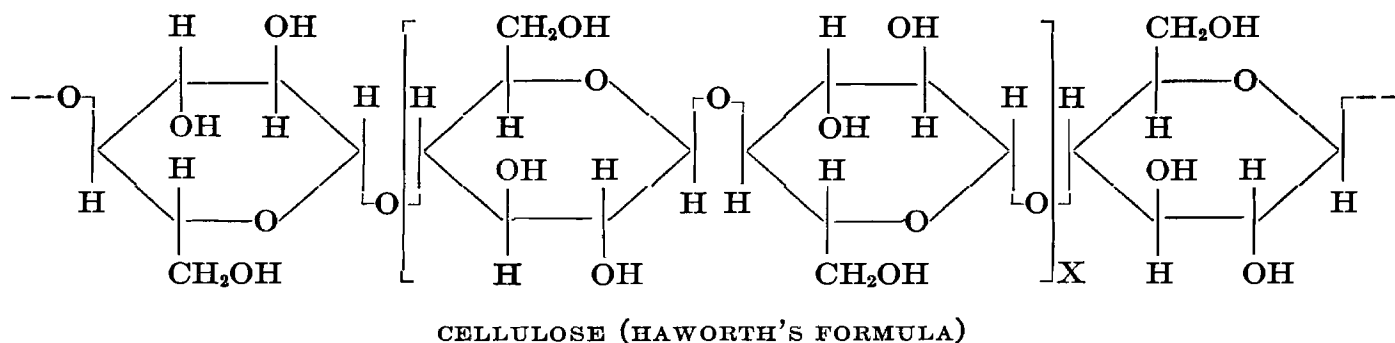
CHEMICAL CONSTITUENTS	CORN STALKS	RYE STRAW	OAK LEAVES	ALFALFA PLANTS	OLD PINE NEEDLES	CYPRESS WOOD
Ether and alcohol soluble fractions.....	5.99	5.33	6.44	10.41	23.92	5.45
Cold and hot water soluble fractions.....	14.14	6.26	13.93	17.24	7.29	3.18
Hemicelluloses.....	17.63	21.10	12.93	8.52	18.98	11.16
Cellulose.....	29.67	38.62	13.78	26.71	16.43	37.62
Lignins.....	11.28	14.63	30.30	10.78	22.68	28.21
Protein.....	1.98	0.81	4.25	8.13	2.19	0.66
Ash.....	7.53	5.09	5.09	10.30	2.51	0.76

the possible combination between cellulose and lignin in the cell wall of the plant; this is claimed, by some, to be physical and, by others, chemical in nature.

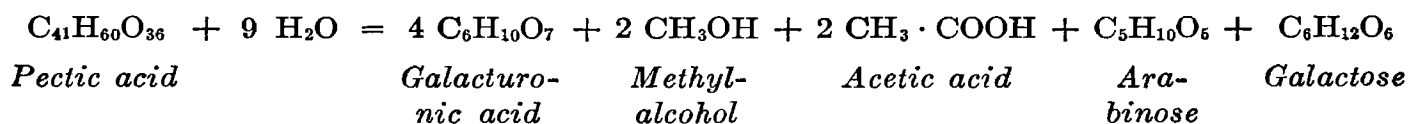
Mature plant residues, which are composed largely of cell wall substances, consist principally of the following chemical compounds:

Cellulose.....	<i>per cent</i> 20-50
Hemicelluloses (pentosans, hexosans, and polyuronides).....	10-28
Lignins.....	10-30
Tannins, coloring substances, cutins, suberins, fats, waxes.....	1-8
Proteins.....	{ 1 (wood, straw, roots) to 15 (leguminous plants)

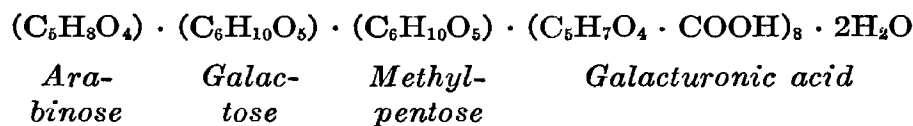
CHART 1. Chemical structure of the major complexes of the cell wall and their constituent groups.



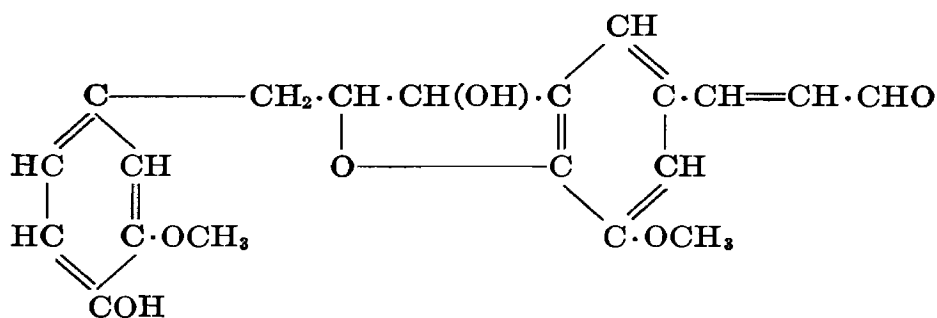
RELATION BETWEEN PENTOSE, HEXOSE AND CORRESPONDING URONIC ACID



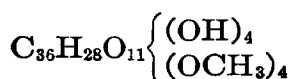
STRUCTURE OF PECTIC ACID AFTER EHRLICH



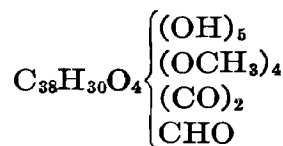
PECTIC ACID AFTER FELLEBERG



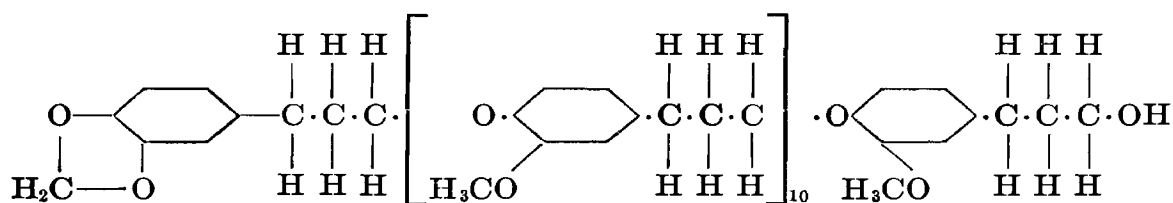
α-lignin of Klason.



*Alkali lignin from straw
(Beckmann et al.)*



*Lignin formula, according to
Powell and Whittaker*



Freudenberg's formula for lignin

VARIOUS FORMULAE FOR LIGNIN AND LIGNIN CONSTITUENTS

Cellulose. It is commonly agreed that true cellulose is of the same chemical nature whatever its origin. The cellulose micelle is believed to consist of 5,000 to 10,000 glucose molecules. Various theories have been suggested concerning their arrangement in the cellulose complex.

The rapidity of the decomposition of cellulose in soils, peats, and composts depends upon: 1. the substances with which it is associated in the plant, especially the lignins, the hemicelluloses including the pectins, or the cutins; 2. the nature of the microorganisms active in the decomposition processes; 3. the presence of available nitrogen and minerals; and 4. the environmental conditions, such as reaction, moisture, and aeration. It is frequently assumed that in the decomposition of cellulose by microorganisms, sugars are at first formed; however, to demonstrate the formation of sugar in soils or in composts is rather difficult, because of their rapid decomposition by a number of soil microorganisms. It has, therefore, been suggested that the decom-

position of cellulose does not go through the sugar stage. In a number of experiments, however, sugar formation has been demonstrated. Various slimy substances are also produced; these are largely products synthesized by microbial activities. A definite relation has been established (435, 1230) between the decomposition of cellulose and the synthesis of cell substance by microorganisms. This phenomenon can best be measured by the transformation of the inorganic nitrogen present in the medium into organic forms through the agency of microorganisms.

Hemicelluloses were formerly considered to be condensation products of sugars only. More recently, however, it was demonstrated (784a, 777a, 774, 954) that they usually contain also uronic acid complexes. This led to the suggestion (406) that hemicelluloses be classified into two groups, the true saccharides and the polyuronides. However, many hemicellulose preparations give mixtures of sugars and uronic acids on hydrolysis. O'Dwyer (784a) isolated two hemicelluloses from beech wood, one (A) of which contained 11 per cent glucuronic acid and the other (B) contained 63 per cent galacturonic acid. Hemicelluloses may thus consist of hexoses, pentoses, and uronic acids, in various proportions, ranging from xylan, or wood gum, almost a pure pentosan, to alginic acid, an abundant constituent of algae, nearly a pure polyuronide (polymannuronic acid). A definite relation has been established (777a) between the hemicelluloses and the cell wall substance.

Since the hemicelluloses are not uniform in chemical composition, they show great differences in decomposability by microorganisms in nature. They are attacked by a great variety of bacteria, aerobic and anaerobic, fungi, actinomyces, protozoa, and other lower invertebrates; some of the bacteria are highly specific, being able to decompose only one type of hemicellulose, as in the case of bacteria attacking certain capsular carbohydrates.

The cellulose and hemicelluloses are the major energy sources for the most active groups of microorganisms in soils, peats, and composts; under favorable conditions they tend to disappear rapidly. However, some of the hemicelluloses of plant origin, as well as some synthesized by microorganisms, are highly resistant to rapid decomposition and frequently play an important part in the formation of humus. Some investigators actually claimed that the composition of humus is similar to that of polyuronide; hence the latter were believed to be the true sources of humus (53).

Proteins. A knowledge of the chemical composition of the plant and microbial proteins is highly essential for an understanding of the decomposition of plant residues and of the formation of the nitrogenous constituents of humus; both plant and microbial proteins take an active part. Unfortunately, the available information concerning the proteins of bacteria, fungi, protozoa, and other invertebrates is still very limited.

The plant proteins comprise: (a) albumins, or water-soluble and heat-coagulable proteins; (b) globulins, insoluble in water but soluble in salt solutions; (c) prolamins, insoluble in water and in salt solutions, but soluble in 70–90 per cent alcohol and in acids and alkalies; (d) glutelins, insoluble in water, salt solutions, and alcohol, but soluble in dilute alkalies and acids. The nitrogen content of most of the proteins ranges from 15 to 19 per cent, although the glutelins may contain as little as 13–14 per cent nitrogen. Proteins also contain 0.5–1.0 per cent sulfur and frequently some phosphorus.

A high nitrogen content is characteristic of the protein molecule; usually the protein content of a material is calculated from the amount of total organic nitrogen, using the arbitrary factor 6.25. Most of the nitrogen present in humus is believed to be in the form of true protein, with a different distribution of the amino acids, however, than in the plant and animal proteins. When proteins are introduced into the soil or compost, they are attacked by a great number of microorganisms and their enzymes, and changed to peptides, amino acids, and finally ammonia. The last is either oxidized in the soil to nitrate, or is assimilated by microorganisms in the presence of available energy and changed into microbial protein. The protein in the humus is partly of plant origin and partly of microbial origin, depending on the extent of decomposition of the plant residues. The protein content of plant residues is between 2.0 and 15 per cent; however, the protein content of humus is between 8 and 35 per cent, with the exception of highmoor peats, which shows that a considerable enrichment of the residual organic matter in protein substances takes place as a result of the decomposition processes.

Lignins. Lignins are cell wall constituents which, unlike the carbohydrates, cannot be readily hydrolyzed to simple compounds; they are recognized by various color reactions, by their insolubility in concentrated mineral acids in the cold and their solubility in alkali solutions under pressure, by the readiness with which they are oxidized, by a characteristic chemical structure (benzol ring, methoxyl, hydroxyl,

and carboxyl groups, high carbon content of 62 per cent or more), and by their relative resistance to decomposition by most microorganisms. Lignins in different plants and frequently in the different tissues of the same plant vary in composition, as shown by a varying methoxyl content and solubility in organic solvents. As many as seven different types of lignin were shown to be present in straw (810). Lignins are absent in filamentous algae and present only to the extent of 3–7 per cent in mosses, 10–18 per cent in cereal straw, and 20–30 per cent in wood (323). The lignin content of the plant increases with the maturity of the plant; at the same time, there is also an increase in the methoxyl content of the lignin (78).

Several methods are commonly used for the preparation of lignin; these yield substances which are designated as 1. acid lignin, 2. alkali lignin, 3. phenol lignin, etc. Lignin thus prepared is usually different from the original or genuine lignin in the plant itself. The various lignin preparations vary in chemical nature not only from one another but also from the genuine lignin. Uronic acids are found (793) in lignified cell walls, which led to the conclusion that lignification is related to uronic acid formation; they are usually absent in isolated lignin. Klason (550), however, found that hemicellulose does not form any compound with lignin, since on hydrolysis with acid, the former is removed while the latter is not affected.

Numerous formulae have been suggested to explain the chemical structure of lignin, as shown in chart 1. According to Klason, genuine lignin consists of α -lignin $[(C_{10}H_{12}O_4)_6]$ and β -lignin $[C_{10}H_{12}O_4 \cdot (C_9H_9O_4 \cdot COCH_3)_2]$. Freudenberg (319) assumed that lignin has a chain structure, resembling, at the end of the chain, a coniferyl alcohol or its hydrate. It is very reactive and can polymerize; this takes place by condensation in the wood after the cells are dead or during the process of its isolation by chemical means. Powell and Whittaker (847a) concluded that the lignin molecule contains four methoxyl groups and five hydroxyl groups capable of acetylation, only three of the latter being phenolic in character.

The methoxyl group (OCH_3) is characteristic of the lignin molecule. The concentration of methoxyl in the lignin depends upon the method of its preparation. In the case of acid lignin of higher plants, it usually varies from 14.1 to 16.3 per cent (1237). The methoxyl content of lignin in lower plants, such as mosses or algae, is very low. The fate of lignin in the decomposition of plant residues has frequently been measured by the changes in methoxyl content (566, 62). When lignin is

treated with an alkali solution and exposed to the air for some time, it is gradually oxidized and transformed to a dark colored substance similar in its properties to the typical "humic acids" (292, 450).

It has been claimed that when cellulose is heated in aqueous or alkali solutions, under pressure, substances resembling lignin are obtained (405). However, these complexes were found (939) to be quite different from genuine lignin, as shown by the difference in the transformation products. Actually, this newly coined term "synthetic lignin" designates the same group of complexes as does the more venerable term "artificial humic acid."

Among the plant constituents, lignin is more resistant to decomposition by microorganisms. However, although the lignins in the natural plant materials still undergo a certain amount of decomposition, isolated lignin is either not attacked at all or only to a very limited extent (1242, 132, 636). Whether this is due to a change in the physical or chemical condition of the lignin molecule still remains to be determined. Those isolated cases where a certain amount of prepared lignin was decomposed by fungi and bacteria (851, 821) were not fully confirmed. Certain specific fungi are capable of decomposing lignin in the plant, as in the case of wood-destroying fungi (279), the edible mushroom *Agaricus campestris* (1233), species of *Coprinus* (1224), and others.

Cutins comprise the epidermal layer or skin of the outer cell wall, which is impermeable to water. Cutins are resistant to hydrolysis with 70 per cent sulfuric acid and are relatively insoluble in fat solvents. They are known to be a mixture of fatty acids which have undergone oxidation and condensation with other substances, such as cellulose. Suberins or corky substances include complexes similar to those found in cutins.

Fats, waxes, and resins. Plant residues contain varying amounts of fats, fatty oils, and waxes, the last being esters of alcohols with fatty acids; glycerol is not found in waxes. These complexes are usually extracted from plant materials by ether, benzol alcohol, and other solvents. They are characterized by a high carbon content (74–82 per cent C) and are differentiated by their saponification number, acid value, iodine number, etc. Some are more readily attacked by microorganisms than others. Resins are plant secretions related to the waxes, but they contain less hydrogen and are predominantly cyclic and aromatic in character.

Other plant constituents. Here belong a number of complexes which occur in most plant residues in lower concentrations than the previ-

ously mentioned substances. Among these we find glucosides, tannins, alkaloids, pigments, and a number of other organic and inorganic materials. They occur in the majority of plant residues to only a limited extent, although at times they may give characteristic properties to certain forms of humus. The mineral constituents of plants include compounds of phosphorus, potassium, calcium, magnesium, and iron, which are highly essential for the nutrition of the microorganisms active in humus formation; compounds of silicon, sodium, and chlorine are of less importance. During decomposition of the plant residues by microorganisms, there is an increase in the relative content of the mineral constituents, some of which enter into chemical combination with the humus complex.

Different plants vary considerably in chemical composition; even the same plant changes considerably with age, as shown in figure 2. These differences are influenced by a number of growth and variety factors. It is the composition of the materials which exerts a controlling influence upon the rate and nature of the decomposition of the plant and upon the amount and nature of the humus formed.

DECOMPOSITION OF PLANT RESIDUES AND FORMATION OF HUMUS

Earlier conceptions. With the advance of our knowledge of the chemical nature of plant residues which undergo decomposition in soils, bogs, and composts, and with a better understanding of the rôle of microorganisms in the decomposition processes, it became recognized that numerous reactions are involved. While de Saussure considered all plant substances as sources of humus, which becomes blackened in contact with moist air, and Braconnot (146) believed that ulmin is formed from wood stems lying in moist places, Sprengel (1074) emphasized that the nature of the plant materials influenced the rapidity of the process of humus formation: residues rich in nitrogen change rapidly into humus, while those rich in fibrous and waxy complexes are transformed into humus more slowly. Mulder (734) also recognized the complexity of the processes of transformation of the various organic constituents in the decomposition of plant residues: cellulose was believed to be dehydrated and changed into humus; sugar transformed to lactic and butyric acids; protein changed into humus, amino acids, and aliphatic acids; and fats and waxes to CO_2 and H_2O .

In the late eighties of the last century evidence began to accumulate that microorganisms play an essential part in humus formation. Kostytchev found (580) that the process of formation of humus from

starch and sugar can serve as direct sources of "humus." He stated that this process might take place indirectly, through the bodies of the microorganisms, since a small part of the cellulose is changed to microbial cell substance; the protoplasm of the fungi and bacteria was considered as a possible source of humus. From this point of view, all organic substances, which can serve as nutrients for microorganisms, may be considered as indirect sources of humus. Trussov also demonstrated that proteins, lignins, tannins, and pigments play an important rôle in the formation of the dark colored substances; he believed that the phenol-containing substances are oxidized by specific enzymes into brown to black compounds, which are soluble in alkalies and precipitated by acids, and show characteristics similar to the "humic acids." In view of the facts that phenolic compounds are formed during decomposition of proteins and that oxidizing enzymes are widely distributed, the origin of the bulk of the dark colored substances, during the decomposition of plant and animal residues, was explained by this process. Fats and waxes did not change into humus, but, because of their slow decomposition, they were believed to become a part of it.

The rôle of lignins, or complexes which are now recognized to be lignins, in the process of humus formation in nature, was suggested by a number of early workers. Definite evidence bearing upon this point was submitted by Hoppe-Seyler (459), by Hébert (211), by Slezkin (1045), and by Wehmer (1261), as will be shown later (p. 109). Trussov (1185) demonstrated definitely that lignin occurs among the products of the decomposition of plant residues which give a brown color in alkali solution and are precipitated by hydrochloric acid. He further suggested that the transformation of lignin into humus consists in the oxidation of those constituents which contain a quinone or polyphenol group, giving condensation products of the nature of oxyquinone.

Recent theories concerning the origin of humus. With the advance in our knowledge of the rôle of microorganisms in decomposition processes and a better understanding of the chemical nature of plant and animal residues, the various hypotheses explaining the processes of humus formation became more concrete. Numerous theories have been proposed during the last two or three decades in an attempt to explain the mechanism of the formation of the dark colored substances which make up humus. Some of these explained the formation of humus by purely chemical interaction or modification of certain organic compounds which either existed in the plant residues or were formed from some of the constituents of the latter. If the rôle of microorganisms in these

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processes was recognized at all, it was only to ascribe to them a part in the formation of those compounds which react to form humus. According to others, the formation of humus from plant residues is a result of the direct or indirect action of microorganisms; the function of the latter was believed to consist both in the decomposition of those organic constituents of the plant material which do not take a direct part in the formation of humus, and in synthesizing new organic complexes.

The purely chemical conceptions of humus formation can be traced back to the earlier ideas concerning the formation of artificial "humic acids" by the interaction of carbohydrates with acids. Some believed that humus is formed by the polymerization of furfural; the latter is commonly produced when carbohydrates, especially pentosans and uronic acid complexes, are treated with hot acids; when furfural or oxy-methyl furfural reacts with hot hydrochloric acid, it is converted into a black insoluble mass, frequently referred to as "humin." Beckley (80) suggested that the action of mineral acids on carbohydrates results in the formation of hydroxymethyl furfural, which, on condensation, gives rise to "humus." Aldoses and hexosans, such as starch, were found to give smaller amounts of furfural, as well as of "humus," than did ketoses. The detection of this furfural in rotting straw and in soil was believed to be sufficient evidence for justifying the foregoing theory. However, this compound was not formed during the decomposition of cellulose by pure cultures of bacteria. The probability of this type of process taking place in soils, in peat bogs, and in composts is invalidated by the lack of concentrated mineral acids under natural conditions; the low decomposition temperatures usually prevailing in soils and in peat bogs make it further doubtful whether one is justified in ascribing any significance to this process in the formation of humus in nature.

The second purely chemical theory, which need be mentioned here, is somewhat more plausible than the first, namely, the formation of humus by the condensation of carbohydrates with amino acids or with polypeptides. It was becoming more definitely recognized that nitrogen is an essential part of humus. André (37, 39) found that this nitrogen is fixed so energetically to the carbon of the humus that when it is boiled with a solution of NaOH or KOH, only a part of it is liberated as ammonia; only prolonged treatment will remove more of this nitrogen. He thus confirmed the earlier observations of Eggertz (253). The function of ammonia in the formation of humus as a result of the

decomposition of stable manures was suggested by Thénard (1149) in 1861 and later by Hébert (408) and Dehérain (211). The process was believed to consist either in the action of ammonia upon lignin-like substances or in its transformation into microbial cell substance. Maillard (664) claimed that microorganisms are of minor importance in the formation of humus in nature. Their sole function in this process was believed to consist in the hydrolysis of proteins to polypeptides and of amino acids and of complex carbohydrates to sugars. The actual formation of humus was considered to be an automatic reaction between these products, in which the microorganisms play no part. The artificial humic substances, which were obtained by the condensation of sugars with amino acids, seemed to be identical with the natural products in chemical composition, especially nitrogen content, and in resistance to decomposition.

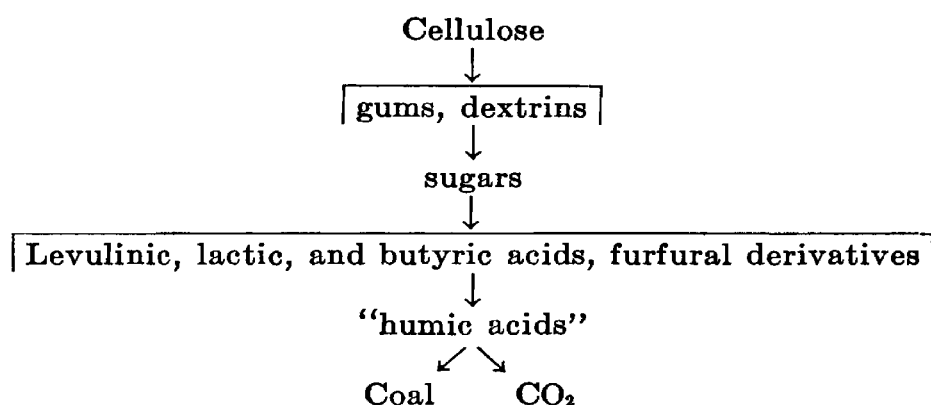
A third theory explained the formation of humus by the oxidation of benzene-ring compounds. Hoppe-Seyler (459) and Reinitzer (874) demonstrated that dark colored substances are formed on boiling phenols and quinones with alkalis. According to Eller (264), the oxidation of phenol, quinone, and hydroquinone in an alkaline solution results in the formation of compounds similar, not only in composition (58.05 per cent carbon), but also in the various physical and chemical reactions, to the natural complexes present in humus and usually described as "humic acids" (p. 52). This conception found further justification in the fact that certain microorganisms produce dark colored substances. Beijerinck (84) demonstrated that *Act. chromogenus* is capable of producing quinone; he believed that this function enables the organisms to play an important rôle in the "humification" process. Muschel (742) found that the black coloration produced by *Bac. mesentericus niger* was due to compounds of the benzene ring series, closely related to o- and p-di-hydroxy-benzene; these apparently give condensation products with amino acids. Similar results were obtained by Perrier (814), who found that when salts of benzoic and salicylic acids and phenol are attacked by fungi and bacteria (*Bact. pyocyaneum*) under aerobic conditions a characteristic dark colored substance is formed. Perrier concluded that the dark colored substances of "humus" are produced by oxidation, at alkaline reactions, of cyclic compounds present in animal excreta and in vegetable substances, after they have been decomposed. These reactions of microorganisms are, however, a part of the natural processes of transformation of organic matter and have little in common with the purely chemical theory of Eller.

More recently, the rôle of lignins and lignin-like materials in the formation of humus has been receiving considerable attention. As far back as the middle of last century, Lesquereux (632) expressed the idea that lignous substances are largely responsible for peat formation. In 1879, Fremy (317) also spoke of lignin as the mother substance of humus compounds in soils and in composts. The work of Hébert and Dehérain and of Hoppe-Seyler, discussed in detail elsewhere, pointed to the important function of lignin in humus formation. It remained for the investigators of the chemistry and origin of coal (294) to obtain further evidence pointing to the important relationship between humus and lignin (p. 54).

Finally, a purely microbiological theory has been proposed (1220, 1223) in which even greater importance is attached to the activities of microorganisms in the formation of humus, as agents both of decomposition and of synthesis. It was found that in the decomposition of plant and animal residues, the carbohydrates tend to disappear rapidly and the lignins accumulate. The former serve as sources of energy for the microorganisms bringing about the decomposition, with the result that considerable cell substance, consisting largely of proteins and certain hemicelluloses is synthesized; these compounds, together with the modified lignins of the plant residues, form the bulk of the constituents of humus. According to this theory, the carbohydrates, proteins, and lignins are associated with the formation of humus, directly or indirectly. The transformation of the celluloses and lignins, the two major constituents of plant residues which contribute to the non-nitrogenous part of the humus, and the microbial synthesis of nitrogenous substances, the major source of protein in the humus, as well as the relation between the proteins, hemicelluloses, and modified lignins in the humus complex require further consideration.

Carbohydrates as mother substances of humus. Although considerable evidence was accumulating that the processes of humus formation in nature are highly complicated and involve numerous transformations and the activities of a great variety of microorganisms, the general conception prevailed among botanists and chemists that cellulose and other carbohydrates form the sole sources of humus, as expressed by Detmer (219) and Czapek (199). Several recent investigators also emphasized the part played by cellulose in the formation of humus. The method of approach was invariably chemical in nature. If the microorganisms were considered at all, they were believed to act as catalytic agents.

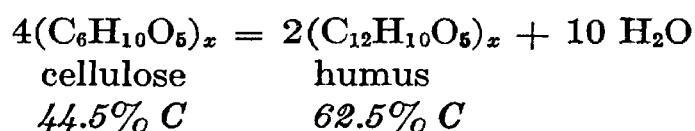
According to Chardet (175), cellulose is decomposed by bacteria, under aerobic conditions, into dextrans and sugars, and these are later transformed into fatty acids and CO₂; under anaerobic conditions, however, as in the case of peat bogs, oxidation processes are excluded and dark colored substances are produced by a process of condensation. The reactions involved in this process were outlined as follows:



Marcusson (674) suggested that, in the degradation of plant residues, the carbohydrates are first converted into furfural; this compound eventually gives rise to benzoid groupings through the formation of a para-di-furfuran ring. This conception was based upon the idea that cellulose is changed into products having a furan structure upon hydrolysis by acids. The "humic acid" was believed to originate from these groups by a process of polymerization.

Burian (162) believed that he demonstrated the presence of furan and furol derivatives in the distillates of "artificial" and "natural humic acids" obtained from cellulose and from Cassel brown respectively. Eller (264), however, denied that the two preparations were similar. Schmidt (952) has also shown, by the formation of maleic acid from the action of ClO₂ on the humus preparations, that a marked difference exists between the dark colored substances obtained from furfural and those from peat.

Bergius (94) considered that both cellulose and lignin act as mother substances of the humus in peat and coal, undergoing the transformation under proper conditions of temperature and pressure. Cellulose was believed to lose water and to result in a product considerably richer in carbon (a conception prevalent in the 19th century):



This process takes place at comparatively high temperatures (250°C.), yielding a preparation which is not soluble in alkaline solutions as long as oxygen is not admitted. Upon treatment with an alkali, oxygen is absorbed and the complex becomes brown and completely alkali soluble. The reaction has been summarized as follows:



One-half of the product is soluble in alcohol and one-half insoluble, which, interpreted in terms of Oden's nomenclature, would indicate that 50 per cent of the material is "humic acid" ($\text{C}_{12}\text{H}_8\text{O}_6$) and 50 per cent "hymatomelanic acid" ($\text{C}_{12}\text{H}_{10}\text{O}_5$). This led Bergius to conclude that the constituents of natural peat can be prepared in the laboratory from cellulose alone. He did not consider the importance of lignin in the formation of the dark colored constituents of humus. The fact that the non-carbohydrate portion of peat produced from sphagnum moss contains little or no "true lignin" was submitted as further evidence of the non-participation of lignins in peat formation.

The transformation of cellulose by the foregoing reaction of dehydration and oxidation was considered as the first step in the formation of peat and coal from plant material. The complete process of coal formation was accomplished in 19 to 42 hours, at 340°C.:



Small quantities of methane and of acetic and formic acids were also produced but were overlooked. The complex, $\text{C}_{20}\text{H}_{16}\text{O}_2$, formed in this reaction was found to be a mixture of $\text{C}_{20}\text{H}_{20}\text{O}_2$ (α -coal), soluble to a large extent (up to 70 per cent) in benzol-alcohol and in NaOH solution, and of $\text{C}_{20}\text{H}_{12}\text{O}_2$ (β -coal), which is insoluble in these reagents.

Lignin was also found to give rise to similar products on heating. Acid lignin, containing 64.5 per cent carbon, 4.52 per cent hydrogen, and 31.0 per cent oxygen, was given the constitutional formula of $(\text{C}_{11}\text{H}_{10}\text{O}_4)_x$. It was suggested that when lignin is transformed into coal by heat, the following reaction takes place:



The elementary composition of lignin from sphagnum moss was considered to be $\text{C}_{11}\text{H}_{18}\text{O}_8$; a complex, $\text{C}_{10}\text{H}_8\text{O}$, obtained from this lignin was found to be similar to the one formed from wood lignin; it was also separated into α - and β -coal.

Bergius suggested that the following processes are responsible for the formation of coal from plant residues: The hexoses take up oxygen, changing to oxy-sugars, products related to glucuronic acid; these oxy-sugars combine with some unchanged sugar to give glucosides, of the type $C_{12}H_{20}O_{11}$. The latter, by splitting off CO_2 and H_2O , change gradually into lignin ($C_{11}H_{10}O_4$) and later into coal ($C_{10}H_8O$). These reactions, summarized in chart 2, were believed to take place at high temperatures in the absence of air ("exclusion of atmospheric agencies") and of bacteria.

The foregoing reactions are purely hypothetical, and it is doubtful whether they play, or have played, any significant part in the formation of humus in soils, composts, peats, or coal. When one considers the fact that it is very seldom that temperatures over $60^\circ C$. are attained under conditions of decomposition in nature, one would be justified in concluding that the products obtained from cellulose at temperatures of $200-350^\circ C$. are mere laboratory preparations.

The function of cellulose as a direct mother substance of humus, under natural conditions, seems insignificant when one considers the work of Hoppe-Seyler and Hébert, carried out more than 40 years ago. Their ideas were soon confirmed in the following statement of Klason (784): "The process whereby dead plants change into the first stage of peat must consist in the fermentation of the carbohydrates; when this takes place under water, in the absence of air, the process must stop here, the active microorganisms being unable to ferment the other plant constituents; peat actually consists of lignin-like substances of plants in a more or less unchanged condition." Beijerinck (85) also considered "lignose," as well as souberin and wood pentosan, as the important plant constituents which contribute to the formation and accumulation of humus. Ehrenberg (256) doubted the idea that cellulose is the mother substance of humus, since he could not obtain any increase in the humus content of the soil in the process of decomposition of cellulose or its derivatives at normal temperatures.

Dehérain (211) outlined as follows the process of humus formation, based to a considerable extent upon the investigations of Hébert: When fresh organic matter is added to the soil, the sugars and dextrins disappear rapidly and completely; the cellulose and hemicelluloses diminish appreciably, whereas the lignin is attacked least; lignin is soluble in alkalies and thus contributes to the formation of black material or humus; the nitrogen part of the humus is derived from ammonia which is assimilated by the microorganisms for the synthesis of microbial

proteins, the available carbohydrates being used as a source of energy. Humus was thus considered to represent a mixture of lignins and proteins. This clear conception of the problem of humus formation under natural conditions was far in advance of the prevailing knowledge at that period and was generally overlooked by subsequent investigators of the subject.

Lignin as a mother substance of humus. Nearly two decades passed before the earlier ideas on the rôle of lignins in the formation of humus were given further consideration. Wehmer (1261) reported in 1915 that, in the degradation of wood by various fungi, the ligno-celluloses are attacked, with the result that the cellulose disappears and the lignin is converted into humus substances. Wehmer (1262) suggested that, in the formation of peat and coal, the plant tissues are transformed into

TABLE 10

Changes in the chemical composition of wood as a result of its decomposition (914)
Per cent of dry wood

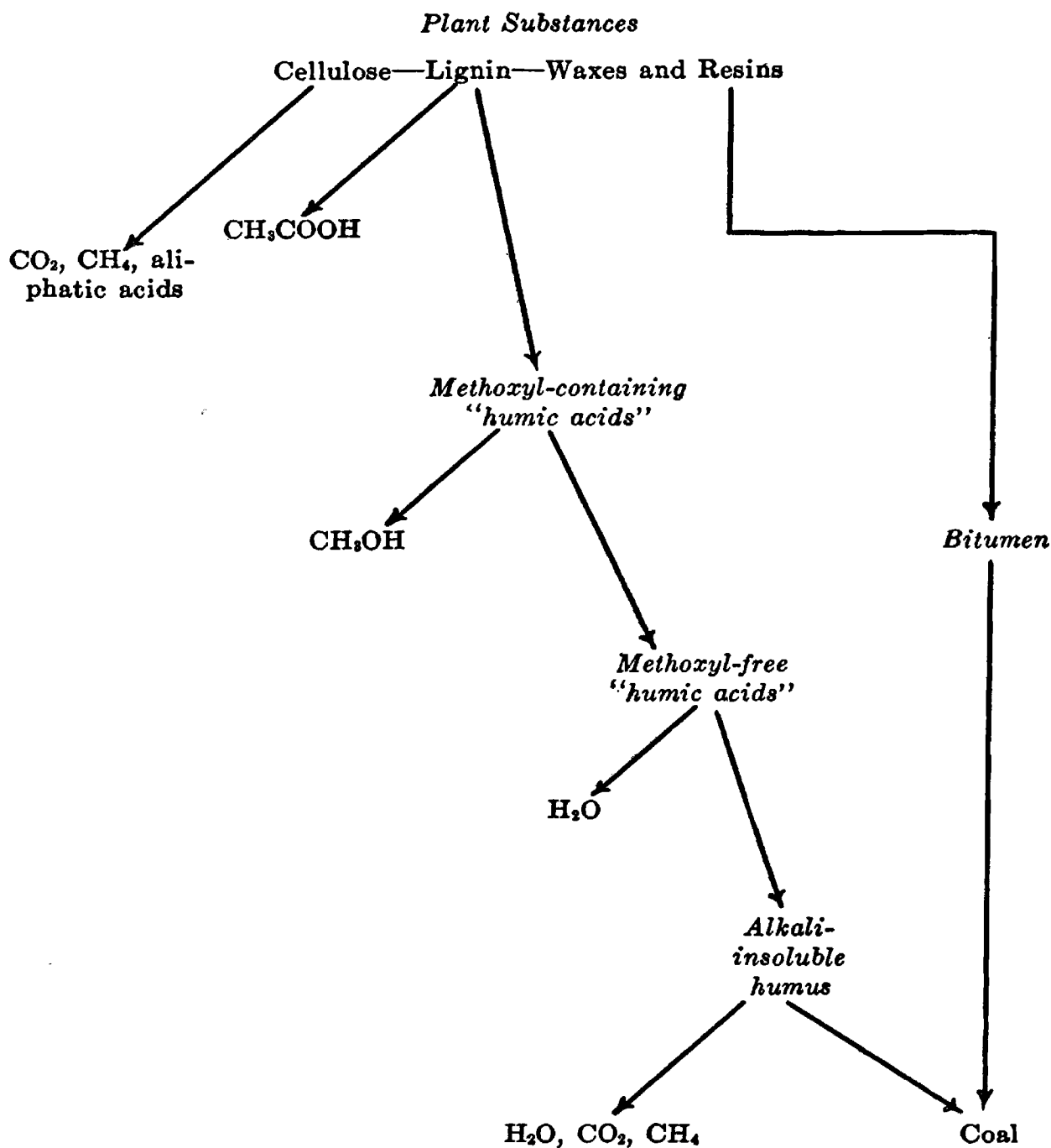
CHEMICAL CONSTITUENTS	CELLULOSE	PENTOSAN	METHOXYL GROUPS	ALKALI-SOLUBLE	METHYL-PENTOSAN
Fresh wood.....	58.96	7.16	3.94	10.61	2.64
Partly decomposed wood.....	41.66	6.79	5.16	38.10	3.56
Fully decomposed wood.....	8.47	2.96	7.80	65.31	6.06

humus bodies, chiefly by the action of fungi, as a first step in the reaction; these organisms are unable to decompose the lignins.

Rose and Lisse (914) compared the chemical composition of healthy and decomposed wood, and found a rapid diminution of the cellulose and pentosan, accompanied by an increase in the methoxyl content (methoxyl is used as an index of the lignin content), as well as in the alkali-soluble material and in the methyl pentosans (table 10). These experiments were repeated by Marcusson (674), who extracted the material first with a 1 per cent alkali solution and determined the lignin in the residue by the method of Wilstätter. He found that while there was a marked reduction in the cellulose content of wood as a result of decomposition, the lignin content remained stationary; the increase in the alkali-soluble material was believed to substantiate the theory that cellulose is the mother substance of humus—the dark colored, alkali-soluble substances. Pure cultures of fungi were also found (151) to decompose cellulose rapidly; the pentosans were partly attacked and

partly left undecomposed; and the lignins remained intact or were acted upon to only a very limited extent.

CHART 2. Mechanism of formation of humus under natural conditions (Fischer).



In the destruction of wood by the shipworm *Teredo navalis*, the cellulose and hemicelluloses were shown (234) to disappear rapidly but the

lignin was not attacked. These results were substantiated by König (565), who demonstrated that, in the digestion of plant tissues by herbivorous animals, the cellulose is attacked much more rapidly than the lignins. Fischer and his associates (294) placed cellulose, lignin, wood, and sphagnum moss in inorganic nutrient solutions; these were inoculated with a soil suspension and incubated at 37C°. Fungous development took place in the moss culture, and later in the wood and in the cellulose, but not in the medium containing lignin. These and other considerations led Fischer (292) to conclude that lignin is the mother substance of natural "humic acids," as illustrated in chart 2.

The lignin theory of the origin of humus in peat and in coal has been substantiated by a number of facts, both chemical and biological, which can be briefly summarized as follows (the term "humic acid" is used here to designate a specific preparation obtained from humus):

1. Decomposing wood and peat increase in lignin content with age.
2. Lignin, as opposed to cellulose, gives rise to aromatic transformation products; "humic acids" as well are found to contain aromatic compounds.

3. Both lignin and "humic acid" contain methoxyl groups; the methoxyl content diminishes with the advance in decomposition. Cellulose contains no methoxyl groups.

4. Both lignin and "humic acid" are acidic in nature; both are able to combine with bases and both are characterized by their capacity of base exchange, to a different quantitative extent, however.

5. Both lignin and "humic acid" are insoluble in cold concentrated acids, the degree of insolubility increasing with an advance in decomposition, such as with the age of peat.

6. When lignins are warmed with aqueous alkali solutions, they are transformed into methoxyl-containing "humic acids," but cellulose is not transformed in this manner. At high temperatures the methoxyl is split off and changed to methyl alcohol.

7. On oxidation under pressure, lignin gives rise to "humic acids" and finally to aromatic carbonic acids (homocyclic ring systems), but cellulose is changed to other products (1179).

8. Oxidation of brown coal under pressure gives benzol carbonic acid and not furan carbonic acid.

One may add further:

9. Both lignin and "humic acid" are oxidized by mild oxidizing agents, such as permanganate and H₂O₂.

10. Both lignin and "humic acid" are soluble in alkalies and precipi-

tated by acids; this relationship is not quantitative, however, and depends upon the nature of the original material and method of preparation.

11. Both lignin and "humic acid" are partly soluble in alcohol and pyridine, depending also on method of preparation; some lignin and some humus preparations are completely soluble in alcohol.

12. Both lignin and "humic acid" are decomposed with great difficulty or not at all by the great majority of fungi and bacteria.

Since the degree of decomposition of peat increases with age and with depth of profile, various layers, taken at different depths of two peat profiles, were analyzed chemically. The results bring out the fact that with an increase in age of peat there is a decrease in cellulose content

TABLE 11
Chemical composition of peat at different depths (294)
Per cent of dry material

NATURE OF PEAT	DEPTH	ASH CON- TENT	METHOXYL CON- TENT	INSOLU- BLE IN CONCEN- TRATED HCl	SOLU- BLE IN NaOH SOLU- TION	BITU- MEN CON- TENT
	<i>meters</i>					
Highmoor peat.....	0	1.8	0.49	29.5	11	2.0
	0.9	1.7	1.22	58.0	20	4.9
	1.8	1.8	1.67	72.5	55	7.7
Lowmoor peat.....	Increasing depth	7.1	2.97	74.5	..	5.3
	Increasing depth	6.8	2.73	77.5	..	6.3
	Increasing depth	6.6	1.66	84.5	..	12.2

and an increase in the methoxyl content, in the alkali-soluble fraction, and in the acid-insoluble fraction (table 11); one must, of course, take recognition of the specific nature of the plant material from which the given layer of peat has been formed.

According to Page (802), the formation of "humic matter" bears a constant relation to the change in the lignin content of the plant material undergoing decomposition. He suggested that the "humification value" of a compost be subtracted from the amount of "total lignin" to obtain the lignin value.

So many formulae have been proposed to explain the chemistry of lignin and of "humic acids" and so much importance has been attached to them, that one is surprised to find that they are largely illusory

Certain experiments (246) can also be cited, which show that during the decomposition of the cellulose in straw by thermophilic bacteria, as in the preparation of artificial manure from straw, dark colored substances are produced. The fact that nitrogen is essential for this process and that no such substances are formed under anaerobic conditions, points to the probable rôle of aerobic microorganisms in this process.

The lignin theory also disregards the function of organic nitrogenous compounds in the formation of humus, especially in soils, in lowmoor peats, and in composts. The organic nitrogen content of humus may be as high as 5 per cent, consequently a large part of the humus constituents comprise nitrogenous compounds. One must conclude, therefore, that although there is no doubt that lignin contributes to a very marked extent to the formation of humus, as will be shown later in detail, other plant and microbial constituents also play an important part in this process.

Physical and chemical properties of lignin vary considerably, depending upon the nature of the material from which it is prepared and upon the methods used for its preparation. Phenol lignin is readily soluble in alcohol. Alkali lignin is only partly alcohol soluble and acid lignin even less so. Alkali and acid lignin can, therefore, be separated into two groups of complexes on the basis of alcohol solubility. Alkali lignin also contains a certain amount of hemicellulose, nitrogenous compounds, and ash, which are extracted from the original straw by the alkali and precipitated by the acid. As a result of treatment with ether and hot alcohol, the alkali-soluble lignin also becomes partly soluble in hot water (962, 1036).

Lignin prepared from straw by alkali extraction was thus found to contain complexes which are commonly associated with humus; namely, the alcohol-soluble (equivalent to "hymatomelanic acid"), the alcohol-insoluble ("humic acid"), the water-soluble ("fulvic acid"), and the hemicellulose portions ("humal acid"), in addition to nitrogenous material and minerals. When one compares in a similar manner the analyses of a "humic acid" preparation obtained from soil by alkali treatment, the same groups of complexes are found, with certain notable quantitative exceptions, such as a much larger amount of organic nitrogen and a lower "hemicellulose" content; this is due largely to the fact that straw is poor in nitrogenous complexes and rich in hemicelluloses, while the humus of the soil is rich in nitrogenous complexes and poor in hemicelluloses. Cassel brown was shown to contain about 75 per cent

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of lignin-like complexes; the remaining portion is composed of mineral substances, nitrogenous compounds, substances soluble in ether and alcohol, as well as a small amount of carbohydrates (see also 230, 1105, 1137).

The rôle of proteins in humus formation. Nitrogen is present in humus in a complex organic form (protein), but not in a free condition, otherwise it would be rapidly decomposed by microorganisms in soils and in composts. These nitrogen complexes are either not readily attacked by the common bacteria and fungi, which are usually active in the decomposition of plant and animal residues, or they are closely bound to a non-nitrogenous complex of a high carbon content, which makes them more resistant to attack by the majority of microorganisms. Once the freshly added plant and animal residues have undergone active decomposition and have become transformed into humus, the latter decomposes slowly. If an abundance of nitrogen is present in the residues, it is liberated as ammonia, while a part of the nitrogen, especially in the presence of available carbohydrate, is transformed into organic forms, which are then rendered resistant to further rapid decomposition by microorganisms.

It is also of interest to emphasize the fact that, in the great majority of soils, the ratio between the carbon and nitrogen in the humus seems to be fairly balanced, ranging usually from 12:1 to 8:1; in the case of composts and lowmoor peats, the tendency is also towards this narrow ratio; however, in highmoor peats the ratio is much wider. It is not sufficient to explain these phenomena by the general statement that nitrogen is present as an impurity of the "humic acids," or that it is due to the absorption of nitrogen by the colloidal "humic acids," followed by its transformation into protein by nitrogen-fixing bacteria (1103). According to Dragunow (236), the nitrogenous constituents of "humic acids" consist partly of proteins and partly of nitrogenous compounds closely bound to the "humic acids."

Detmer, Eller, and Oden succeeded in reducing the nitrogen content of these "humic acid" preparations by repeated treatments with strong alkali solutions. This does not prove the existence of nitrogen as an "impurity," however; it may merely indicate that the nitrogen-containing fractions of the soil humus can be more readily hydrolyzed by mineral acids at high temperatures than the non-nitrogenous fractions. Berthelot and André (103, 109) and others demonstrated that the organic matter brought into solution on treatment of soil with alkalies has a wider ratio of nitrogen to carbon than the organic matter frac-

tions left in the soil or precipitated by a mineral acid. But this again is hardly sufficient reason to assume that definite chemical compounds exist in humus in the form of "humic acids," which are free from nitrogen, or that the nitrogen is present in the form of extraneous complexes. It has been claimed (114a) that "humic acid" preparations can be freed from nitrogen by means of electroosmosis; these results need, however, further confirmation.

Microbial cell substance and the formation of humus. The formation of microbial proteins can illustrate better than any other transformation the function of microorganisms in the origin of humus in nature. These organisms play at least a threefold part in humus formation: 1. the decomposition of fresh plant and animal residues; 2. the decomposition of the various constituents of the humus itself; 3. the contribution of the synthesized microbial cell substance to the humus. The presence in humus of microbial cells or their disintegration products has been definitely established. However, the extensive contribution of this cell substance to certain types of humus, as in composts or in forest soils, has been but seldom recognized and has received only recently due consideration.

According to v. Post (857) and Müller (737), the humus bodies obtained from soil often consist of chitinous remains of insects and animal excreta. Kostytchev (581) and Ollech (789) suggested that the remains of bacteria and fungi often contribute to humus formation. Attention has already been called to the ideas of Hébert and others concerning the important rôle that the constituents of microbial cells may play in the formation of humus (1112, 1292).

Shmook (1004-6) advanced the theory that protein was present in the soil largely in the bodies of bacteria and protozoa. The function of microbial cell substance as a source of humus has also been demonstrated by Trussov (1184-5). Schreiner and Shorey (979) suggested that various chemical substances found to be characteristic constituents of soil humus may actually be synthesized by microorganisms. This idea was emphasized by a number of other investigators (85, 1262, 415, 599, 1099). According to Donath and Lissner (231), cellulose decomposition by bacteria is not a simple process at all, but may be accompanied by the formation of bacterial products; the pectin-like slime produced by these organisms was found to play an important rôle in the formation of humus substances (775, 777).

Falck (280-2) differentiated several processes of decomposition of plant residues in forest soils, leading to the formation of different types

of humus: (a) The complete destruction of the organic matter by fungi, whereby the yearly addition of plant residues is just balanced by the amount of decomposition taking place, without any increase in the total humus content. This is accompanied by extensive synthesis of fungous protoplasm, which serves as excellent fertilizer for the forest trees. The cellulose tends to disappear completely, whereas the lignins are more resistant. In some cases, however, as in the process of corrosion brought out by Basidiomycetes, the lignins and cellulose alike are completely decomposed; this process predominates in acid humus soils. (b) Decomposition of organic matter is begun by fungi and then interrupted by lower invertebrates and bacteria; the fungous mycelium, as well as the partly decomposed plant residues are devoured by larvae of various insects and worms, with the result that a dark mass of humus is produced. This humus is readily attacked by bacteria, in the presence of bases, the action resulting in the liberation of carbon as CO_2 and of nitrogen as ammonia; this process results in the formation of a mull soil. (c) The process of formation of a forest humus layer, frequently referred to as "surface peat," a process less clearly understood; Falck explains this process by the absence of abundant fungous development.

Waksman (1221) called attention to the similarity between the carbon-nitrogen ratio in soil humus and in the protoplasm of microorganisms, especially fungi, and suggested that this is due to the fact that microbial protoplasm makes up a large part of the humus. When cellulose is added to the soil, it decomposes only in proportion to the available nitrogen, because of the fact that the fungi and bacteria which decompose the cellulose in soils and in composts synthesize an amount of cell substance which is in direct proportion to the quantity of cellulose decomposed. The ratio between the cellulose decomposed and the available nitrogen required for synthetic purposes is about 30 to 1; i.e., for every 30 parts of cellulose consumed by fungi and bacteria, 1 part of nitrogen is changed from an inorganic form into microbial protoplasm.

In the presence of sufficient nitrogen, the decomposition of cellulose by pure cultures of aerobic microorganisms takes place very rapidly; the same is true not only of pure cellulose but also of straw, corn stover, and other plant residues rich in cellulose and in pentosans and poor in nitrogen. This phenomenon accounts largely for the injurious effect of straw on plant growth. Available nitrogen is required by microorganisms because, under aerobic conditions, a considerable part of the

carbon of the cellulose decomposed, frequently as much as 30 per cent, is changed into microbial protoplasm. Since microbial cell substance contains about 3 to 10 per cent nitrogen, the synthesis of considerable amounts of microbial substance results in the consumption of large quantities of soluble nitrogen and its transformation into organic compounds (fig. 3). The constant synthesis of proteins and other complex organic nitrogenous substances by microorganisms in soils and in

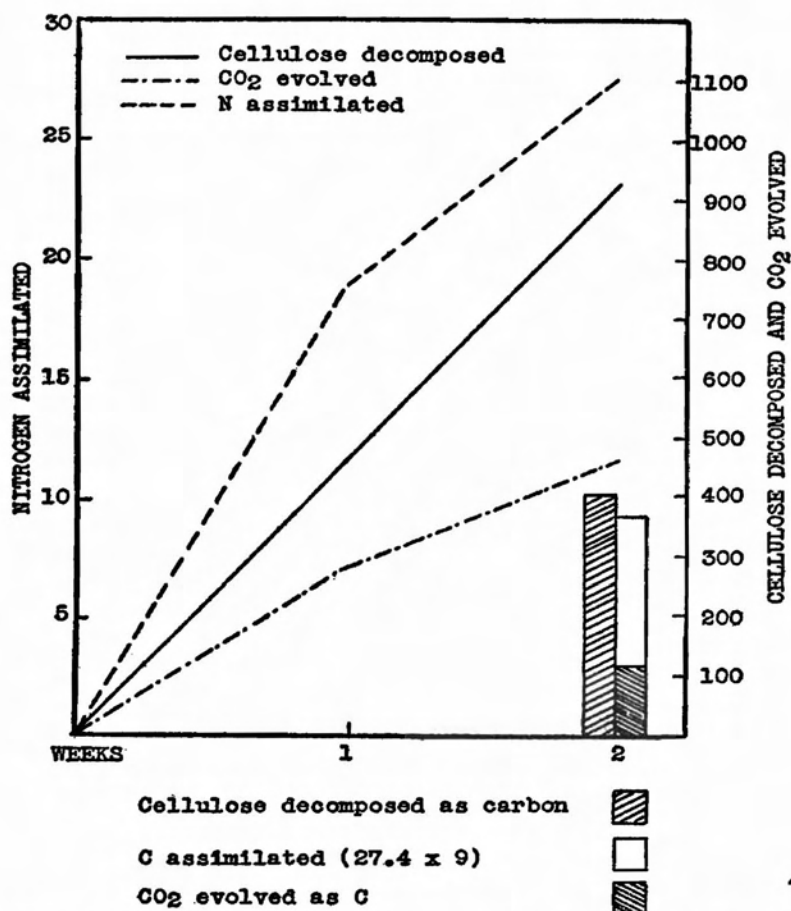


FIG. 3. Relation between cellulose decomposition by microorganisms and nitrogen assimilation, or its transformation into microbial cell substance (Waksman and Heukelekian).

composts, whether carbohydrates or proteins are used as sources of energy, has been recorded previously by Dehérain, Lathrop, and others (239). These synthesizing activities account for a large part of the nitrogenous complexes in the humus, as well as of certain hemicelluloses or uronic acid complexes. The latter is substantiated by the fact that various microorganisms produce extensive quantities of mucus (1020) and other slimy material, which, on further analysis, is found to belong to the hemicelluloses.

Numerous other references could be cited in regard to the contribution of microorganisms, through their cell substance as a whole or through some of the constituents of the latter, to the humus complex. Alkali-soluble and acid-precipitated complexes, comparable to "humic acids" or α -humus, have been isolated (1067) from the dead bodies of microorganisms. Some of these synthesized complexes are highly resistant to decomposition and hence tend to persist in the humus. Thom and Phillips (1155) have shown that the dark brown masses of growth produced by fungi contain material of a lignin-like character whereas colorless or light colored fungi produce little of this material. *Alternaria* was found to contain 17.25 per cent and *Cladosporium* 29.27 per cent of this complex, while the brown *Trametes pini* and the black *Fomes igniarius* were even richer in this type of "lignin."

The brown-black pigment of the spores of certain fungi, such as *Aspergillus niger*, was found (854) to exhibit an acid character. This was believed to be due to the presence in the molecule of phenolic, hydroxyl and carboxyl groups. When heated to 150–250°C. it loses CO₂ and water and becomes less soluble in alkalies. This suggested the analogy of the pigment to the humic acid complexes.

Formation of humus. When plant and animal residues are added to the soil or are placed in composts, under conditions favorable to decomposition, they are immediately attacked by a large number of microorganisms, including fungi, bacteria and protozoa, as well as various other invertebrates. However, the residues do not decompose as a whole, but the various chemical constituents may be attacked independently of one another. Some of the microorganisms are able to decompose a variety of complexes, whereas others are able to utilize very few constituents and will frequently act only upon complexes of a specific chemical structure.

Some of the plant constituents, such as the starches, sugars, proteins, and amino acids, are rapidly attacked by a great variety of organisms. The production of intermediary compounds, such as alcohols and organic acids, takes place largely under anaerobic conditions; under aerobic conditions, the materials are decomposed chiefly to carbon dioxide, ammonia (in the case of the nitrogenous substances), and water. Considerable synthesis of microbial cell substance accompanies these transformations. Cellulose is attacked by certain specific aerobic and anaerobic bacteria and by a number of filamentous and mushroom fungi, actinomyces, and possibly protozoa. The cellulose is decomposed quantitatively, without the production of intermediary dark colored substances, other than those of the synthesized microbial cells.

Since the hemicelluloses represent a variety of chemically different substances, it is difficult to make any general statement concerning the nature of the organisms capable of decomposing them and the rapidity with which they are decomposed. A greater variety of microorganisms are capable of utilizing hemicelluloses than cellulose. Certain polysaccharides commonly classified with the hemicelluloses, such as various galactans and uronic acid complexes, are more resistant to decomposition than is cellulose; these hemicelluloses are especially abundant

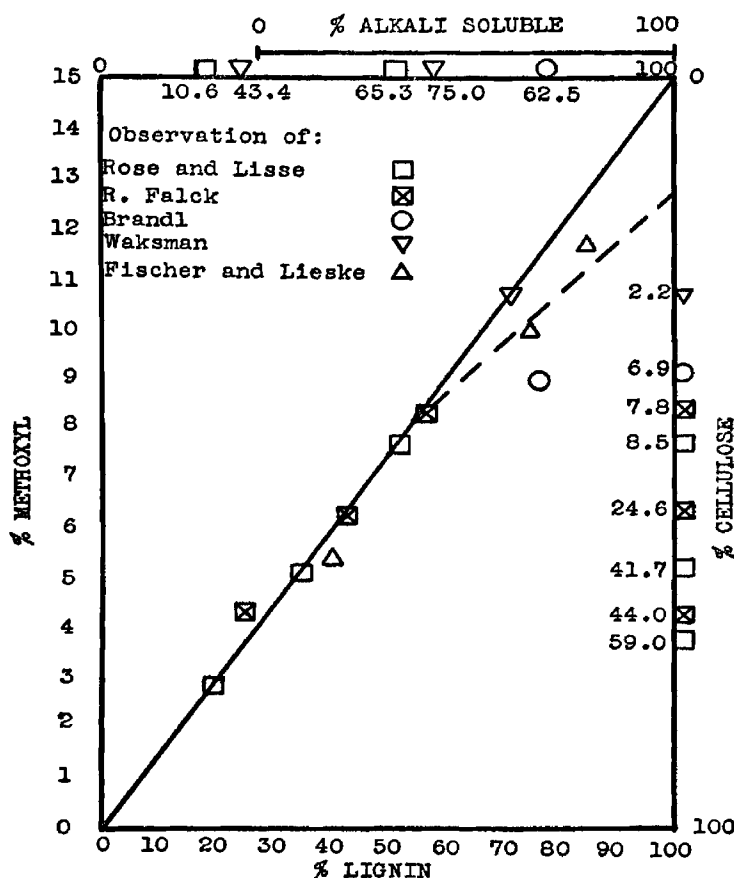


FIG. 4. Lignin and cellulose transformation in the process of decomposition of plant residues by microorganisms (Fuchs).

among the lower plants, such as mosses and algae. The following phenomenon is frequently observed during the decomposition of plant residues by a mixed microbial population. The hemicelluloses as a group begin to decompose more rapidly than the cellulose, but after a certain period of time the cellulose completely disappears, while a large amount of the hemicelluloses still remains in the decomposing plant residues or in the resulting humus, notwithstanding the fact that in the original material the cellulose predominated quantitatively over

the hemicelluloses. An explanation for this is to be found in the fact that some of the plant hemicelluloses are resistant to decomposition and that certain hemicellulose-like compounds which were synthesized by the microorganisms responsible for the decomposition processes persist and can be detected in the humus residue.

Of the various plant constituents, the lignins are most resistant to decomposition by microorganisms. König (566) demonstrated that the decomposition of plant residues in the soil is accompanied by a disappearance of pentosans and an accumulation of lignin, as measured by the methoxyl content. The resistance of the lignins to decomposition is particularly evident under anaerobic conditions (1242), when the activities of practically all fungi and actinomyces are excluded. Under aerobic conditions, however, the lignins undergo considerable decom-

TABLE 12

*Transformation of chemical complexes during the decomposition of rye straw (1242)**

CHEMICAL CONSTITUENTS	AT BEGINNING OF DECOMPOSITION	DECOMPOSED FOR 2 MONTHS UNDER AEROBIC CONDITIONS
Total material.....	100.0	58.0
Cellulose.....	41.5	18.3
Pentosan.....	26.0	10.3
Lignin.....	22.5	20.0
Protein.....	1.2	3.4

* Calculated on the basis of original 100 gm. dry, ash free material.

position, although not to the same extent as the cellulose and hemicelluloses; lignins of different plants vary considerably in this respect. The nature of the organisms capable of bringing about the decomposition of the lignins, especially in field soils, is still imperfectly understood.

However, even if the lignins are more resistant to decomposition than the other plant constituents, they are considerably modified during the process of decomposition, either through chemical agencies (961) or as a result of specific microbial action (1262, 214), as shown by the fact that they become much more readily soluble in dilute alkali solutions. The fact that there are certain modifications in the structure of the lignin molecule has been considered as evidence for the prevalent idea that "humic acids" are formed from lignin. Lignin of the original plant substance is only sparingly soluble in cold alkali solutions; high temperatures (150–180°C.) are required to accomplish this. However,

the modified lignin of the decomposed plant materials is readily soluble in dilute solutions of NH_4OH or NaOH , frequently to the extent of 30 to 75 per cent.

Wehmer has shown that wood-destroying fungi (*Merulius lacrymans*, *Polyporus vaporarius*, *Coniophora cerebella*) change lignin, in an acid medium, into "humic acid." In the decomposition of plant residues by microorganisms, the methoxyl content, the lignin content, and the amount of alkali-soluble substances increase, while the cellulose content decreases, as shown in tables 10, 12, and 13, and in figure 4. This can lead to but one conclusion, namely, that the lignin of the plant residues is an important source of the "humic acid" in the humus.

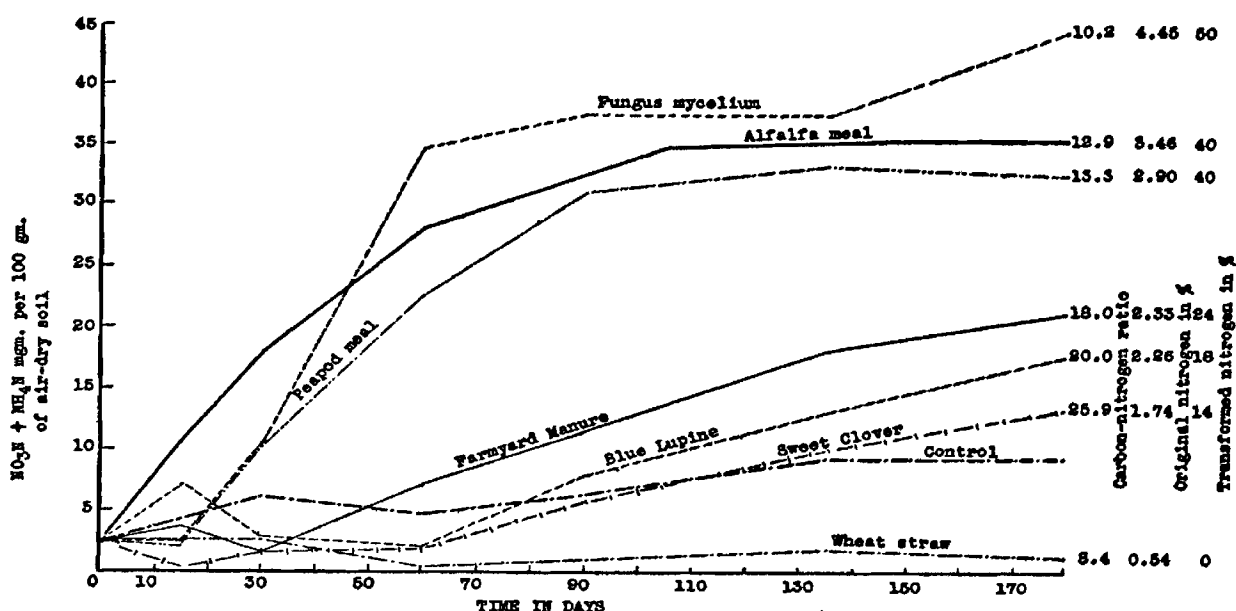


FIG. 5. Influence of C/N ratio of plant material upon its decomposition, as measured by the liberation of nitrogen in an available form (Jensen).

According to Fuchs (324-6), the "humic acid" molecule is twice as large as the lignin molecule and is poorer in hydroxyl and methoxyl groups. The reduction in the methoxyl content of the lignin, in the process of decomposition by microorganisms, has actually been demonstrated by Pringsheim and Fuchs (851). One may conclude, therefore, that the formation of humus from plant residues consists in a rapid reduction of the cellulose and hemicelluloses, a relative increase in the content of lignin and modified lignin complexes, and an absolute increase in the protein content when the residues are poor in nitrogen. The new protein is synthesized through the activities of the microorganisms.

The rapidity of decomposition of plant and animal residues by

microorganisms in soils and in composts is controlled by the relative concentration of total nitrogen in the residues (1242). If the nitrogen content is high, as in dried blood and cottonseed meal, the excess of this element will be rapidly liberated as ammonia; if the nitrogen content is low, additional inorganic nitrogen will have to be introduced in order to bring about rapid decomposition. This is brought out in figure 5. When the plant residues contain about 1.7 per cent nitrogen, there is just sufficient nitrogen to enable the microorganisms to bring about active decomposition, without any additional nitrogen required from the outside and without any nitrogen being liberated as ammonia, until considerable reduction in bulk of material has taken place. The

TABLE 13
Formation of "humus" during the decomposition of straw (1143)
Per cent of dry material

DAYS OF INCUBATION	PENTOSAN	CELLULOSE*	ALKALI SOLUBILITY†	HUMUS CONTENT‡
Original	31.3	39.9	48.5	22.4
14	25.7	39.9	49.5	23.4
28	19.0	35.9	56.7	26.3
64	14.4	27.9	65.0	30.9
82	11.1	23.8	67.8	31.6
102	10.1	16.4	71.1	32.8
146	7.9	70.6	32.3

* Cross and Bevan method.

† Loss on treatment with 3 per cent NaOH solution in reflux condenser.

‡ Precipitate obtained on acidifying the alkali extract; contains hemicelluloses and lignin. The carbohydrate fraction in the humus (Eller's procedure) was 28.0–48.6 per cent, the lignin fraction 51.4–72.0 per cent.

fact that no ammonia is formed during this decomposition does not prove that the nitrogenous complexes present in the plant residues are not attacked, but merely that all the nitrogen liberated in the decomposition of the proteins is immediately reassimilated by the organisms attacking the non-nitrogenous substances and is synthesized into microbial cell substance. In the anaerobic decomposition of plant residues the amount of available nitrogen is less significant than in aerobic decomposition (8a).

These processes of decomposition of the major constituents of the plant and animal residues are accompanied also by the decomposition of numerous organic compounds which occur in less abundance, such

as the oils, fats, waxes, tannins, glucosides, and pigments. The nature and extent of decomposition of the major and minor groups of plant and animal constituents are markedly influenced by the nature and age of the material and by the conditions of decomposition, the latter influencing the nature of the microorganisms active in the decomposition processes. Figure 6 shows the marked effect exerted by aeration upon the decomposition of plant residues and their various constituent

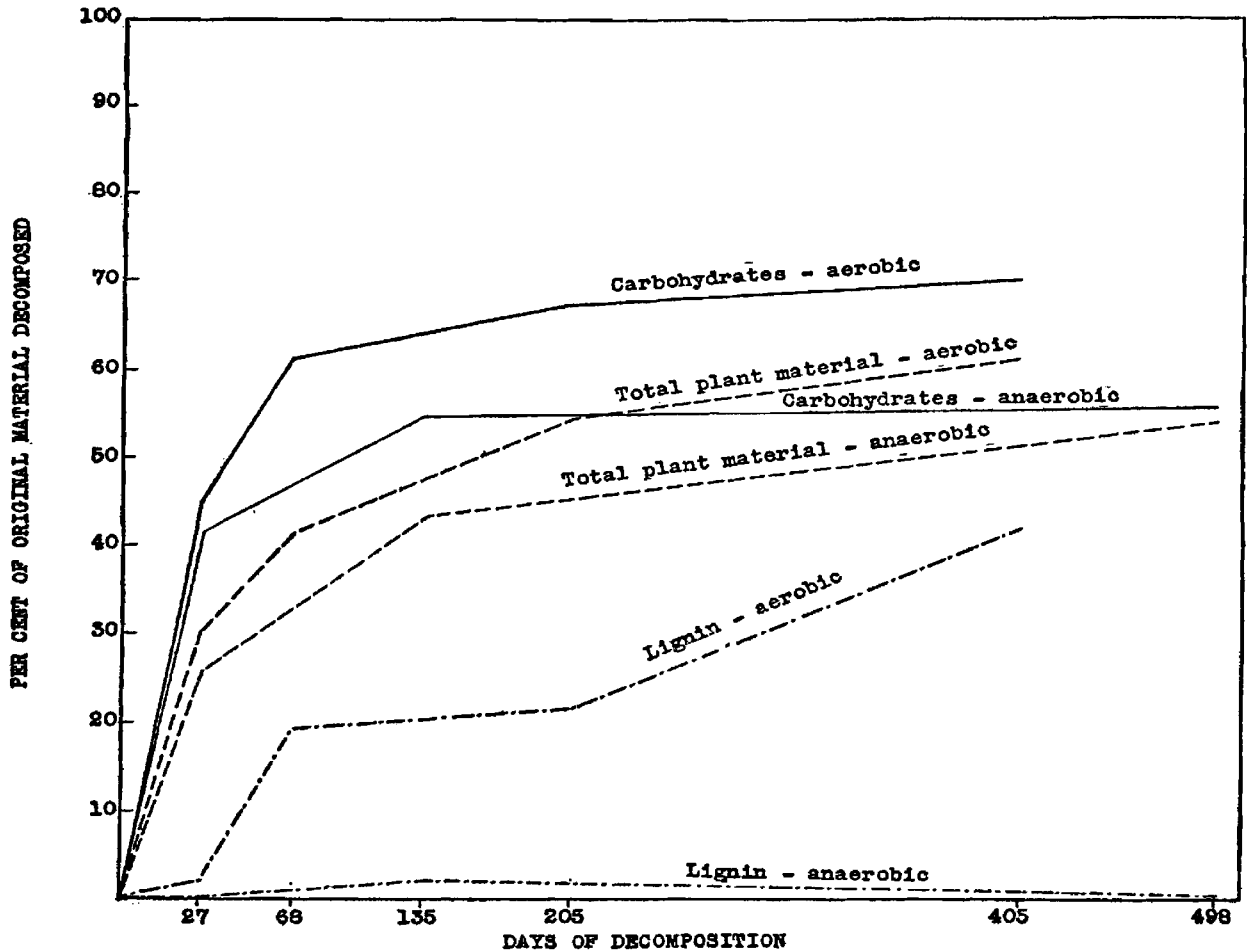


FIG. 6. Influence of aeration upon the decomposition of the whole alfalfa plant, the total water-insoluble carbohydrates, and the lignins under aerobic and anaerobic conditions (Tenney and Waksman).

complexes; the lignins, for example, undergo some decomposition under aerobic conditions, but remain practically undecomposed under anaerobic conditions. This phenomenon has an important effect upon the accumulation of humus under peat bog conditions.

It thus becomes evident that when complex plant and animal materials find their way into the soil, either through natural forces or through the agency of man, or are allowed to undergo decomposition

in composts, numerous processes are set in motion by thousands of different organisms. Following the decomposition of these materials, there results a dark brown residual mass, which is commonly described as humus. One should recognize the great complexity of the processes involved in the decomposition of organic residues in soils, peat bogs, and composts, in order to appreciate how complex humus may actually be. Various substances are formed as a result of the processes of hydrolysis, oxidation, reduction, and condensation, and a diversity of new compounds are synthesized by microorganisms. Moreover, humus is never found in a static condition, except when prevented by natural agencies from decomposing further, as in the case of coal formation. The mere fact that a portion of the humus is soluble in alkalies or is oxidized readily by certain reagents is hardly sufficient reason for claiming that this represents an entirely new compound which can be conveniently labelled "humic acid," "humus," or even "pure humus." There is slight justification for referring to this fraction of the humus as the "humified" portion and for labelling the remaining fraction as "unhumified."

The nature of the various forms of humus is determined by the composition of the undecomposed plant material from which they originate. The organic matter of rotted wood, of composted straw, of soil, and of peat does not represent a mixture of mysterious compounds, requiring special names such as "humic bodies," but comprises a great many chemical complexes which have their origin either in the plant residues or in the microorganisms active in the decomposition processes. This is emphasized in table 14, where the comparative composition of forest soil humus and of oak leaves decomposed under controlled laboratory conditions is given.

Sauerlandt (941) calculated that when 30 tons of manure are added per hectare of soil every 4 years, 550 kg. of lignin will be introduced into the soil each year. The plant residues add another 300–500 kg. of lignin per hectare annually. The humus content of the soil is, on the average, 2 per cent humus, amounting to 60,000 kg. of humus per hectare. If one assumes an annual decomposition of 5 per cent humus, 3,000 kg. will be found to be decomposed each year. Only one-third of this loss can, therefore, be replaced by the lignin in the manures and in the plant residues. These calculations point to other sources, besides the lignins, as mother substances of humus. The results previously presented leave no doubt as to that, since the other constituents of the manure and of the plant residues also contribute to humus either

directly, in the form of hemicelluloses, fats, and proteins, or through microbial synthesis (1231).

Summary. During the decomposition of plant and animal residues in soils or in composts by microorganisms, some organic constituents are attacked more readily than others; some are extremely resistant to decomposition. Accompanying these decomposition processes, numerous microorganisms synthesize new complexes in the form of microbial cell substance. The nature and the rapidity of the processes of decomposition are modified by the environmental conditions, which influence the type of microorganisms active in the decomposition processes, as well as the mechanism of decomposition and the nature of products formed. The mass of plant residues undergoing decomposi-

TABLE 14

Comparative chemical composition of forest soil humus and of decomposed oak leaves (1949)

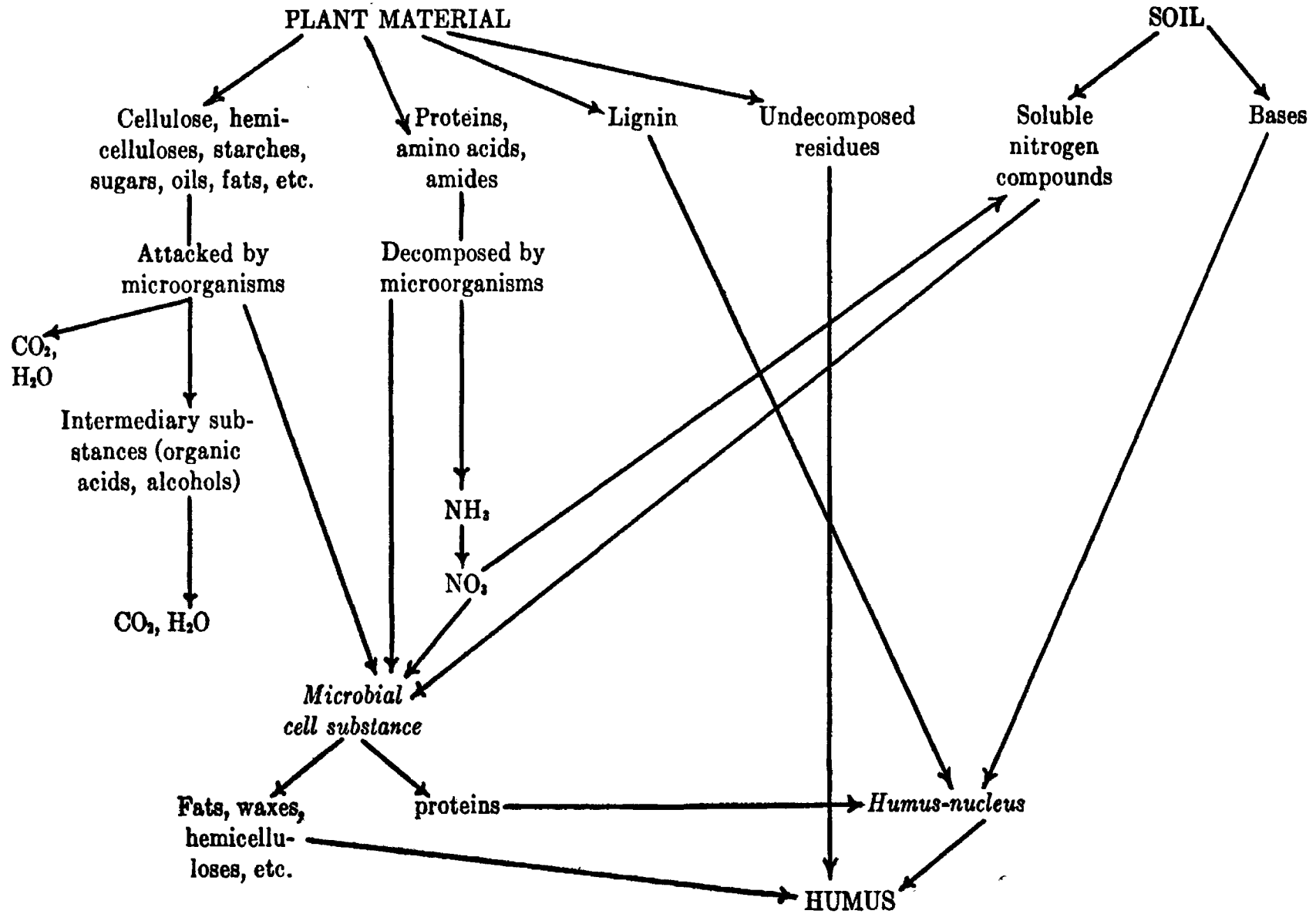
Per cent of dry, ash-free material

CHEMICAL CONSTITUENTS	HUMUS LAYER OF FOREST SOIL	OAK LEAVES DECOMPOSED 6 MONTHS IN LABORATORY
Water soluble fraction.....	7.00	13.84
Hemicelluloses.....	18.52	8.71
Cellulose.....	11.44	8.00
Lignin.....	47.64	54.21
Protein.....	10.06	12.33
Ether-soluble fraction.....	5.34	3.04
pH.....	5.60	5.93

tion, together with the synthesized cell substance and certain intermediary products, form a dark mass of material which is commonly referred to as humus. This humus has no definite chemical composition, but changes constantly as a result of the continuous processes of decomposition.

Plant residues, in the form of roots and stubble, give rise to the characteristic humus in arable soils; under specific conditions certain grasses and trees give rise to the humus of lowmoor peats and of forest peats, characterized by a high content of lignin and protein and low content of cellulose. Under conditions of highmoor formation, sphagnum plants give rise to the humus of highmoor peats, which are low in protein, low in ash, high in hemicelluloses and cellulose, and high in fats and waxes. The allochthonous formations, or sedimentary peats,

CHART 3. Schematic representation of mechanism of formation of humus in the decomposition of plant residues in soil



CHAPTER VI

ISOLATION OF DEFINITE ORGANIC CHEMICAL COMPOUNDS FROM HUMUS

“An essential difference between soil and a mere mass of sand or disintegrated rock is that the former contains some organic matter.”—
SCHREINER AND SHOREY.

When one considers the diversity of the complex chemical constituents of plant and animal residues from which humus is formed, the numerous processes of hydrolysis, oxidation, reduction, and condensation involved in the decomposition processes, as well as the synthesis of considerable quantities of microbial cell substance, in itself complex in chemical composition, one can logically expect to find in humus a great variety of organic compounds. Our knowledge of the chemistry of these humus constituents has progressed along two distinct lines: first, evidence has accumulated concerning the presence in humus of a number of well-defined organic compounds which vary both in nature and in abundance; second, the humus constituents have been separated into several groups of complexes, defined by certain common and characteristic properties.

Although the existence in humus of a great variety of complexes was becoming generally known, it was only with the publication of the investigations undertaken by the Bureau of Soils in Washington, under the leadership of Schreiner and Shorey, that satisfactory methods were developed for the isolation and identification of the humus constituents and knowledge of these substances became definitely systematized. An outline of the general procedure employed in these investigations on the humus of soils and peats is shown in chart 4. After extraction with alkali solutions, certain humus fractions were precipitated with acids. The humus was divided into several groups, which were similar to those commonly studied previously under the names of “humic acid,” “crenic acid,” “humin,” etc. These groups were used for the isolation of the specific chemical compounds indicated in the chart.

The results obtained by the general method of separation may be conveniently compared with those of Berthelot and André, who also

CHAPTER VI

ISOLATION OF DEFINITE ORGANIC CHEMICAL COMPOUNDS FROM HUMUS

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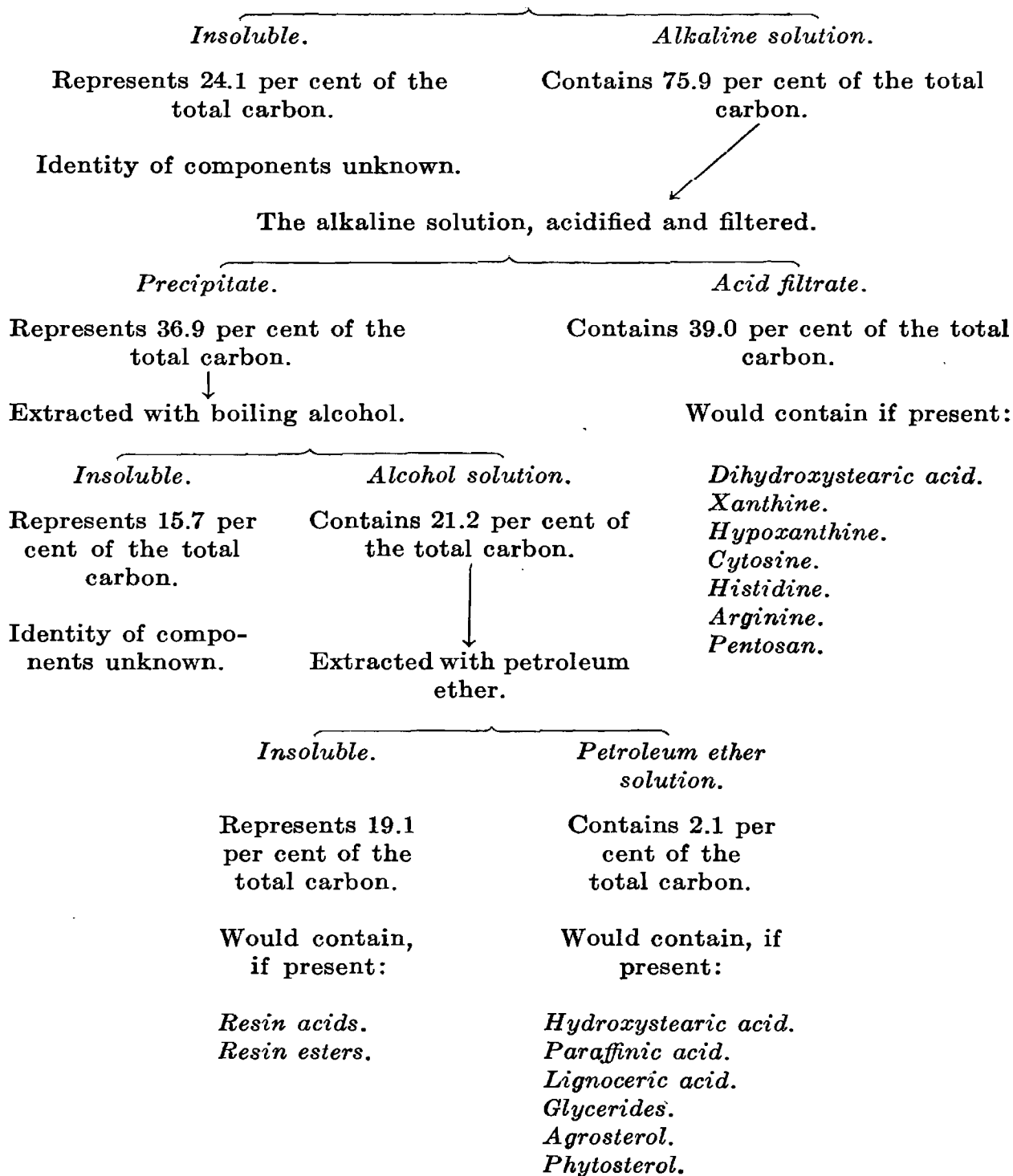
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CHART 4. Distribution of organic compounds in soil humus (Schreiner and Shorey).

Soil, containing 0.955 per cent organic carbon, was extracted with 2 per cent sodium hydroxide.



separated the soil humus into three fractions, on the basis of alkali treatment, and calculated the carbon and nitrogen distribution in these fractions (table 15). The total humus of their soil contained 56.1 per cent C and 4.9 per cent N, with a C:N of 11.4:1. Although the complexes which they obtained were characterized by certain general properties, they did not represent specific individual compounds. They would vary in composition with the source of humus and with the methods used in extraction.

The compounds isolated from humus by Schreiner, Shorey, and their associates, represent well-defined chemical substances. Some of these compounds were constituents of the plant and animal residues which resisted decomposition, or were being transformed slowly; some were products of microbial decomposition; some were constituents of the synthesized microbial cell substance. It was found that some of these

TABLE 15

Carbon and nitrogen distribution among different fractions of soil humus (109)

PREPARATION	CARBON OF FRACTION, PER CENT OF TOTAL CARBON	NITROGEN OF FRACTION, PER CENT OF TOTAL FRACTION	NITROGEN PER 100 PARTS OF CARBON
Insoluble in cold alkali.....	31.7	1.25	4.0
Soluble in alkali, but precipitated by acid.	27.6	1.52	5.6
Soluble in alkali and not precipitated by acid (hydrolyzed products).....	40.7	3.9	9.7

compounds occurred in the humus in a free state, while others were present in a combined state, being liberated only as a result of treatment of the humus with various chemical reagents. Some of the compounds demonstrated in the humus were shown to be beneficial to the growth of higher plants and microorganisms, whereas others were decidedly injurious (1030, 184).

A summary of the nature and abundance of the various organic compounds which have so far been isolated from the humus of soils and peats is presented here. Although this information does not give a complete picture of the chemical nature of humus as a whole, it emphasizes the fact that humus is extremely complex and variable in chemical composition.

I. PARAFFIN HYDROCARBONS

Hentriacontane, $C_{31}H_{64}$, was isolated by Schreiner and Shorey (981), by extracting a peat soil with boiling 95 per cent alcohol. This compound forms a hard, waxy mass, melting at $68^{\circ}C.$; the sp. gr. is 0.78

at the melting point. The substance is soluble in ether and in petroleum ether, difficultly soluble in hot alcohol, and slightly soluble in cold alcohol. It was suggested that hentriacontane appears in the soil humus as an unchanged plant residue.

II. STEROLS

1. *Agrosterol*, $C_{26}H_{44}O \cdot H_2O$, was first isolated from the soil. Schreiner and Shorey (976) demonstrated its presence in a North Dakota soil rich in organic matter. It was extracted from the soil by boiling 95 per cent alcohol. This sterol was believed to have been contained in some plant which grew on this soil. It is also possible that this compound was formed in the soil by the action of microorganisms on some of the constituents of the plant residues, such as certain fatty acids. The fact that microbes are able to synthesize various sterols, including ergosterol, also suggests that the microbial cell substance, which is synthesized in the soil, was a probable source of this compound. This sterol was found to exist in the soil in a free state.

2. *Phytosterol*, $C_{26}H_{44}O \cdot H_2O$, the most common sterol in plants, was extracted from a peat soil with boiling ethyl alcohol (976). Since it was obtained by a process of saponification, it appeared likely that this compound occurred in the humus in combination with other organic complexes, probably as an ester of a higher fatty acid. Phytosterol may also enter the soil in the plant residues and remain there in an unchanged form.

III. FATS, WAXES, AND ESTERS

When a soil is treated with ether, chloroform (315), benzol-alcohol, or other solvent, varying concentrations of fats and waxes can be extracted; the actual amount of these depends on the nature of the humus and its abundance in soil. Some of these compounds are introduced with the plant residues, and others occur in the cells of the soil-inhabiting microorganisms. Probably some of the sterols and the various other alcohols, as well as some of the acids, do not exist in the humus in a free condition, but only in the form of fats and waxes. The presence of the following two groups of esters was definitely demonstrated in humus:

1. *Glycerides of fatty acids*, containing a small amount of unsaponifiable material and possibly also some free acid; these were found in all of the soils examined (980). Their presence in humus is due either to their introduction in the form of plant and animal residues or to their synthesis by microorganisms.

2. *Resin esters*, soluble in alcohol and ether, but insoluble in water and in aqueous alcohol. Compounds belonging to this group were isolated (979) in the form of a resinous brown powder, melting at 95°C. and containing 68.88 per cent carbon, 10.24 per cent hydrogen, and 20.88 per cent oxygen.

In addition, various other fats and waxes, under the general name "bitumens," were demonstrated in other forms of humus, especially in that from peat and coal. The presence of carotenes and chlorophyll in soil has also been established (71a).

IV. ORGANIC ACIDS

A number of organic acids belonging to several chemical groups were shown to be present in varying concentrations in the humus of peats and soils. These acids are not to be confused with the dark-colored "humic acids," of unknown composition. Since organic acids of known constitution are present in plant residues and since numerous microorganisms, especially certain fungi and bacteria, are capable of producing a variety of acids in the decomposition of organic matter, one would expect to find this group of compounds abundantly represented in humus. Most of the acids do not accumulate in the soil but are further decomposed by microorganisms, especially in the presence of sufficient bases, such as calcium and magnesium. In some instances, the same organism which produces a certain acid is able to decompose it further; *Aspergillus niger*, for example, produces gluconic and citric acids, which are later transformed to oxalic acid and finally to CO₂. Other organisms, especially anaerobic bacteria and yeasts, produce butyric, propionic, lactic, and other acids, which are attacked further by aerobic bacteria and by fungi, especially in the presence of neutralizing bases.

The following acids have actually been discovered in humus:

1. *Oxalic acid*, (COOH)₂, isolated by Shorey (1010) from the acidified filtrate of the alkaline extract of soil, was also obtained by treating the soil with dilute hydrochloric acid. Shorey suggested that this acid is present in the soil in the form of calcium oxalate, frequently in rather high concentrations. Although an abundance of oxalic acid is introduced into the soil in the various plant residues and is also produced by a variety of fungi and bacteria, ordinarily it is rapidly decomposed further to carbon dioxide. It is not found as a constant humus constituent, but appears occasionally.

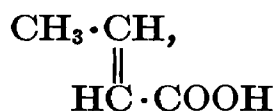
2. *Succinic acid*, (CH₂)₂(COOH)₂, was demonstrated (1010) in soil from California. The fraction obtained after neutralization of the

alkali extract of the soil with sulfuric acid and removal of the precipitate contained this complex. It is less abundant than oxalic acid in plant residues, but it is formed by a number of organisms.

3. *Saccharic acid*, $\text{COOH} \cdot (\text{CHOH})_4 \cdot \text{COOH}$, is widely distributed in the soil. It was isolated by Shorey (1010) from the alkali extract of a soil, after the precipitate formed on acidification had been removed. In view of the fact that this compound is not known to occur in plant or animal tissues, it was believed to originate in the humus through the action of microorganisms.

4. *Acrylic acid*, $\text{CH}_2 : \text{CH} \cdot \text{COOH}$, was isolated from the same soil as the saccharic acid (1010). This compound, as well, does not occur in plant and animal tissues; it was suggested, therefore, that it is probably also produced in the soil through the agency of microorganisms.

5. *α -crotonic acid*,



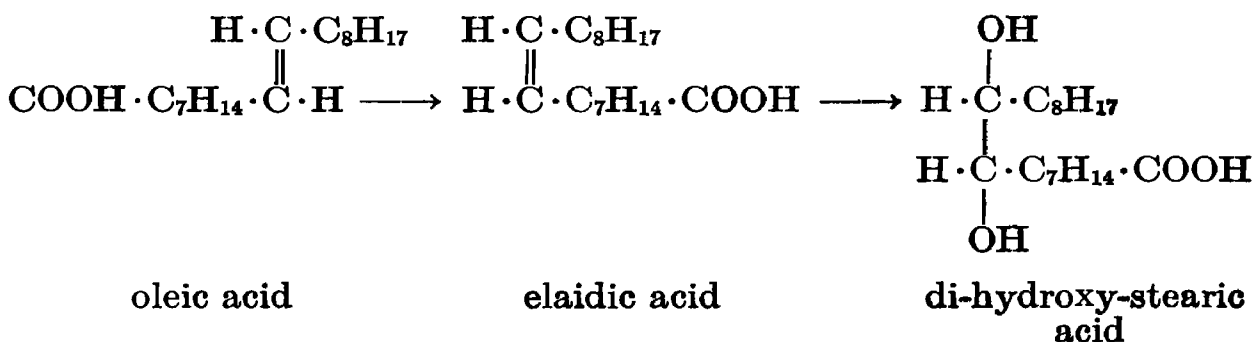
was isolated by Walters and Wise (1249) from a sandy loam soil from Texas. It is soluble in water, in ether, and in alcohol. It reduces potassium permanganate in cold alkaline solution. Ninety-four milligrams of this compound were obtained from 50 pounds of soil, although considerable loss occurs in the process of its preparation. The presence of this acid in the soil was traced to several sources: it can be formed during the decomposition of cellulose by bacteria, in the transformation of β -hydroxy acids of the aliphatic series, or by hydrolysis of allylcyanide, which is present in the essential oils of certain plants. It may be of interest to call attention here to the fact that the butyric acid bacteria, so commonly found in the soil, produce a polymer of β -hydroxy-butyric acid in their cell substance (627).

6. *α -mono-hydroxy-stearic acid*, $\text{CH}_3 \cdot (\text{CH}_2)_6 \cdot \text{CHOH} \cdot (\text{CH}_2)_9 \cdot \text{COOH}$, was isolated by Schreiner and Shorey (979) from the so-called "hymatomelanic acid" fraction of the soil humus. The alkaline extract of the soil is acidified and the precipitate formed is filtered off, washed, and treated in a moist state with boiling 95 per cent alcohol. The alcohol extract is evaporated and the residue is washed and dried, then treated with petroleum ether. This extract is evaporated to remove the ether and the residue is digested with hot alcohol; when the alcoholic solution is allowed to cool, the acid crystallizes out. This compound was found in a Maryland soil, very low in organic matter as shown by a carbon

content of 0.53 per cent and a nitrogen content of 0.066 per cent. This member of the fatty acid series is not known among the plant and animal constituents; its origin in the soil was ascribed to the action of microorganisms upon some organic compounds; it may also be formed by direct microbial synthesis.

7. *Di-hydroxy-stearic acid*, $\text{CH}_3(\text{CH}_2)_7\text{CHOH}\cdot\text{CHOH}(\text{CH}_2)_7\cdot\text{COOH}$, was isolated (974) by extracting with ether the filtrate left after the alkali extract of soil has been acidified with acetic acid and the precipitate removed. Fifty milligrams of this material were obtained from one kilogram of soil. One-third of the soils examined contained this acid; it was found by Schreiner and Lathrop (970) in virgin and in cultivated soils, in cropped and in pasture soils, including soils obtained from various parts of the United States. It may, therefore, be considered as a common constituent of humus. The same compound was found in the roots of an oak tree infected with fungous mycelium. Its presence in various plant residues such as straw and timothy has also been demonstrated (184).

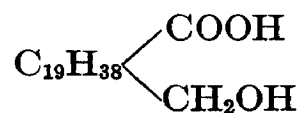
This acid was believed to originate in the soil either through microbial synthesis or the oxidation of organic compounds found in plant tissues, such as oleic acid, which is a constituent part of certain fats and lecithin; the following reactions have been suggested:



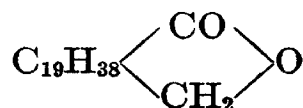
The presence in soil humus of oleic, elaidic, stearic, and palmitic acids was actually demonstrated in 1916 by Khainski (542).

The di-hydroxy-stearic acid is highly toxic to plants growing in nutrient solutions. In view of the fact that it was found largely in poor, unproductive soils and seldom in fertile soils, Schreiner and his associates attempted to establish a relationship between the occurrence of this soil acid and soil fertility. Its presence was believed to be an indicator of conditions which cause the soil to become less productive. However, Fraps has shown (310) that di-hydroxy-stearic acid has little injurious effect upon corn or sorghum plants in soil, even when

acid to crystallize out. This compound was obtained at the rate of 1,000 pounds per acre of soil. It was found to be related to the acid



isolated as the lactone,



from carnauba wax.

Other organic acids of higher molecular weights were also demonstrated in the soil but have not been studied further.

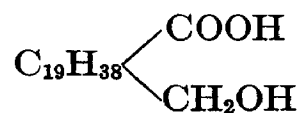
12. *Paraffinic acid*, $\text{C}_{24}\text{H}_{48}\text{O}_2$, was isolated (977) from the cold alcoholic extract, which yielded the α -hydroxy-stearic acid referred to previously. This compound was found in most soils but only in small amounts. Its origin in humus is probably a result of oxidation of hydrocarbons of the paraffin series known to occur in various plant residues.

13. *Lignoceric acid*, $\text{C}_{24}\text{H}_{48}\text{O}_2$, was obtained (977) first by distillation of soil in a closed tube; later it was shown to be present in the hot alcohol extract of soil, thus establishing its existence in humus in a free state. It is soluble in aqueous alkali solutions and is precipitated unchanged when the latter are neutralized with a mineral acid. The fact that lignoceric acid is also found in wood distillate suggests its possible formation in soil through the action of microorganisms upon plant residues, possibly upon lignin complexes. This compound is very abundant in humus; Schreiner stated in a private communication that its yield was at times found to be equivalent to nearly 20 per cent of the total humus.

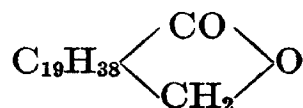
14. *Humoceric acid*, $\text{C}_{19}\text{H}_{34}\text{O}_2$, was isolated (51) from peat by the use of benzol. It is an unsaturated acid, M.P. 72–73°C.; it reacts readily with alkaline KMnO_4 solution and crystallizes from alcohol in the form of needles or leaflets.

15. *Resin acids*. Three resin acids of unknown chemical composition were obtained (979) from the alcohol-soluble portion (“hymatomelanic acid”) of the “humic acid” fraction of soil humus, after the α -hydroxy-stearic acid and the paraffinic acids had been removed with boiling

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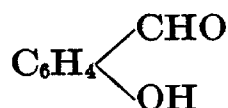
petroleum ether. These acids were found to form a large fraction of the humus.

Many definite organic acids and other compounds have thus been isolated from the "hymatomelanic acid" and the "crenic" or "fulvic acid" fractions of soil humus; other compounds can be readily isolated from the "humin," or alkali-insoluble fraction, and probably also (1235) from the "humic acid" fraction. These results point further to the absurdity of considering such preparations as definite chemical entities.

V. ALDEHYDES

Aldehydes were shown to be rather constant constituents of humus. Only three specific aldehydes have been identified, but certain unidentified compounds belonging to this group have been found in practically all of the soils examined (988).

1. *Salicylic aldehyde*,



was isolated (1010) from the filtrate obtained on acidifying the alkali extract of soil. The presence of this aldehyde in humus may be due to its direct introduction in the plant residues; it may also be formed during the decomposition of certain plant constituents, such as salicin. It was found only in a relatively small number of productive soils. Schreiner and Skinner (987) have shown that this compound has a harmful influence, much more so than vanillin, upon plants grown in culture solution. When added to soil cultures, however, it was found to have no detrimental effect in the case of some soils, especially those that were limed and possessed a high bacterial activity (337), but it was harmful in other soils.

2. *Vanillin*, $\text{OH} \cdot \text{C}_6\text{H}_3(\text{OCH}_3) \cdot \text{CHO}$, was obtained (1011) from the same preparation as the previous aldehyde. Twenty-five kilograms of soil yielded only a few milligrams of this compound; in some cases, the yield was 0.001 to 0.00048 per cent. By grinding the soil and extracting it directly with alcohol, more vanillin was obtained than by the preliminary process of alkali extraction; it was concluded, therefore, that this compound exists in humus in a free state. The fact that vanillin contains a methoxyl group and can be prepared from lignin (598) suggests the probability that lignin gives rise to the vanillin found

in humus. The total amount of methoxyl present in soil is considerably greater than that indicated by the vanillin content; a large part of it must be due either to lignin itself or to various lignin derivatives. Sullivan (1118) actually demonstrated the presence of vanillin in rotten oak wood and in various other plant residues (184).

The injurious effect of vanillin upon plants has been definitely established (1041, 310); it is less harmful in soil than in solution culture; it acts differently in different soils and under different conditions, because of its greater persistence in some soils than in others. Robbins (897) found that when vanillin is added to soil there is at first a depression in bacterial numbers followed by a marked increase; in sterile soil this compound remained harmful to plants, but when such soil was inoculated with an infusion of normal soil, the toxic effect tended to disappear. This suggests the probability that vanillin is destroyed in the soil by certain microorganisms; its persistence in some soils was believed to be due either to a lack of vanillin-destroying organisms or to conditions unfavorable for their development. The addition of vanillin to a fertile soil produced no injurious effect upon plants, but it proved to be injurious in an infertile acid soil; this injury was overcome by the addition of lime, or of lime and phosphate (1182, 1043).

3. *Tri-thio-benzaldehyde*, $C_6H_5C(SH)_3$, was isolated (1010) from the filtrate of the alkali extract of soil acidified with acetic acid. This compound was found infrequently in soil, having been demonstrated only in a California soil and in a salt marsh soil, the former containing 0.59 per cent total sulfur and several hundred pounds of the specific aldehyde per acre-foot.

VI. CARBOHYDRATES

Carbohydrates are present abundantly in humus, especially in that of forest soils and peat. A detailed study of the occurrence and relative distribution of these compounds in different types of humus is reported later. Only a brief summary of some of the specific compounds is presented here. Large amounts reach the soil in the form of plant and animal residues, and some are also synthesized there by the numerous microorganisms active in the decomposition processes.

1. *Pentosans and pentoses*, $(C_5H_8O_4)_n$. Nearly all types of humus give furfural on boiling with 12 per cent hydrochloric acid, which proves that they contain pentosans, uronic acid, or other furfural-yielding compounds. The presence of pentosans, frequently in considerable abundance, in the humus of peat and of forest and mineral soils

has been demonstrated by von Feilitzen and Tollens (285), Sestini (999), de Chalmot (174), and others. Table 16 shows the quantitative distribution of pentosans in a variety of soils and their relation to the total humus content.

The fact that furfural may be derived, not only from pentosans, but also from other compounds that yield pentoses, such as nucleoproteins, and from uronic acids makes it essential to establish the nature of the furfural-yielding complex. Shorey and Lathrop (1015), for example, actually demonstrated that xylose is formed as one of the products of hydrolysis of humus. Schreiner and Lathrop (969) found pentose

TABLE 16
The pentosan content of a series of mineral soils (1015)
Per cent of dry soil

SOIL TYPE	TOTAL CARBON CONTENT	TOTAL PENTOSAN CONTENT	RELATION OF PENTOSAN CARBON TO TOTAL CARBON
Elkton silt loam.....	0.522	0.176	15.13
Sassafras silt loam.....	0.315	0.055	7.93
Chester silt loam.....	1.510	0.182	5.49
North Carolina peaty soil.....	27.102	1.090	1.83
Marshall loam.....	6.971	2.750	17.93
California peaty soil.....	11.478	0.341	1.30
Norfolk fine sandy loam.....	0.822	0.027	1.46
Santa Paula, Calif., loam.....	1.308	0.061	2.14
Portsmouth loam.....	3.854	0.219	2.57
Susquehanna clay loam.....	1.048	0.659	28.53

sugar in all of the soils tested; they concluded, therefore, that pentoses or pentose-containing complexes, in addition to pentosans, are common constituents of the soil organic matter. According to Leavitt (615), pentoses, as well as glucose, are present in humus in the form of anhydrides.

2. *Uronic acids.* The occurrence of uronic acid complexes in humus, frequently in considerable abundance, has also been definitely established (1017). The relation of these complexes to humus as a whole and to the pentoses in particular, will be discussed in detail later.

3. *Cellulose*, $(C_6H_{10}O_5)_n$, is found abundantly in forest soil (1243) and in peat, especially certain types, such as highmoors (285, 907). The quantitative distribution of this important compound in humus is discussed later.

4. *Glucosides*. The presence in soil of a glucoside of rhamnose, methyl pentose, $\text{CH}_3 \cdot (\text{CHOH})_4 \cdot \text{CHO}$, has been established (1010). This glucoside was present in comparatively large concentration in the colored material precipitated by lead acetate from the acid filtrate of the alkali extract of soil.

5. *Sugar alcohols*. Mannitol, $\text{C}_6\text{H}_{14}\text{O}_6$, was isolated from the soil humus by Shorey (1010).

VII. LIGNINS

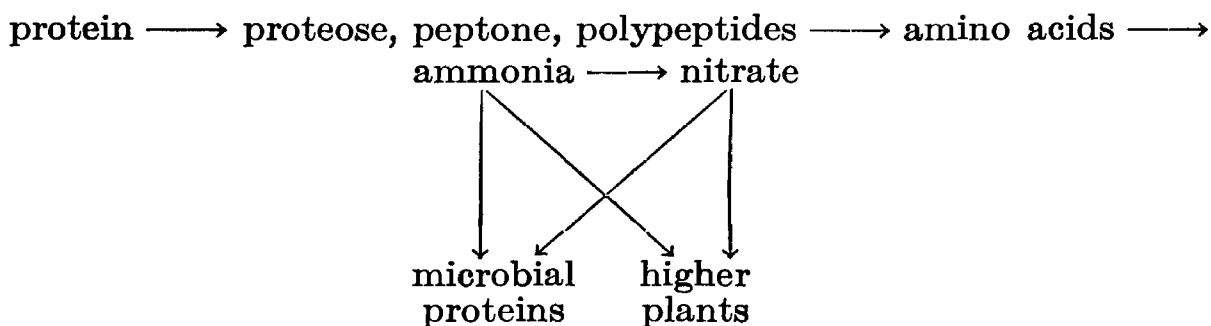
In view of the fact that the chemistry of lignin still presents a number of confusing questions, it is difficult to estimate the exact amount of lignin present in humus. There is no doubt that it is present there in rather high concentrations in an unaltered form, in a modified form, or as condensation products with other complexes. The various "humic acid" preparations commonly obtained by alkali extraction of soils, peats, and composts possess certain specific properties which are known to be characteristic of the lignins. This, as well as the fact that lignin is more resistant to microbial decomposition than are most of the other plant constituents, points to a connection between the two. Attention should also be called here to the occurrence of methoxyl in humus (1016), which adds further weight to the idea that lignin exists in humus, either in an unmodified or in a modified form. Just what modifications the lignin molecule undergoes before it is recognized to have changed into a characteristic "humic compound" is merely a matter for speculation. If humus is considered as the sum total of organic residues undergoing decomposition under natural conditions, lignin becomes a part of humus, no matter whether it is present in the original state or whether it has become modified, as shown by a loss in methoxyl content, by greater solubility in alkali solutions, and by darker color.

VIII. ORGANIC NITROGENOUS COMPOUNDS

1. *Proteins, proteoses, and peptones*. The earlier prevailing conception, as expressed by Ritthausen (895) and by Grouven (375), was that the nitrogen content of humus was originally ammonia which became absorbed by the "humic acids" (649). However, only 2 per cent of the total nitrogen present in humus could be removed by heating the soil with milk of lime, and 5 per cent by heating with potassium hydroxide solution. Detmer (219), Sivers (1039), and others concluded that the nitrogen was present in soil organic matter chiefly in the form of

proteins. Since then, the protein nature of most of the nitrogen in humus has become more or less definitely established. According to Valmari (1197), 88.4 to 96.2 per cent of the nitrogen in peat and in garden soil is in the form of proteins.

The constitution of plant and animal proteins is usually determined by the products formed on acid hydrolysis; in a similar manner, the protein compounds of the humus are hydrolyzed with acids and the products analyzed qualitatively and quantitatively. After proteins are added to the soil, as plant and animal residues, they are attacked by microorganisms and undergo a chain of reactions:



The proteins of the soil are thus found to be of plant, animal, and microbial origin, the last being most significant. Proteins as such have not been isolated to any large extent from soil humus, and considerable difficulty is involved in any such extraction; it is doubtful, therefore, whether proteins exist in humus in a free state; they probably occur in the form of complexes with other compounds, especially lignins, as will be shown later. Protein transformation products can be readily demonstrated in humus, frequently in great abundance. Walters (1247) reported the occurrence in soil of primary decomposition products of proteins, namely, proteoses and peptones. Jodidi (500) extracted 2.92 per cent of the nitrogen in humus with boiling water in 10 hours, and 9.96 per cent, in 24 hours. Shmook (1004) found that 19.10 per cent of the total nitrogen of a Russian lateritic soil was water soluble.

Suzuki (1119) made a study of the nitrogen distribution in the "humic acid" fraction of peat; the preparation was hydrolyzed with concentrated acid, and the individual amino acids were determined by means of Fischer's procedure. The presence of alanine, leucine, aspartic acid, and other amino acids was definitely established. The conclusion was reached that "humic acid" is of a protein nature, is a mixture of protein decomposition products, or is a compound of proteins with other organic

complexes. Morrow (728) failed to isolate any appreciable quantity of alcohol-soluble or salt-soluble proteins from humus; he demonstrated, however, that the distribution of organic nitrogen in the humus of various soil types is very uniform.

In the course of the decomposition of proteins in soil, Lathrop (611, 612) found that new proteins were formed which appeared to be more resistant to decomposition than either plant or animal proteins. These new proteins could not be extracted with distilled water, but when the soil was treated for 24 hours with a 1 per cent solution of sodium hydroxide, the presence of proteins and protein-like substances could easily be established. These soil proteins were believed to be either complexes synthesized in the cells of microorganisms, or certain proteins added in the plant and animal residues which resisted rapid decomposition. During the process of decomposition of organic residues, large quantities of microbial cell substance are synthesized and considerable quantities of inorganic nitrogen are transformed into organic nitrogenous compounds (435). The proteins of certain plant residues, as oak leaves and pine needles, seem to be highly resistant to microbial attack, by reason either of their specific nature or of their formation of complexes with other plant constituents.

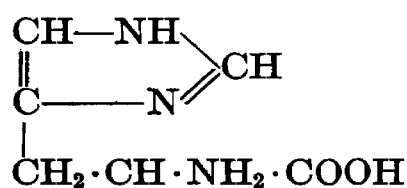
When peat was extracted with 20 per cent hydrochloric acid, only 80 per cent of the nitrogen was made soluble (204). The peat protein yielded three to five times as much amide-nitrogen as did pure vegetable or animal proteins, a phenomenon also observed by others.

2. *Amino acids.* Sestini demonstrated the presence of amino compounds in material extracted from soil with nitrous acid (1000). These compounds are not found very extensively in a free state (504, 843, 845, 900). They are formed largely from the more complex substances (polypeptides and proteins) when humus is treated with alkalies and acids. The amino acids, as well as the acid amides, are the building stones of humus proteins; when the proteins are gradually decomposed by microorganisms, they give rise to amino acids, which are attacked further and reduced to the ammonia stage. An analysis of four soils by the Sörenson method showed that 49 to 68 per cent of the total nitrogen in humus is in the form of amino acids (175). Potter and Snyder (844), however, were able to demonstrate, by the use of the Kober technique, the presence of only small quantities of free amino acids in humus. There was also no tendency for this form of nitrogen to accumulate in the process of decomposition of the organic substances, as is usually found to be the case for ammonia. Manure containing

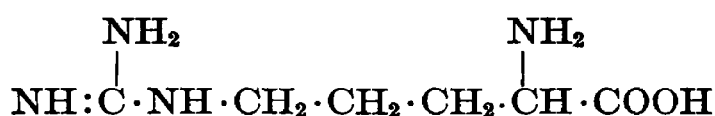
0.522 per cent total nitrogen and 0.015 per cent ammonia nitrogen had only 0.003 per cent amino acid nitrogen. A dilute acid extract of soil contained no amino acids, whereas dilute alkalis extracted appreciable quantities of amino acids. One may conclude from these results that the amounts of amino nitrogen present in humus in a free state are very small in comparison to the quantities produced on hydrolysis of the humus with boiling mineral acids or alkalis.

The presence of a number of mono-amino acids has been demonstrated in soil, such as leucine, iso-leucine (899) and others. Although the total concentration of this group of acids in humus is greater than that of the basic or diamino compounds, the occurrence of the latter has received more attention. Several of the diamino acids, namely, arginine, histidine, and lysine, were found in a weak alkali extract of soil.

Histidine (α -amino- β -imidazole propionic acid) and *arginine* (α -amino- δ -guanidine valerianic acid) have the following structural formulae:



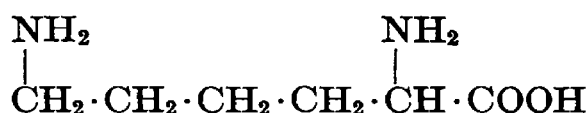
Histidine



Arginine

Both were isolated (979, 982) from the soil, the method of isolation depending upon their precipitation by silver salts from alkali solutions. The first compound was obtained in larger concentrations and from a greater number of soils than the second.

Lysine (α - ϵ -di-amino caproic acid),



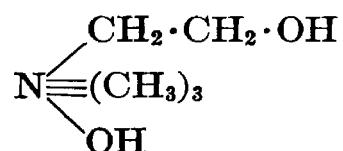
was isolated from a California soil (1010). It was shown to occur in humus only in limited amounts. Lathrop (612) found histidine in 18 out of 24 soils examined; arginine was present in two soils, and lysine in only one soil. The first compound is more resistant to decomposition by microorganisms than the other two because of the fact that their nitrogen is present in ring formation in histidine and in chain structure in arginine and lysine. This explains why arginine and lysine are not so characteristic of humus as is histidine, although the first two are present in almost all of the proteins added to soil.

3. *Amides*. When the nitrogenous compounds obtained on acid hydrolysis of humus in soils and in peats are compared with those found on hydrolysis of animal and vegetable proteins, considerably higher concentrations of amide nitrogen are found in the former than in the latter (612, 501, 503, 536, 844). Between 16 and 30 per cent of the total hydrolyzable nitrogen in the humus is composed of amides which occurred, not in a free state, but in protein combinations. Baumann (72) observed in 1887 that a soil rich in organic matter contained only a trace of ammonia; however, on boiling this soil with hydrochloric acid, he found that a large amount of ammonia was liberated, which led him to conclude that amino compounds and amides are present in the humus. Berthelot and André (108) treated a soil containing 0.174 per cent nitrogen with hot 20 per cent hydrochloric acid, for 2 hours; 31.8 per cent of the total nitrogen was thereby made soluble; of this, 7.1 per cent was liberated as ammonia. They concluded that the nitrogenous complexes of humus consist chiefly of insoluble amides, which are converted into soluble amides and ammonia by the action of acids, alkalis, and even water. Warrington (1252) has also shown that small quantities of amides are present in soil; in this case they were obtained by treatment of the soil with hypobromite and nitrous acid. The presence of urea in forest soils, as well as in other soils rich in humus, has also been established (306). This adds further weight to the theory, already mentioned (p. 105), that the organic nitrogenous compounds of the soil are largely of microbial origin, since microorganisms are known to synthesize considerable quantities of urea and other amides.

4. *Amines*. Several amines and related compounds have been isolated from humus. The following three deserve particular consideration:

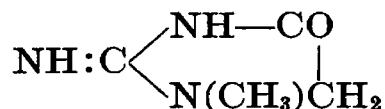
a. *Trimethylamine*, C_3H_9N , was found by Shorey (1010) in a salt marsh soil from Georgia; the soil was made alkaline and distilled under reduced pressure. In view of the fact that this compound is present both in animal and in plant products, its occurrence in soil may be due to its introduction into the soil with such materials or to its formation in soil during the decomposition of certain compounds, such as choline.

b. *Choline*,



or tri-methyl-hydroxy-ethyl ammonium hydroxide, was isolated by Shorey (1010) from a silt loam soil. This compound was found in humus in comparatively low concentrations. It occurs in soil either as a result of its introduction or formation there during decomposition of more complex compounds.

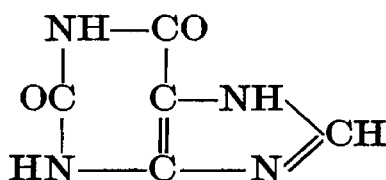
c. *Creatinine*,



was isolated (983, 1018, 1008) from the filtrate left on acidifying the dilute alkali extract of soil, as well as by simple extraction of soil with water. Creatinine is present in stable manure, urine, and fresh leguminous plants; it may also be produced by direct bacterial action. Its concentration in soil is equivalent to several parts per million, frequently as high as the nitrate content or even higher. This compound can be regarded as a normal soil constituent, and it is known to have a favorable effect upon plant growth (1040).

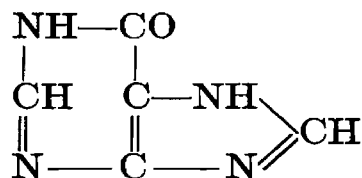
5. *Purine bases*. A number of purine bases have been demonstrated in the soil; namely, adenine, xanthine, and hypoxanthine; these are products of microbial decomposition of nucleic acids.

a. *Xanthine*, 2-6-dioxy-purine,



was isolated (979) from the alkali extract of a soil. It may have been introduced into the soil in the plant residues, but it is more than probable that it was formed there during the process of decomposition of the nucleic acids and nucleo-proteins.

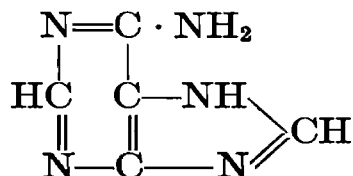
b. *Hypoxanthine*, 6-oxy-purine,



was isolated from a number of soils (979). The purine bases are readily converted into one another by various bacteria and their enzymes;

the presence of any one base in the soil may indicate the predominance of one specific organism.

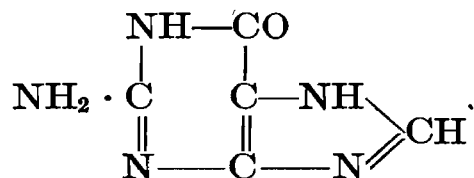
c. *Adenine*, 6-amino-purine,



is not of so common occurrence in humus as the other two bases (1010). Out of 24 soils examined (612), 12 contained hypoxanthine, which was usually associated with cytosine. Xanthine was found in four of the soils and was associated with hypoxanthine in three of them, while adenine occurred in only two of the soils and was associated in one case with xanthine.

Xanthine forms on oxidation uric acid which is readily decomposed in soil by microorganisms. Adenine is changed by deamination into hypoxanthine; the latter is the more resistant to decomposition by bacteria. These facts explain the more general occurrence of hypoxanthine in humus.

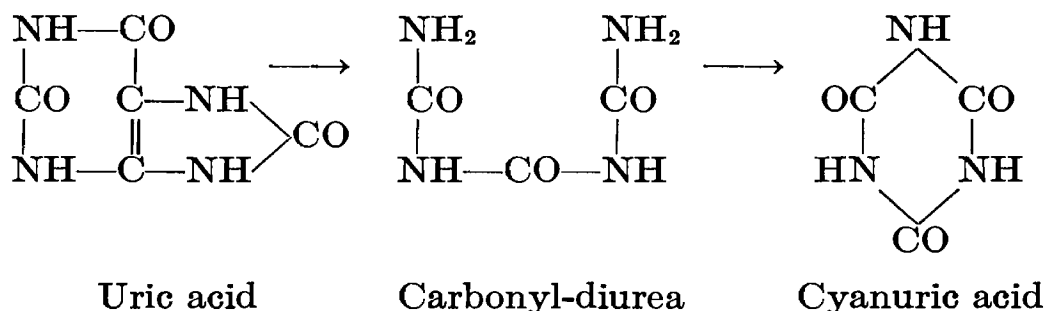
d. *Guanine*, 2-amino-6-oxy-purine,



was isolated (610) from a soil that had been heated in the autoclave under steam pressure; it was found in the filtrate obtained from the acidified alkali extract of soil. It may be produced in the soil from guanosine, guanylic acid, or other nucleic acids. Since guanine was not present in the unheated soil, it must have been formed in the process of heating from some other nitrogenous body, probably nucleic acid.

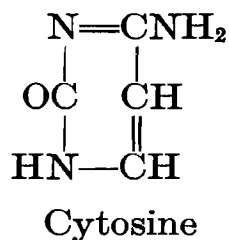
e. *Tetra-carbonimid*, $\text{C}_4\text{H}_4\text{N}_4\text{O}_4$, was isolated from soil by Shorey and Walters (1019); like guanine, it also occurred in the acid filtrate of the alkali extract of soil. This compound is not an uncommon constituent of humus. Thirty milligrams of the pure substance were obtained from 18 kg. of soil, with a probable loss of at least 50 per cent. Its content in soil fluctuates, depending on the conditions. Because of the fact that uric acid has not been demonstrated in the soil, its transformation into tetra-carbonimid has been suggested.

According to Walters and Wise (1250), tetra-carbonimid is actually cyanuric acid. Its formation from uric acid was explained as follows:



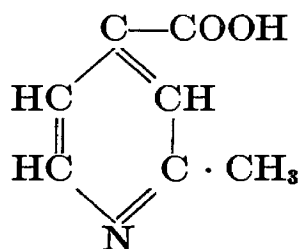
Cyanuric acid or its precursor is widely distributed in humus. A soil containing 0.0744 per cent total nitrogen was treated with 2 per cent sodium hydroxide solution; the extract contained 56 per cent of the total nitrogen. When the extract was acidified with sulfuric acid and filtered, 31 per cent of the nitrogen was left in the acid filtrate. On treatment with an acid solution of HgSO_4 , a precipitate was formed which contained 14 per cent of the nitrogen. The cyanuric acid accounted for 0.30 per cent of the total nitrogen of the soil.

6. *Pyrimidine derivatives.* Cytosine, or 2-oxy-6-amino-pyrimidine, $\text{C}_4\text{H}_5\text{ON}_3 \cdot \text{H}_2\text{O}$, was isolated from the soil by Schreiner and Shorey (978).



This compound has been demonstrated in several soils and was found to be a common constituent of humus.

7. *Pyridine derivatives.* Berthelot and André (104) were the first to establish the presence of a pyridine compound in the soil. In 1906, Shorey (1007) isolated from the soil a compound, α -picoline- γ -carboxylic acid, $\text{C}_7\text{H}_7\text{NO}_2$. It was later again isolated by Schreiner and Shorey (973). Its structural formula was given as



This compound may originate in humus as a result of the decomposition of proteins and the reduction of melanoids or "humins" substances, as shown by Samuely (938). When tryptophane is boiled with acids or with water it is changed to dark colored complexes, which may be other sources of this compound. Picoline-carboxylic acid was found in fairly large quantities in a number of soils. It is somewhat toxic to plants in nutrient solutions.

In addition to these compounds, a number of other organic nitrogenous complexes can be readily demonstrated to be present in humus. It is sufficient to mention such compounds as nucleic acids and chitin. The latter is synthesized in considerable quantities by soil-inhabiting insects and by fungi; it would ordinarily be found in the "humins" fraction of the humus. The presence of chitin in forest soils was first demonstrated by P. E. Müller (737). H. von Post (857) found that as much as 15 to 20 per cent of the dry weight of peat may consist of chitin. Höveler (464), however, could not find this compound in peat soils.

In summarizing the occurrence of nitrogenous compounds in the soil, Lathrop (609, 612, 613) stated that histidine, hypoxanthine, cytosine, xanthine, nucleic acid, creatinine, and cyanuric acid may be considered as compounds of common occurrence; arginine, lysine, adenine, choline, and trimethylamine occur infrequently. Although arginine is present in nearly every protein, it is more readily attacked by microorganisms, and therefore does not accumulate in humus; however, compounds like histidine, which contain an aromatic complex in their molecule, are attacked with difficulty.

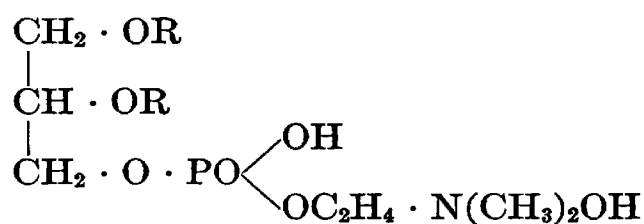
IX. ORGANIC PHOSPHORUS COMPOUNDS

Phosphorus compounds are added to soils in plant and animal residues. They are also synthesized in soils and in composts by microorganisms. An idea of their abundance may be derived from the fact that 50 per cent of the total ash of *Azotobacter* and other bacteria is composed of phosphoric acid. The organic phosphorus compounds of humus may be conveniently classified into three groups: 1. nucleoproteins, 2. phosphatides including lecithin, and 3. phytin, or the calcium-magnesium salt of inositol-phosphoric acid. The presence of phosphorus in soil humus was reported by early investigators (735, 955). Aso (58) demonstrated the presence of nuclein and lecithin in soil; Shorey (1010) isolated nucleic acid from humus and Bottomley isolated a similar compound from peat (137). The presence in humus

of choline, a decomposition product of lecithin, and of inositol, a decomposition product of phytin, has also been reported (61, 245, 358, 677a, 966). The abundance and chemical nature of humus influence considerably the availability of phosphates in the soil for plant nutrition (333a).

1. *Nucleic acid* was isolated from the acid filtrate of a dilute (1 per cent) sodium hydroxide extract of a number of soils; it differed considerably in chemical composition, according to the nature of the soil from which it was obtained. In addition to phosphoric acid, it gave a pentose, one or more of the purine bases, and a pyrimidine derivative. The presence of di-nucleotides in peat humus was demonstrated more recently (204). The fact that nucleic acids are prominent constituents of the cells of bacteria and fungi can thus be correlated with the extensive development in the soil of microbial cell substance, which makes up an important part of humus.

2. *Lecithin*, a compound analogous to glycerides, was first demonstrated in the soil by Aso (58), and later by Stoklasa (1096a).



X. ORGANIC SULFUR COMPOUNDS

Organic sulfur compounds are also contained in plant and animal residues; they are synthesized by microorganisms in soils and in composts. In the decomposition of proteins, the sulfur is first liberated as the amino acid cysteine; further decomposition leads to the formation of thiolactic acid, mercaptans, ethyl sulfide, and hydrogen sulfide, depending on the nature of the organisms concerned in the process and on the environmental conditions, especially oxidation-reduction potentials.

Sulfur is also contained in the essential oils, as thio-carbamides. The isolation of tri-thio-benzaldehyde from humus has already been mentioned.

XI. OTHER COMPOUNDS

The presence in certain types of humus of compounds having injurious or beneficial effects upon plant growth has been definitely estab-

lished (p. 351). Their nature is still incompletely known. Among them is the "peat disease" studied by Elema and Hudig in Holland. It is claimed to have been isolated (1050) by the following procedure: the soil was boiled with two to three volumes of 80 per cent alcohol under a reflux condenser, the extraction being repeated several times; the combined filtrates were distilled under reduced pressure. The first third of the distillate was treated with a few cubic centimeters of an aqueous solution of copper sulfate; a precipitate was formed, which was filtered off, washed with alcohol and water; the residue was suspended in alcohol and decomposed with hydrogen sulfide; the filtrate was then concentrated to a small volume and allowed to stand; the specific substance then crystallized out. The same compound was obtained from the Everglades peat in Florida; it is of interest to note that this type of peat responds well to additions of copper.

XII. ELEMENTARY CARBON

The presence of elementary carbon in humus has been demonstrated by a number of investigators (967, 1274, 904). It probably does not originate from microbial activities, but is a product of the ignition of organic matter. Although there are certain indications that carbon can be oxidized by microorganisms, the subject needs further study.

Summary. As opposed to the idea of the simple chemical nature of humus in soils, peats, and composts, a number of investigators have definitely established the fact that humus is highly complex in composition, and that a large number of chemical compounds can be separated from it. Schreiner and Shorey have isolated from the acid precipitate of the alkali extract of soils (the so-called "humic acid" fraction) various glycerides, resin acids, resin esters, certain sterols, lignoceric acid, and other compounds; from the acid filtrate (the so-called "crenic acid" and "fulvic acid" fractions) they obtained pentosans, amino acids, purine bases, and other substances. Some of these compounds are found in humus in a free state, while others are combined with inorganic bases, with acids, or with various organic substances in the form of esters; still others probably form a part of a large molecule or a complex; for their separation, the latter must first be broken down by proper chemical reagents.

Some of the compounds thus far isolated were no doubt originally present in the plant and animal residues added to the soil; some were formed as a result of decomposition of these residues by the numerous bacteria, fungi, protozoa, worms, and insects inhabiting the soil; some

were synthesized by the microorganisms, forming important constituents of their cell substance and becoming liberated during its decomposition. The fate of these various organic compounds in humus varies. Some are readily decomposed in the soil with the liberation of carbon dioxide and ammonia; some are more resistant to decomposition and persist for longer periods of time, being gradually transformed by microorganisms. Some of the compounds are beneficial to plant growth, whereas others are toxic to plants. Both will in course of time be further decomposed by the various soil inhabiting organisms or by atmospheric agencies, by processes of oxidation, reduction, hydrolysis, and condensation.

The chemical complexes so far shown to exist in humus represent only a fraction of the total organic constituents. With the development of suitable technique of isolation and separation, numerous other compounds will no doubt be obtained. This information is important not only for an understanding of the chemical composition of humus, but also for the elucidation of the processes of humus formation and transformation; these compounds, however, are not sufficient to characterize humus as a whole.

CHAPTER VII

CHEMICAL NATURE OF HUMUS AS A WHOLE

“Der Humus enthält dieselben Bestandtheile wie die Pflanzen- und Thierreste, aus welchen er entstanden ist, aber in einem zum Theil anderen Mengenverhältniss, je nach Grade und den äusseren Factoren der Zersetzung.”

—E. WOLLNY.

Humus represents a heterogeneous complex consisting of numerous compounds of plant, animal, and microbial origin, and of their decomposition and transformation products. Although numerous chemical compounds can be isolated from humus, the latter is characterized by certain general groups of constituents, which vary qualitatively and quantitatively, depending on the nature and origin of the humus. One is, therefore, justified in speaking of humus not as of a known chemical complex but as of a state of matter. Just as plant or animal substance can be subjected to chemical analysis and separated into several large groups of chemical compounds possessing similar properties, such as fats, carbohydrates, and proteins, so can humus also be divided into specific groups of complexes.

Most of the constituent groups of humus have their counterpart among the plant constituents but they vary considerably in chemical nature and in relative abundance. Some of these groups are better known chemically than others; in some instances there is still incomplete knowledge concerning the exact chemical nature and origin of some of the constituents of humus. Just as the carbohydrates are represented in some plants principally by cellulose and pentosans, in other plants by mannans or galactans, and in still other plants by cane sugar or starch, with other carbohydrates present in smaller amounts, the carbohydrate groups predominating in humus of different origin may not be alike in chemical composition, either qualitatively or quantitatively. Differences in the chemical nature of humus become especially apparent when one compares the humus of highmoor and lowmoor peats, of composts, of forest soils, and of mineral, field, and garden soils.

In view of the fact that humus originates from the decomposition of

plant, animal, and microbial residues, one may expect to find in it numerous organic complexes. The nature of these substances changes as decomposition progresses. This can be readily demonstrated in certain forest soils, of the so-called "raw-humus" or "acid humus" type, where a definite distinction has been established (432) between the layers of organic matter at different stages of decomposition. The humus present in these different layers, as in the true mineral horizons, varies considerably in physical and chemical characteristics. The transition from plant residues to humus is gradual but marked. The same is true of the transformation of plant residues in different types of peat. Even in the case of inorganic or mineral soils, one may be able to recognize various organized bodies, which can be classified (967), into: 1. plant residues, such as roots, leaves, twigs, branches; 2. insects, worms, and their products; 3. fungous mycelium and spores; 4. bacterial cells, protozoa, algae; 5. particles of coal, charcoal, lignite. Some of these materials no doubt represent partially decomposed residues.

For most practical purposes, a study of the chemical composition of humus can be limited to the broad groups of compounds which have their counterpart among the plant and animal constituents. In special cases, it may become essential to determine the presence or absence in humus of certain compounds which may be present in very small concentrations, as in the study of substances which are toxic or stimulating to development of plants.

Chemical groups of humus constituents. Significant amounts of the following four broad groups of substances are found in humus:

1. Fats, waxes, and resins, or substances soluble in ether, alcohol, benzol, chloroform, and similar solvents. Quantitatively this group contains the smallest portion of the humus constituents, although it includes, in addition to the aforementioned compounds, also sterols, higher alcohols, fatty acids, tannins, pigments, and similar substances.

2. Carbohydrates and related compounds. Here belong various polysaccharides, such as cellulose, pentosans, galactans, mannans, and polyuronides, both of plant and microbial origin; starches; sugars; and glucosides.

3. Proteins and their derivatives. This group includes the true proteins; the proteoses and peptones; amino acids; amines; various purine, pyridine, and pyrimidine bases; and a number of other organic nitrogenous complexes.

4. Lignins and their derivatives. This group comprises not only the

true lignin of higher plants, but also compounds that possess properties similar to this type of lignin, as in the case of the lignin-like complexes present in mosses, algae, and fungi; they are characterized by insolubility in concentrated acids (72–80 per cent sulfuric, 42 per cent hydrochloric), by solubility in alkali solution, by a ring structure, by rapid oxidation with various chemical agents, and by a varying methoxyl (OCH_3) content. Since the chemistry of lignin still presents many obscure problems, it is difficult to establish definitely the exact chemical relation of the dark colored humus constituents, which have some of the properties of lignin, with the corresponding lignins in plants. In the process of decomposition of plant residues, the lignins undergo marked modifications, including a loss of certain groups (methoxyl) and combination with proteins, as will be shown later. The lignin-like complexes in humus are also more readily soluble in alkalies and are darker in color; when lignin is oxidized, in alkali solution, it changes to dark colored substances. To what extent soil microorganisms play a part in these reactions and to what extent these are brought about by chemical agencies still remains to be determined. However, in spite of the accumulated knowledge of the rôle of lignin complexes in the formation of humus and their relation to those preparations formerly known as "humic acids," the presence in humus of a dark colored fraction, which is readily soluble in dilute ammonium hydroxide solution or is non-soluble in acetyl-bromide, is still believed by some (822, 373) to indicate the presence of "humic acid," "humin," or "pure humus." There is no doubt now that this complex originates in natural humus principally from the lignin constituents of the plant residues, by various biological and chemical modifications; this fraction may therefore be included in the lignin group.

There is definite evidence to indicate that the major part of these groups of substances does not exist in the humus in a free state, but occurs in various combinations in which the soil bases may enter. Some of these compounds are well-defined chemical entities, others are colloid chemical in nature (336, 385).

Certain inorganic elements, such as P, S, Fe, Ca, and Mg, form an essential part of the humus, probably to an extent even greater than in the case of plant, animal, or microbial substances. Since mineral soils have a predominance of inorganic matter, it is frequently difficult to distinguish between the inorganic constituents of the humus and the mineral part of the soil itself. Iron and ammonia, for example, may enter into combinations in which they are no longer detected by

chemical reagents. They may be available, however, as in the case of iron, for plant nutrition.

The relative quantitative distribution of these four groups of humus constituents in different types of humus, as compared with the distribution of similar complexes in undecomposed plant residues, is shown in tables 17, 18, and 19. Further and more detailed information bearing upon this subject, whereby different analytical procedures are employed, are reported later. A qualitative analysis of the various individual organic constituents of these groups of complexes would have brought out even more striking differences between the composition of plant residues and humus, on the one hand, and between different

TABLE 17

Chemical composition of several types of peat as compared with that of fresh plant materials (1940)

Per cent of dry material, ash-free basis

NATURE OF MATERIAL	ETHER-SOLUBLE SUBSTANCES	CARBOHYDRATES	PROTEINS	LIGNINS AND LIGNIN-LIKE COMPLEXES
<i>Cladium</i> , green plants.....	1.18	51.83	7.49	30.30
<i>Carex</i> , green plants.....	2.62	48.00	7.30	21.73
<i>Sphagnum</i> plants.....	1.52	53.56	6.06	7.18
Sound wood (Cypress).....	3.53	48.78	0.66	28.21
Lowmoor peat.....	1.22	9.94	20.80	55.92
Highmoor peat.....	4.02	36.69	6.67	38.83
Woody peat.....	3.32	8.36	14.73	62.61
Sedimentary peat.....	0.89	19.91	27.59	31.56

types of humus, on the other. This is particularly apparent in the results obtained with the humus of the different peats and of the different horizons of the forest soil profile. The humus formations of the mineral soils do not show at first glance any striking differences; however, as will be shown later, these vary not only in total humus content, as shown by the amounts of total carbon and nitrogen, but also in the nature of the humus, as shown by the distribution of the different fractions.

ETHER- AND ALCOHOL-SOLUBLE COMPLEXES IN HUMUS

Considerable information has accumulated concerning the abundance in humus of fats, waxes, resinous substances, and sterols; however, this

information still remains more or less uncoordinated. H. von Post (857) reported that a soil rich in organic matter contained 0.52 per cent of fats and waxes. According to Reinitzer (874), the ether extractives of a forest soil consist largely of waxy substances, since the ether-soluble fraction (0.184 per cent of soil) was made up of 84 per cent wax and of 16 per cent fat. The analysis of 24 mineral soils from Texas gave, on the average, 0.0203 per cent ether-soluble material and 0.0174 per cent chloroform (following the ether)-soluble substances (315). The ether-soluble fraction gave 50 per cent unsaponifiable matter and 40 per cent saponifiable, with a loss of 10 per cent, while the ether ex-

TABLE 18

*Chemical composition of the humus in the surface layer of forest soils (1243)**
Per cent of dry, ash-free material

NATURE OF FOREST	LAYER	ETHER-SOLUBLE SUBSTANCES	TOTAL HEMICEL- LULOSES	PENTOSAN	CELLULOSE	PROTEINS	LIGNIN-LIKE COMPLEXES
Hardwood spruce.....	F-layer	4.85	16.61	7.04	10.26	9.11	43.19
Hardwood spruce.....	H-layer	3.39	13.77	3.22	2.84	8.53	57.26
Mixed conifers.....	F-layer	5.66	17.79	8.37	8.72	41.72
Mixed conifers.....	H-layer	4.60	20.31	4.36	8.19	43.36
Spruce with hypnum.....	F-layer	3.81	19.23	4.99	10.57	7.28	44.96
Spruce with hypnum.....	H-layer	4.43	19.01	3.90	6.20	5.78	50.42

* The ash content of these humus formations was 9.20, 11.61, 7.94, 13.67, 6.05, 10.57 per cent, reading from top to bottom.

tract of fresh plant material usually contains a higher concentration of the first and a lower of the second constituent. The fatty acids present in the humus had a neutralization number of 177 for all of the 24 soils. This number can be compared with that of 167.9 for erucic acid, 177.6 for di-hydroxy-stearic acid, 179.8 for archidic acid, 198.9 for oleic acid, and 197.5 for stearic acid. The chloroform extract of the soil humus gave more of the unsaponified and less of the saponified material than a corresponding extract of grasses, the difference being small, however.

The humus of a series of brown and black prairie soils was reported (1241) to contain, on an average, 0.46 to 4.71 per cent ether-soluble and 0.58 to 1.53 of alcohol-soluble material. It is to be recalled that

Schreiner and Shorey isolated from these fractions a number of hydrocarbons, glycerides, sterols, fatty acids, resin acids, and esters.

A detailed study of the relative abundance and chemical nature of this group of humus constituents has been made for various types of peat and coal. The nature of the peat, as influenced by the plant material which gave origin to it, by its age, by preliminary treatment, and by conditions of extraction, has a considerable influence upon the nature and abundance of this group of complexes frequently spoken of as "bitumen." Lowmoor peat is usually found to contain the lowest amount, while highmoor peat is much richer in these complexes. As much as 9.46 to 17.21 per cent of dry highmoor peat was found in the

TABLE 19
Chemical nature of humus in different mineral soils (1223)

NATURE OF SOIL	HORIZON OR DEPTH	REACTION	TOTAL HUMUS (C X 1.724)	NITROGEN IN HUMUS	CHEMICAL COMPOSITION OF HUMUS				
					Ether-and alcohol soluble substances	Water-soluble	Carbohydrates	Proteins	Lignin-like complexes
					per cent	per cent	per cent	per cent	per cent
Michigan podsol.....	A ₁	4.6	41.6	2.57	3.29	4.00	16.54	16.08	55.62
	A ₂	5.1	1.1	4.73	4.58	6.36	10.28	27.82	46.32
Chernozem, Mannitoba.....	A	...	7.4	5.34	1.30	11.37	33.36	42.83
Chernozem, Texas.....	A	6.9	2.29	5.68	2.03	2.36	13.88	35.50	35.81
Chestnut soil.....	0-15	6.8	1.93	5.23	3.14	2.58	11.97	32.70	39.95
Serozem, Arizona.....	0-15	7.2	0.28	8.03	7.63	3.50	4.34	50.22	34.76

ether- and benzol-alcohol-soluble fractions. Pollen peat was reported (712) to contain nearly one-third of the total organic matter in the form of this group of complexes. The abundance of the ether-extractable material in peat was found to increase with the age of the peat, since the bitumens are highly resistant to decomposition under conditions prevailing in the peat bog (957).

A Florida saw-grass peat profile was shown (289) to contain 2.32 to 3.02 per cent of the ether- and alcohol-soluble substances, whereas a heath peat from North Carolina contained 9.09 to 16.44 per cent of these complexes. In most of the analyses reported in the foregoing, the treatment of the peat with ether and alcohol precedes any treatment with acid. If, however, after extraction with the aforementioned

reagents, the peat was treated with hot dilute hydrochloric acid (2–4 per cent) and then with ether and alcohol, a further yield of these complexes was obtained, namely, 2.46–3.26 per cent for the Florida peat and 2.89 to 19.70 for the North Carolina peat. When the peat is first extracted with ether, only the free fats and fatty acids go into solution; the treatment with hot mineral acid liberates the combined fats and fatty acids, which make up the second yield.

The temperature at which the peat is extracted also has a marked influence upon the yield (957). The bituminous substances extracted from peat and coal at ordinary temperatures in Soxhlets do not contain any oil; the extracts made under pressure, however, contain oil, the yield of which increases with temperature. This points to decomposition processes which take place under these conditions.

Stadnikoff (1083) reported that as much as 22 per cent bituminous substances can be extracted from certain sphagnum peats by means of benzol-alcohol; this yield was increased, by treatment of the peat with 10 per cent hydrochloric acid, to 27 per cent. This process was recommended for the preparation of Montan wax and resins. The peat bitumen consists of a mixture of free acids, their corresponding esters, and possibly anhydrides of saturated and unsaturated compounds. The presence of Montan wax in forest peat has also been demonstrated (1153). It is to be recalled, in this connection, that the use of pressure or preliminary treatment with hot acid results in an alcohol extract of a part of the humus fraction, referred to previously as "hymatomelanic acid."

The nature and abundance of fatty and waxy substances in humus of forest soils depends upon the type of forest vegetation, upon the extent of its decomposition, and upon the soil conditions, especially aeration and reaction. In the decomposition of 200 gm. of dry oak leaves under aerobic conditions (1243), the ether-soluble substances diminished from 9.50 gm., at the beginning of the experiment, to 2.64 gm. after 6 months and to 0.87 gm. after 12 months, whereas under anaerobic conditions the reduction was only to 7.04 and 4.09 gm. respectively. The influence of vegetation and of extent of decomposition are further brought out in table 18.

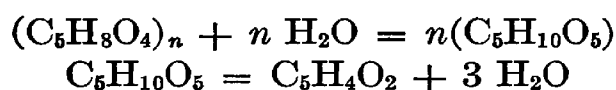
CARBOHYDRATES

The carbohydrates form quantitatively by far the major group of plant constituents. Among the carbohydrates, cellulose occupies the leading place, followed by pentosans and other polysaccharides, as

well as polyuronides, the latter being especially abundant in mosses and in algal residues. The distribution of carbohydrates in humus, however, is totally different. Here, cellulose may either be entirely lacking or present only in very limited amounts; on the other hand, pentosans and other hemicelluloses, especially polyuronides are rather abundant. This is due largely to the fact that, in the case of the great majority of plant residues, the true cellulose is decomposed rapidly and more or less completely by a great variety of microorganisms, whereas some of the hemicelluloses, especially certain galactans and polyuronides, are more resistant to decomposition. Further, as a result of continuous synthesis of new microbial cell substance, in the process of humus formation, considerable amounts of hemicellulose are produced, in the form of the so-called microbial gums and slimes. In the case of humus which is still rich in partially decomposed plant residues, such as the F and H layers of the raw-humus forest soil profile and highmoor peats, considerable quantities of true cellulose may still be present.

Most of the available information on the abundance of carbohydrates in humus are limited to determinations of pentosans, based upon the furfural yield from soils or composts upon being boiled with 12 per cent hydrochloric acid. In view of the fact that other substances, especially the polyuronides, also give considerable amounts of furfural by this method of determination, it is doubtful whether the results commonly reported represent true pentosans. One is more justified in speaking of "furfural-yielding" substances, unless the presence of true pentosans is actually demonstrated by the detection of pentose sugar formed as a result of the acid hydrolysis. Some of the pentoses may also be derived from the nucleic acids present in humus.

Pentosans. The quantitative determination of pentosan in humus is usually based upon its hydrolysis to pentose, and the subsequent transformation of the latter to furfuraldehyde, on boiling with 12 per cent hydrochloric acid:



De Chalmot was among the first to show (174) that certain pentosans persist in soil humus, and may frequently be found there in appreciable quantities. The pentosan carbon was found (1015) to make up as much as 1.3 to 28.5 per cent of the total carbon content of humus. The average pentosan content of the soil was reported (313) to increase with an increase in the nitrogen compounds, the ratio between these

two groups of humus constituents being nearly constant, namely, about 0.75 to 1. The surface soils contained more pentosan than the subsoils and had a somewhat wider pentosan-nitrogen ratio (0.77:1 against 0.70:1). It was found that different pentosans are not decomposed at the same rate in soil. When soil was boiled with dilute mineral acid, such as 1.28 per cent sulfuric, and the sugar determined in the filtrate, the pentose obtained was equivalent to only 60 per cent of the total pentosan in the humus, as calculated from the results of furfural distillation method; this emphasizes further the need for precaution in interpreting the "pentosan" content of humus.

TABLE 20

Chemical composition of humus in decomposed wood, in peat and in soil (706)

Per cent of dry material

MATERIAL	ASH CONTENT	TOTAL NITROGEN	TOTAL CARBON	PENTOSAN	METHYL PENTOSAN	METHOXYL CONTENT	IN PER CENT OF TOTAL CARBON IN HUMUS	
							Pentosan	Methoxyl
Decomposed oak wood.....	4.89	1.66	48.31	4.22	2.40	2.96	8.73	6.13
Decomposed pine wood.....	1.38	0.49	52.19	3.42	3.61	3.49	6.55	6.69
Peat from Modium.....	4.44	2.93	58.14	7.49	1.45	1.33	12.88	2.29
Peat soil from Sandefjord.....	86.20	0.55	6.09	0.45	0.23	0.04	7.39	0.66
Peat soil from Larvick.....	85.13	0.59	6.69	0.54	0.23	0.04	8.07	0.59
Peat soil from Aas.....	90.21	0.39	4.88	0.36	0.17	0.06	7.38	1.23
Soil from Aas.....	81.53	0.74	9.21	0.70	0.32	0.12	7.60	1.30
Soil from Telemark.....	90.72	0.32	5.60	0.10	0.16	0.04	1.79	0.71
Soil from Lauchstädt.....	94.99	0.15	1.94	0.09	0.12	0.03	4.64	1.55
Chernozem soil.....	84.37	0.53	6.11	0.36	0.23	0.05	5.89	0.82

Michelet and Sebelien (706) reported (table 20) that from 1.79 to 7.60 per cent of the total carbon of humus in mineral soils is pentosan carbon; in the case of humus in peat and peat soils, from 7.38 to 12.88 per cent of the total carbon is present in pentosan. Various soils and peats also contain appreciable amounts of methyl pentosan, which may exceed in some cases the content of pentosan. A large portion of the total pentosans which reach the soil in stable manures and in plant residues is rapidly decomposed; however, the soil humus may still contain appreciable amounts of this carbohydrate. The percentage of the total humus carbon recovered as pentosan carbon in experiments

by Balks (64) was 8.24 to 11.63. The amount of methyl pentosan in the soil remained more or less constant; the concentration of this complex in humus is not influenced to any great extent by the addition of organic matter in the form of stable manure to soils, as brought out in figure 7.

Pentosans are particularly abundant in peat. This was first demonstrated by von Feilitzen and Tollens (285). A definite parallelism was shown to exist between the reduction in amount of the pentosan and the composition of the peat; it was suggested, therefore, that the pentosan content of peat be used as an index of the degree of its decomposition. This assumption was not fully justified, as shown later by Gorbenko (352). Keppeler (537) treated peat with 72 per cent sulfuric acid, in the cold, thus hydrolyzing all the hemicelluloses and cellulose;

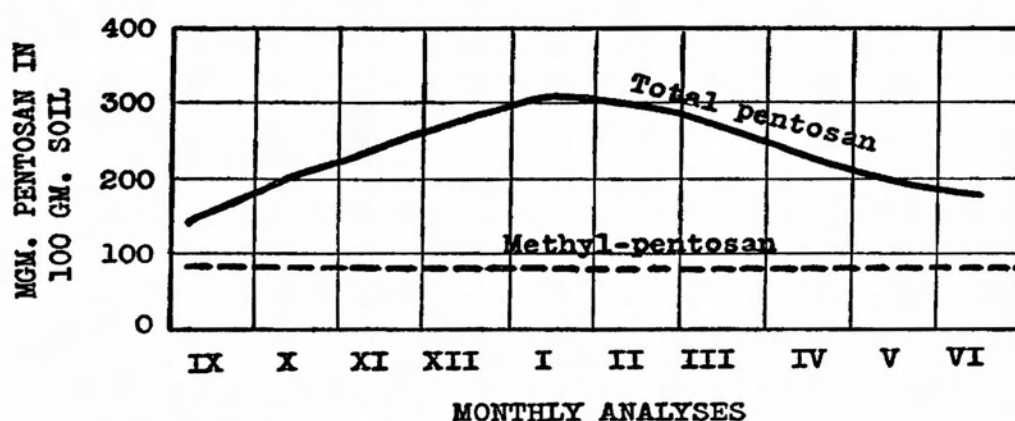


FIG. 7. Pentosan and methyl pentosan transformation in the soil, as a result of decomposition of organic residues (Balks).

the hydrolyzate was analyzed for total reducing sugar and for pentose sugar. The pentosan content of the peat was found to diminish with increase in the degree of decomposition (table 21); this decrease was even more rapid than that of the hexosans, including the true cellulose and hexosan hemicelluloses. In proceeding from the younger to the older sphagnum formations of a typical highmoor peat, a pronounced difference is observed in the pentosan content. The specific nature of the carbohydrates in the sphagnum plant and the characteristics of the environment in the highmoor peat profile determine the rates of disappearance of the pentosans and the other carbohydrates in this type of peat.

Although the pentosans are known to make up the major fraction of the hemicellulose group in most of the plant residues, especially in

cereal plants and grasses, they comprise only a small fraction of the hemicelluloses in the humus of mineral soils and peats. A lowmoor peat, practically free from cellulose, was shown (1240) to contain 11.03 per cent total hemicellulose, as determined by the formation of reducing sugar on hydrolysis with hot dilute mineral acid; of this only 2.52 per cent was pentosan. A highmoor peat, containing 12.35 per cent cellulose and 15.76 per cent hemicellulose, had only 3.60 per cent pentosan.

The pentosan content of the humus in a forest soil profile was found to vary with forest type and profile layer (table 22). In the case of a hardwood-spruce forest the pentosans made up 42 per cent of the total hemicellulose in the F layer and 23 per cent in the H layer; in

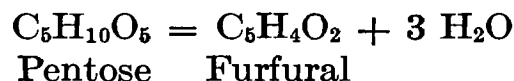
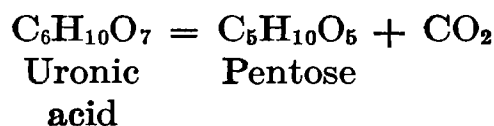
TABLE 21

Pentosan content and degree of decomposition of organic matter in a peat profile (538)

DEPTH OF PEAT	PENTOSAN	HEXOSAN	$\frac{\text{PENTOSAN}}{\text{HEXOSAN}}$	DEGREE OF DECOMPOSITION
<i>cm.</i>	<i>per cent</i>	<i>per cent</i>		
0-10	12.4	37.5	1:3.0	17.4
10-30	14.0	38.8	1:2.8	13.2
30-55	12.4	36.9	1:3.0	17.9
80-100	12.3	36.4	1:3.0	20.0
130-160	5.7	20.0	1:3.5	57.8
160-190	5.3	18.0	1:3.4	61.8
190-220	4.3	16.0	1:3.7	66.6
220-250	3.2	16.5	1:5.1	67.6
250-280	3.2	13.1	1:4.0	73.2
280-310	2.8	10.4	1:3.8	78.2
310-340	2.7	12.4	1:4.6	73.5

the case of a spruce forest with undergrowth of hypnum moss the corresponding concentrations were 26 and 21 per cent. Here, as well, the proportion of the pentosan to the other hemicelluloses is narrower in the more decomposed layers. These results are due either to the fact that the pentosan disappears more rapidly than the other hemicelluloses or, more probably, to the fact that the furfuraldehyde obtained on treating humus with 12 per cent hydrochloric acid is not derived entirely from pentosan and may come from totally different humus constituents. Although the pentosans may actually diminish more rapidly than the other hemicelluloses during the decomposition of the plant residues, certain new hemicelluloses become synthesized by the microorganisms.

Uronic acid complexes. The uronic acids, of the general formula $C_6H_{10}O_7$, are not found to any large extent in a free state in any of the plant and animal residues added to the soils or to composts; they are, however, abundantly distributed in these residues, in the form of complex molecules, usually designated as "polyuronides." These either form polymers of a single uronic acid or more commonly of uronic acids with hexose or pentose sugars or both. They are found among the plant products in the form of pectins, gums, and mucilages; they are especially abundant in the microbial gums and slimes. Their presence in humus is due to their introduction in plant residues and to their extensive synthesis by microorganisms. The uronic acids in these polyuronides consist chiefly of glucuronic, galacturonic, and mannuronic acids. On boiling a uronic acid with HCl, furfural is liberated, after the molecule passes through the pentose stage, as shown by the following reactions:



Shorey and Martin (1017) found that the carbon dioxide produced from the uronic acid complexes in humus varied from 0.07 to 0.41 per cent in the case of mineral soils, and from 1.69 to 1.80 per cent in the case of peats. On the basis of 37 per cent total carbon in the uronic acid molecule, the relative concentration (per cent) of uronic acid carbon to the total organic carbon in the humus may be calculated to be 12.8 to 28.4 in the mineral soils, and 5.15 to 9.25 in the peats. The quantitative determination of uronic acid in these analyses was carried out by treating 25 gm. of soil or 10 gm. of peat with 200 cc. of a 1 per cent HCl solution, heating the flask to boiling and keeping it at that temperature for 1 hour in a current of air freed from CO_2 , then removing the CO_2 by absorption in barium hydroxide solution; this CO_2 was assumed to be derived from carbonates. Enough HCl was then added to make the solution 12 per cent HCl, the flask was placed on an oil bath and heated, at 140° – $145^\circ C.$, for 5 hours, and the CO_2 was absorbed in fresh barium hydroxide solution. This CO_2 is liberated from the uronic acid groups, according to the foregoing reaction. The furfural yield is not quantitative, however, because of the incomplete decarboxy-

lation of the uronic acids. The relation between the furfural yield and the theoretical amount calculated from the uronic acid content of peat was found to be 49 to 57.5 per cent. These experiments emphasized the fact that what has been formerly considered as pentosan in soil may consist largely of uronic acid complexes, existing in humus in combination with other compounds and not in a free state.

TABLE 22

Relation of uronic acids to total hemicelluloses in fresh plant materials, in composts, in peats and in soil (1236)

Per cent of dry material

NATURE OF MATERIAL	CONDITION	ASH CONTENT	HYDROLYSIS WITH HOT DILUTE ACID		PENTOSAN IN TOTAL MATERIAL	URONIC ACID ANHYDRIDE
			Total hemicellulose (sugar × 0.9)	Pentose sugar		
Oak leaves.....	Fresh	5.1	20.1	11.8	11.7	11.5
	Decomposed 3 years	16.5	10.9	5.5	7.1	12.3
Rye straw.....	Fresh	4.2	25.0	22.3	28.5	4.6
	Decomposed 3 years (nutrients added)	17.9	14.0	9.2	10.5	4.6
Lowmoor peat.....	Florida, Everglades	6.9	9.2	5.1	6.6	9.7
Highmoor peat.....	Orono, Maine	2.3	26.6	9.7	11.9	15.6
Pine forest soil.....	Needles	2.7	20.9	8.5	6.4
	Litter*	4.0	20.7	9.8	7.0
	F-layer*	13.0	15.8	7.6	7.7
	H-layer*	19.0	13.5	5.7	7.6
	A ₁ horizon*	75.0	11.8	4.5	9.2
	B ₁ horizon*	91.2	9.1	2.3	32.4
Manured soil.....	Unlimed*	10.4	8.4	19.2
Unmanured soil.....	Unlimed*	5.8	4.6	31.7
Manured soil.....	Limed*	7.7	5.3	12.9
Unmanured soil.....	Limed*	5.3	4.1	20.0

* Calculated on ash-free basis.

The results presented in table 22 show that with the decomposition of plant materials a progressive diminution in the pentosan content and a relative increase in uronic acid complexes occur. The nature of the soil, fertilization, and treatment have an influence upon the uronic acid content of humus. This is brought out in a striking manner in the case of the pine forest profile; with the advance of decomposition,

the humus gradually becomes enriched in uronic acid complexes. Liming of soil, both manured and unmanured, results in a marked reduction in its uronic acid content.

Hexosans. In addition to the pentosans and uronic acid complexes, humus of soils, peats, and composts also contains hexosans which are usually classified with the hemicelluloses. The hexosans are quite distinct from cellulose since they are more readily hydrolyzed with dilute acids and upon hydrolysis give sugars other than glucose, such as mannose, galactose, and levulose. Glucose may also be formed as a hydrolytic product, as in the case of the dextrans or glucans found in the mycelium of fungi. The hexosans in humus are derived partly from plant residues and are partly synthesized by microorganisms. It is doubtful whether they exist to any large extent in humus in a free state; they are probably combined there with other complexes, such as uronic acids, to give more complex hemicelluloses.

On hydrolysis of highmoor peat with dilute acids (1 per cent sulfuric for 1.5 hours at 130–135°C.), von Feilitzen and Tollens (285) obtained the following sugars: mannose, galactose, levulose, and pentose, which corresponded to the hemicelluloses mannan, galactan, levulan, and pentosan or polyuronide. Information concerning the occurrence of hexosans in humus of forest soils, as well as in field and garden soils, is very limited; there is no doubt that they occur there, because of the fact that the plant residues, especially the products of certain trees and lower forms of life, such as mosses and algae, are rich in these carbohydrates. Hexosans occur in marine humus as a result of their abundance in the cells of marine algae; such material offers large stores of natural material for further investigation of the hexosans.

Cellulose. The presence of cellulose in peat was first demonstrated by von Feilitzen and Tollens (285). Its relative concentration was found to diminish with depth of peat and with the extent of its decomposition. The sphagnum plants of a highmoor peat contained 21.11 per cent cellulose; the peat produced from this sphagnum contained, at a depth of 20–100 cm., 15.20 per cent cellulose and, at 100–200 cm. depth, only 6.87 per cent. This points to a marked reduction of the cellulose content in humus with the advance of decomposition.

A number of different methods have been employed, since this early work, for measuring the cellulose content of humus in peats, soils, and composts. Oden and Lindberg (784) treated peat with ether, sulfurous acid, and ammonia, under pressure, then extracted the cellulose from the residue by means of Schweizer's reagent. Marcusson (677) fol-

lowed the ether and benzol-alcohol treatment by 1 per cent sodium hydroxide solution, then with chlorine and sodium sulfite, according to the method of Cross and Bevan; the cellulose content and the pentosan content of the residue were then determined. Peat was thus shown to contain 6–13 per cent pentosan and 7–15 per cent cellulose.

According to Hess and Komarewsky (427), the cellulose measured by these procedures cannot be considered as true cellulose. They extracted air-dry highmoor peat with ether and with benzol-alcohol, the first reagent removing 6 per cent and the second 10 per cent of the total peat. The residue was then treated with 1 per cent sodium hydroxide solution and shaken, the alkali being renewed at various intervals, until the solution was no longer colored; this reagent removed 49 per cent of the peat. The residue was now treated eight successive times with chlorine dioxide followed by 2 per cent sodium hydroxide solution, to remove the coloring substances and the lignin (953); this resulted in a loss of another 23 per cent of the constituents of the peat. The residue still contained some ash and represented impure cellulose; it was dissolved in ammoniacal copper solution, and the cellulose was precipitated with a dilute alcoholic solution of acetic acid; the precipitate was washed with dilute acetic acid, alcohol, and ether. The preparation thus obtained proved to be pure cellulose. It made up 10 per cent of the total air-dry peat.

Komarewsky (560) also established that the cellulose content of peat diminishes with depth. He believed that the amount of cellulose found in peat can be taken as an index of the degree of decomposition of the peat. This method is as inapplicable as a similar method previously proposed by Keppeler (538). The nature of the peat influences its cellulose content as much as does its age or the extent of its decomposition; lowmoor and sedimentary peats contain no cellulose or only traces of it, whereas highmoor peats contain large quantities of cellulose. On removing the hemicelluloses first, by prolonged boiling with dilute mineral acid, then treating the washed and dried residue with 72 or 80 per cent sulfuric acid in the cold, the cellulose will be hydrolyzed to glucose. The amount of glucose thus obtained may be considered as a fairly accurate index of the cellulose content of peat. Even if this procedure does not yield pure cellulose, the method is satisfactory for practical quantitative purposes (289, 318).

The humus of forest soils, especially the upper layers, which are in an active stage of decomposition, contains considerable quantities of cellulose, as shown in table 18. The F layer, which is just below the

litter, is found to contain 8.37 to 10.57 per cent of cellulose; however, the H layer, in which the structure of the original plant constituents can no longer be recognized, contains only small amounts of cellulose, ranging from 2.84 to 6.20 per cent of the total humus.

As to the presence of cellulose in humus of mineral soils, it is sufficient to refer to the results of Pichard (822a), who found (table 26) that manured as well as unmanured soils, with a total carbon content of 2.55 to 4.79 per cent, contained 7.08 to 8.40 per cent cellulose, on the basis of the total humus. The manuring of the soil was found to exert little influence upon its cellulose content. The pentosan content, however, was markedly affected by the manure treatment, the respective content of pentosan in the humus of the unmanured and manured soils being 3.32 and 13.07 per cent.

NITROGENOUS SOIL CONSTITUENTS

The nitrogenous complexes of soils and peats are predominantly organic in nature. The inorganic or mineralized forms of nitrogen make up only a fraction of a per cent to 2 or 3 per cent of the total; a part of this nitrogen is usually present in the form of nitrate and a part as ammonia. Since the total nitrogen in most forms of humus is about 5.0 to 5.5 per cent [2.54 to 6.43, according to Eggertz (253)], the nitrogenous complexes, calculated as protein, make up about one-third of the total humus in ordinary field and garden soils, as shown in table 19. In the case of peats, the protein content of the humus may be as low as 6 per cent for highmoors, and as high as 28 per cent for sedimentary peats. In forest soils, the protein content increases with an increase in the degree of decomposition. In composts of stable manure, the ammonia nitrogen may be very high at the early stages of decomposition; it gradually diminishes with the advance of decomposition and is transformed into organic compounds, through the synthesizing activities of the microorganisms, which are active in the decomposition processes.

The nitrogenous constituents of humus give, on hydrolysis, amino acids and acid amides. Hot hydrochloric acid will extract as much as 75 per cent of the total nitrogen in the humus; boiling water usually removes only 3 to 10 per cent of the nitrogen. "Humic acid" or α -humus preparations from soils and from lowmoor and sedimentary peats, obtained by precipitation of the alkali extract with a mineral acid, are usually found to contain 2 to 4 per cent total nitrogen.

The products of hydrolysis of the organic nitrogenous complexes

in humus can be conveniently divided into four groups: 1. amide nitrogen, 2. basic or di-amino nitrogen, 3. mono-amino nitrogen, and 4. "humin" nitrogen.

The amide nitrogen is measured by the amount of ammonia formed during the acid hydrolysis of humus. It is possible that some of the ammonia is liberated from other unknown constituents of the humus by the magnesium oxide used in determining the ammonia. The di-amino nitrogen is measured from the precipitate obtained from the acid hydrolyzate of the humus with phosphotungstic acid; this fraction includes arginine, histidine, lysine, and cystine, in addition to some unidentified nitrogenous bases which are also precipitated by this reagent. The mono-amino nitrogen is commonly determined by the Van Slyke method, which involves the measurement of the volume of nitrogen gas liberated on diazotizing the hydrolyzate with sodium nitrite; according to Shorey (1014), the only certainty that exists, in the case of humus, is that this fraction contains amino compounds which lose nitrogen on diazotization at room temperature. When the acid hydrolyzate of humus is made alkaline with magnesium or calcium oxide, a precipitate is formed, the nitrogen fraction of which is designated "humin nitrogen." This nitrogen may be partly a secondary product, which results from the polymerization or condensation of some of the primary products of hydrolysis. The pentose-yielding constituent of humus liberates furfural when heated with acid; this furfural then reacts with certain amino compounds to give condensation products. Frequently that part of the nitrogen which is left in the humus unhydrolyzed by acid is also included in the "humin nitrogen" fraction, largely on account of the fact that the early designation of "humin" was attached to the most resistant part of humus. This term has thus played its part in the confusing nomenclature of humus compounds. Kossel (575) applied the term "melanoidinic acid" to the mixture of dark colored substances formed on treatment of proteins with mineral acids. In some cases the "black insoluble humin" formed during protein hydrolysis from the tryptophane group was differentiated (356) from the "soluble humin" derived from tyrosine in the presence of formaldehyde. As much as 3.95 per cent "humin nitrogen" was found in blood meal and 15.79 per cent in alfalfa hay (369).

The total amount of humus nitrogen made soluble by hydrolysis with mineral acids and the nature of the hydrolytic products are influenced by the nature and concentration of the acid, by the temperature at which hydrolysis takes place, and by the time of hydrolysis. Ac-

According to Dojarenko (227), 21 to 71 per cent of the nitrogen in humus is present in the form of amino compounds, 5 to 20 per cent as amides, and about 2 per cent as ammonia; the total nitrogen content of humus ranged from 2.6 to 4.6 per cent. Shorey (1007) reported that 78 per cent of the total nitrogen in soil humus can be brought into solution by treatment with a mineral acid; more than half of this nitrogen was in the form of "humin" nitrogen, and the remainder occurred as ammonia, di-amino acid, and mono-amino acid nitrogen. Jodidi (499) heated a lowmoor peat with 25 per cent sulfuric acid solution and measured, at frequent intervals, the relative amounts of total and amino nitrogen, as determined by the Van Slyke method, brought into solution. Continued heating not only increased the amount of nitrogen brought into solution but it also resulted in the further hydrolysis of the dissolved nitrogen compounds. The relative concentrations of the various forms of nitrogen in solution were as follows:

	<i>per cent</i>
Ammonia.....	1.22- 1.97
Nitrate.....	0.07- 1.46
Acid amides.....	25.23-33.03
Di-amino acids.....	11.61-13.00
Mono-amino acids.....	22.20-55.66

Soils receiving organic fertilizers were found to contain the largest amounts of amide nitrogen. A soil treated with a 2 per cent sodium hydroxide solution gave only 49 to 68 per cent of its total nitrogen in the form of amino acids, as determined by Sørensen's procedure (175). Composting of peat usually results in a decrease in its amide and di-amino nitrogen and in an increase in the water-soluble forms of nitrogen.

In general it was found that only 65 to 75 per cent of the total nitrogen in the humus can be brought into solution by repeated and prolonged treatment with concentrated acids. Shmook (1006) found that 21.2-25.5 per cent of this nitrogen was in the form of amide, 13.02-14.72 per cent as di-amino, and 60.6-65.0 as mono-amino nitrogen. The arginine and lysine accounted for 82.5 per cent of the total di-amino nitrogen, while the mono-amino acids accounted for 86 per cent of the total mono-amino nitrogen. Different soils behaved differently, a lateritic soil giving a much larger amount of "humin" nitrogen of non-protein origin. "Humic acid" isolated from soil by extraction with a dilute alkali solution and precipitation with an acid, contained 60.22 per cent carbon, 3.20 per cent nitrogen, and 2.62 per cent ash.

About 45 per cent of the nitrogen in the preparation was hydrolyzed with hydrochloric acid; the nitrogen in the hydrolyzed fraction consisted of 25.35 per cent amide, 9.86 per cent di-amino acid, and 64.79 per cent mono-amino acid compounds.

The organic nitrogen in the humus of some Hawaiian soils yielded, upon hydrolysis with strong hydrochloric acid (536), 23.91 per cent amide, 9.98 per cent di-amino, and 64.57 per cent mono-amino nitrogen. Similar results were reported by other investigators (844, 728), as shown in table 23; the term "humin" is used here to designate that part of the nitrogen which remains in the residual material after acid hydrolysis.

TABLE 23
Nitrogen distribution in the organic matter of peat (728)
Per cent of total nitrogen

FRACTION	SPHAGNUM PEAT	SPHAGNUM PEAT AND SUBSOIL	CALCARE- OUS BLACK PEAT	"MUCK"
Ammonia N*.....	23.27	25.52	19.26	19.49
Total basic N.....	9.73	10.98	10.60	13.55
Basic amino N.....	5.26	7.29	6.35	9.13
Non amino basic N.....	4.47	3.69	4.25	4.42
Total non-basic N.....	43.00	38.96	42.40	38.81
Non basic amino N.....	40.45	33.82	39.46	33.82
Non amino non basic N.....	2.55	5.14	2.94	4.99
Total humin N.....	26.38	26.96	26.07	27.61

* Derived from the amides.

Remezov (876) found that the use of 5 per cent hydrochloric acid and a temperature of 200°C. in an autoclave, gives more uniform results. The nitrogen in the humus was thus separated into three groups: 1. water-soluble organic compounds, 2. acid hydrolyzable, and 3. acid non-hydrolyzable. The first group comprises 4 to 30 per cent of the total nitrogen; it depends upon the total organic nitrogen in the soil and upon the exchangeable cations; the higher the nitrogen content of the soil and the greater the relative abundance of mono-valent cations over the divalent, the greater is the percentage of water-soluble forms; this is the most readily decomposable fraction. The second is characteristic for different soil types, the amide form of nitrogen predominating in the gray and podsol soils, but not in the chernozems and peat soils; some of the chernozems are characterized by a high

mono-amino and a low di-amino acid content. The third form of nitrogen represents the oldest part of the organic matter and does not show any correlation with soil type.

The nitrogen distribution in different forms of humus is thus found to be rather uniform. This is a phenomenon characteristic of humus, in which the nitrogenous complexes are quite different from those of plant and animal proteins. The percentage of acid amide and humin nitrogen is much larger in the humus proteins, and the amount of di-amino and mono-amino nitrogen is smaller than in the common proteins (900). When protein-rich material is added to soil, the various nitrogenous constituents are not decomposed at the same rate; some are reduced rapidly while others accumulate, as shown in table 24.

TABLE 24

Rate of decomposition of the various nitrogen constituents in dried blood added to soil (612)

Per cent of total hydrolyzable portion of residual material

FORM OF NITROGEN	TIME OF INCUBATION, DAYS					
	0	18	44	86	148	240
Amide.....	7.01	9.56	14.84	22.56	19.47	19.25
Melanin.....	4.77	6.38	10.77	9.45	7.66	10.91
Arginine.....	7.60	6.48	7.49	7.18	7.57	8.33
Histidine.....	13.37	16.28	13.66	12.10	13.42	12.01
Lysine.....	10.09	9.55	2.71	1.78	2.98	5.81
Mono-amino acid.....	58.22	50.81	45.85	37.26	44.75	42.92
Non-amino.....	0.31	1.41	4.13	9.10	4.16	1.77

When dried blood was added (611) to the soil, there was a loss of 83.26 per cent of the total hydrolyzable nitrogen in 240 days, 76 per cent having disappeared in 86 days. Of the mono-amino acid nitrogen, 89 per cent disappeared during the longer period. The lysine was destroyed to the extent of 96 per cent within 86 days, but later increased somewhat; 83 per cent of the histidine nitrogen disappeared in 240 days; the arginine at first decreased more rapidly than the total hydrolyzable nitrogen, but later increased. The amide nitrogen diminished only slowly, so that at the end of the decomposition period, there was a considerably greater concentration of this form of nitrogen than at the beginning. The mono-amino acids underwent the greatest amount of decomposition.

Shorey classified the nitrogenous constituents of humus on the basis

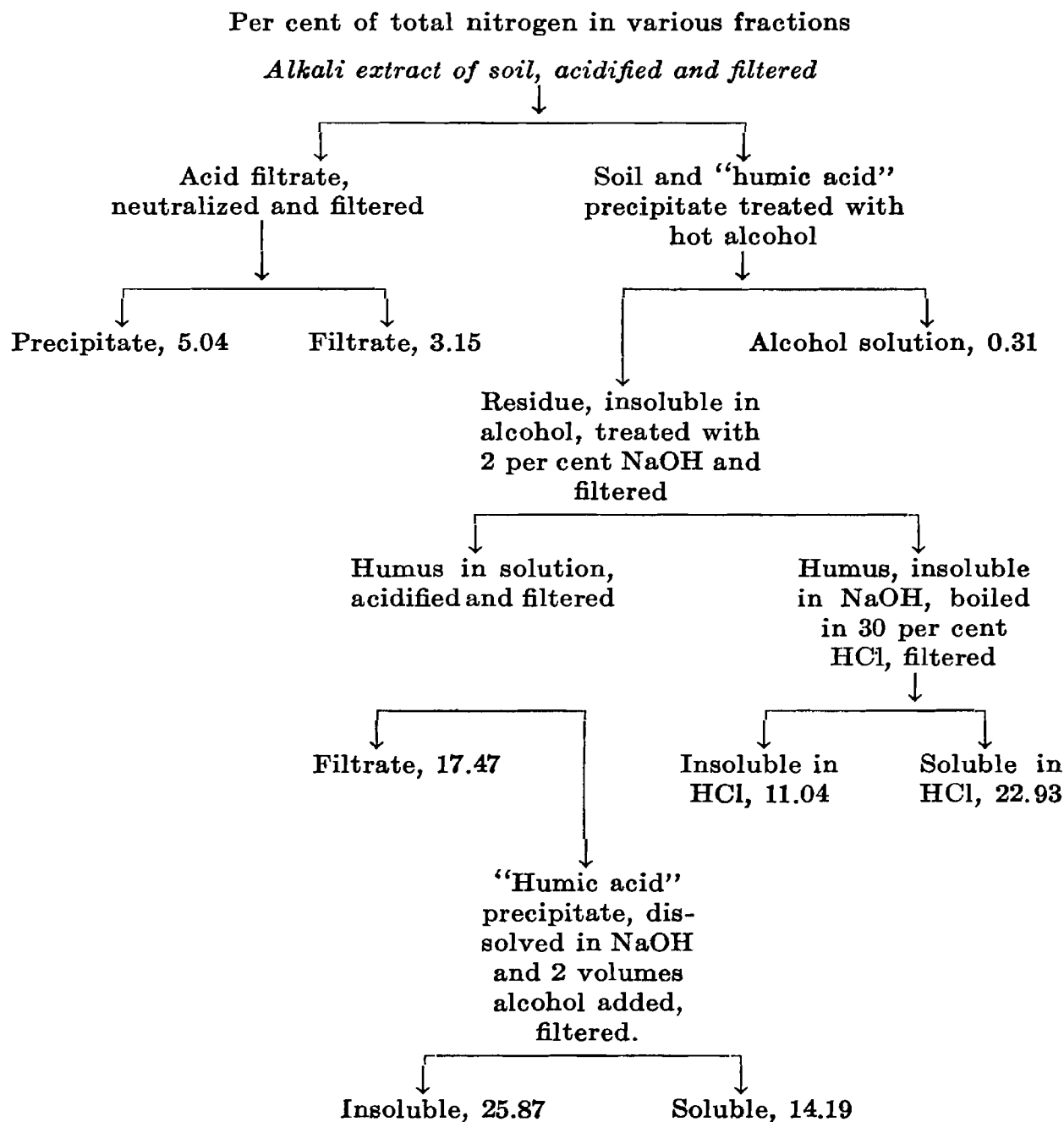
of their solubility in alkalies, acids, and alcohols. The soil is first treated, for 24 hours, with a 2 per cent sodium hydroxide solution, then acidified; upon filtering, an extract is obtained free from soil and from precipitated humus. As shown by the subsequent treatments indicated in chart 5, the humus is divided into eight fractions. Fraction 1 consists largely of complexes of aluminum, iron, and calcium, with an admixture of certain organic substances. On dissolving the precipitate in a small quantity of sulfuric acid and adding 6 to 10 volumes of alcohol, aluminum sulfate is precipitated. If the alcohol is evaporated, water being added to maintain the volume, and the suspension filtered, a mixture of resinous and waxy material is obtained, similar to that of fraction 3. Fraction 2 contains a large number of compounds, both nitrogenous, such as purine and pyrimidine bases, and non-nitrogenous, such as fatty acids; the latter can be obtained by shaking with ether or by precipitating with metallic salts. Fraction 3 contains the least amount of the nitrogen, most of the complexes found in this fraction being either nitrogen free, or contaminated by a small amount of nitrogen. Fractions 4 and 5 represent the nitrogenous substances which are not dissolved or dispersed in the 2 per cent sodium hydroxide solution. Two-thirds of these substances are made soluble by hot hydrochloric acid; this extract is fractionated as ammonia, mono-amino, di-amino, and humin nitrogen. Fraction 6 gives no more precipitate on neutralization, since the aluminum was removed in fraction 1. The treatment of the soil with hot alcohol made possible a further dissolution or dispersion of the material by an alkali solution; a larger percentage of the nitrogen was obtained in the filtrate. Fractions 7 and 8 represent the nitrogen of the so-called "humic acid" and "hymatomelanic acid" preparations.

On extraction of soil with a dilute alkali solution for 16 hours, about 50 to 80 per cent of the nitrogen was recovered (450) in the "non-humic fraction" (after precipitating the "humic fraction" with an acid). Of the non-humic nitrogen, 30-40 per cent was in the form of polypeptides, 5 per cent as free amino nitrogen, 12 per cent as ammonia. The peptides are largely colloidal and are precipitated by basic lead acetate and by phosphotungstic acid. The remaining 40-50 per cent of the non-humic nitrogen was mainly non-basic and was precipitated by basic lead acetate. These nitrogen complexes were believed to be incorporated in the humic-clay gel, so that they go into solution only when the humic matter is dissolved, and in proportion to the latter.

The results obtained by these procedures point to the complexity of

the nitrogenous substances in humus and to the possibility of their separation for further study. They establish beyond doubt the pro-

CHART 5. Distribution of nitrogen forms in the humus of a Maine soil (Shorey)



tein nature of these complexes. The next question which arises is whether this protein exists independently in the humus or whether it is intimately connected with other substances, thus accounting for

the resistance of the proteins to decomposition by microorganisms. Further, the fact that the humus protein is not acted upon by the proteolytic enzymes, as shown by Boysen-Jensen for marine humus (144) and by Hobson and Page (451, 452) for soil humus, points to its presence in humus in a combined state. It has actually been determined that protein forms humus-like complexes with lignin, as will be shown later.

LIGNIN-LIKE COMPLEXES IN HUMUS

The presence of lignins and lignin-like substances in the humus of soils, peats, and composts is definitely established. The relation of these complexes to the major portion of humus, namely, the so-called "humic acid" complexes or "humic matter," is of the greatest importance for an understanding of the origin and chemistry of humus, as has been pointed out (p. 109).

Most of the methods proposed for the determination of lignin in plant materials are based either upon its insolubility in concentrated hydrochloric acid (41 per cent) or sulfuric acid (66–80 per cent), or upon its solubility in hot alkali solutions, or upon its characteristic methoxyl content (519, 323, 598, 318). Various other methods have been suggested, such as oxidation with chlorine dioxide, solubility in sulfurous acid, and oxidation with ammoniacal solution of hydrogen peroxide, but each of these methods is open to criticism, since substances different from lignins are also thus oxidized and removed. The majority of these methods have also been used for determining the amount of "humified" organic matter in soils and in composts. If one has to exercise exceptional care in the use of these methods in the analysis of plant substances, the chemistry of which is more or less understood, it should be emphasized that particular care is indispensable for the profitable application of some of these methods to the analysis of humus, the chemistry of which still presents many puzzling problems. In the case of plant substances, especially wood and straw, which are low in protein, hot alkali solutions are frequently used to extract the lignin; this is then precipitated with an excess of hydrochloric acid; some of the hemicelluloses which are also extracted by this procedure can be hydrolyzed and removed from the precipitate by boiling the acidified extract. In the case of humus, however, alkalis extract, in addition to the lignins and modified lignin complexes, a number of different other substances, especially the proteins; it is difficult, therefore, to differentiate between lignin of plant origin, the lignin-like

complexes formed through the agency of microorganisms, the substances produced by the oxidation and partial transformation of lignins, and the compounds produced by the interaction of the lignins with the proteins. The differentiation between lignin and "humus" based on the insolubility of the former and the solubility of the latter in cold ammonium hydroxide solutions (371) still leaves room for speculation concerning modifications that the lignin molecule undergoes during

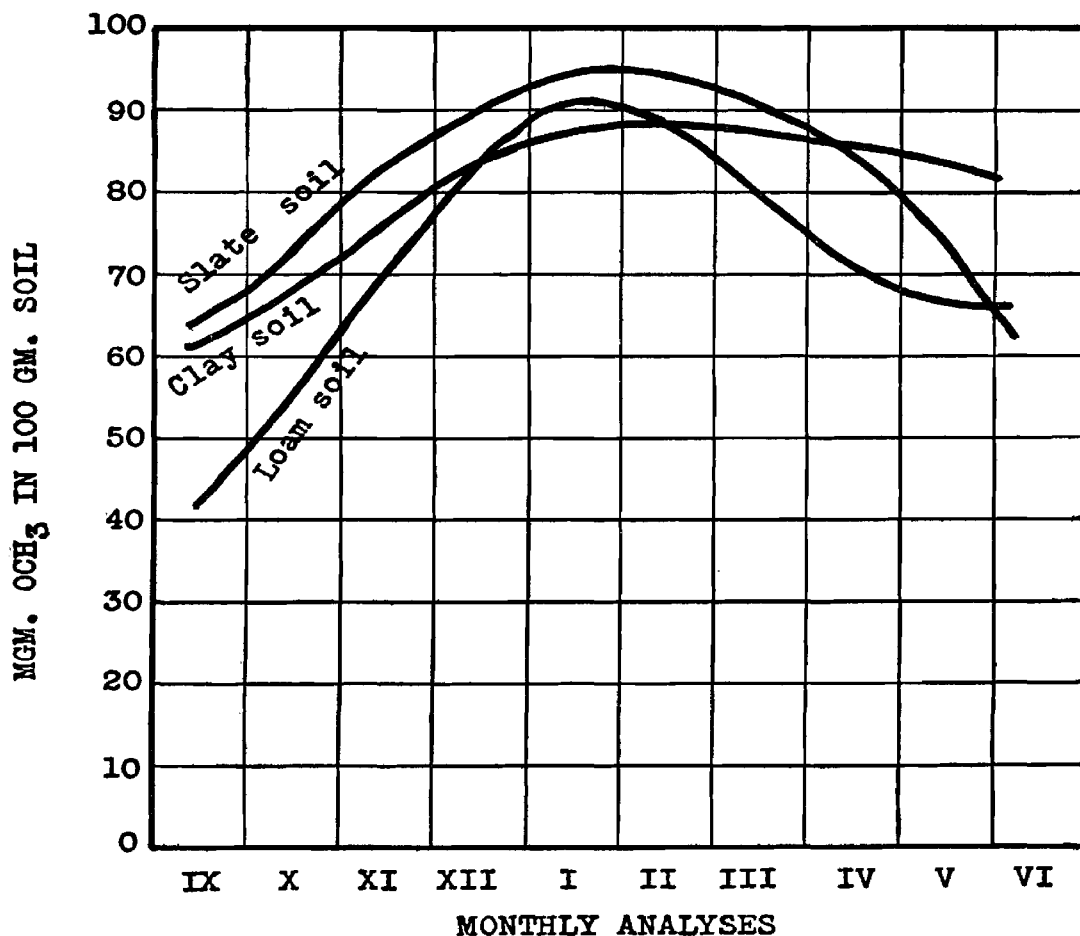


FIG. 8. Methoxyl transformation of different soils throughout the year as a result of decomposition of organic residues (Balks).

the decomposition of plant residues, which would render it soluble in this reagent.

The occurrence of lignin in humus can be demonstrated by a number of procedures which are based upon the chemical properties of lignin; namely, its aromatic structure, methoxyl content, and others. Hoppe-Seyler (459) isolated from humus, the ring compounds pyrocatechuic acid and pyrocatechin. This was later confirmed (907). The presence

of some amounts of methoxyl in the humus of soils and peats, ranging from 0.59 to 1.55 per cent of the total carbon in the soils and 2.29 per cent in the peats was also established (706), as shown in table 20. The methoxyl content of soil was shown (64) to first increase as a result of addition of manure and then to decrease gradually (fig. 8). It was actually suggested that the abundance of lignin in soil be determined by multiplying the methoxyl content by the factor 6.25. The course of transformation of the pentosan and lignin (measured by the methoxyl content) in the decomposition of manure in soil is illustrated in table 25 and figure 9. Further details have been reported previously (p. 123).

TABLE 25

Influence of manure upon the pentosan and methoxyl content of soil (62)

DATE	1000 PARTS OF CARBON IN SOIL	
	Carbon in form of pentosan	Carbon in form of methoxyl
Before manuring.....	40.2	11.9
1/21/24, after manuring.....	70.1	18.8
4/ 7/24.....	55.8	15.8
6/ 2/24.....	41.9	13.4
11/ 3/24.....	37.0	15.0
7/23/25.....	36.2	13.8

In the case of humus-rich natural materials, with a comparatively low ash content, such as peats, surface layers of forest soils, and composts, the abundance of lignin can best be determined by treating the material with concentrated mineral acids, such as 72 to 80 per cent sulfuric, in the cold, thus removing all carbohydrates and most of the proteins; the lignin, in addition to some ash and nitrogen, is left in the residue. Keppeler (538) found that with an increase in age of peat, such as increasing depth of a profile, there is an increase in the amount of organic matter which is not acted upon by 72 per cent sulfuric acid. This confirms Fischer's results (p. 112) on the increase in methoxyl content with depth of peat. A comparison of the abundance of lignin in plant materials and in peat formed from such plants showed a marked increase (1240) with the advance in the decomposition of the peat. As much as 56 to 62.6 per cent of the total organic matter in a lowmoor and woody peat was found to be composed of lignin or lignin-like materials (lignin-humus). These results were confirmed (289) when high-

moor peat was shown to contain 18 to 28 per cent of the lignin-humus complex, and woody and lowmoor peats, 35.6 to 68.5 per cent.

The presence of lignin or modified lignin complexes in forest soils can also be demonstrated by the same methods of analysis. The results presented in table 36 show that this complex makes up 41.7 to 45 per cent of the total organic matter in the F layer of raw-humus soils and 43.4 to 57.3 per cent of the H layer, increasing rapidly with an advance in the decomposition of the forest litter. The presence of

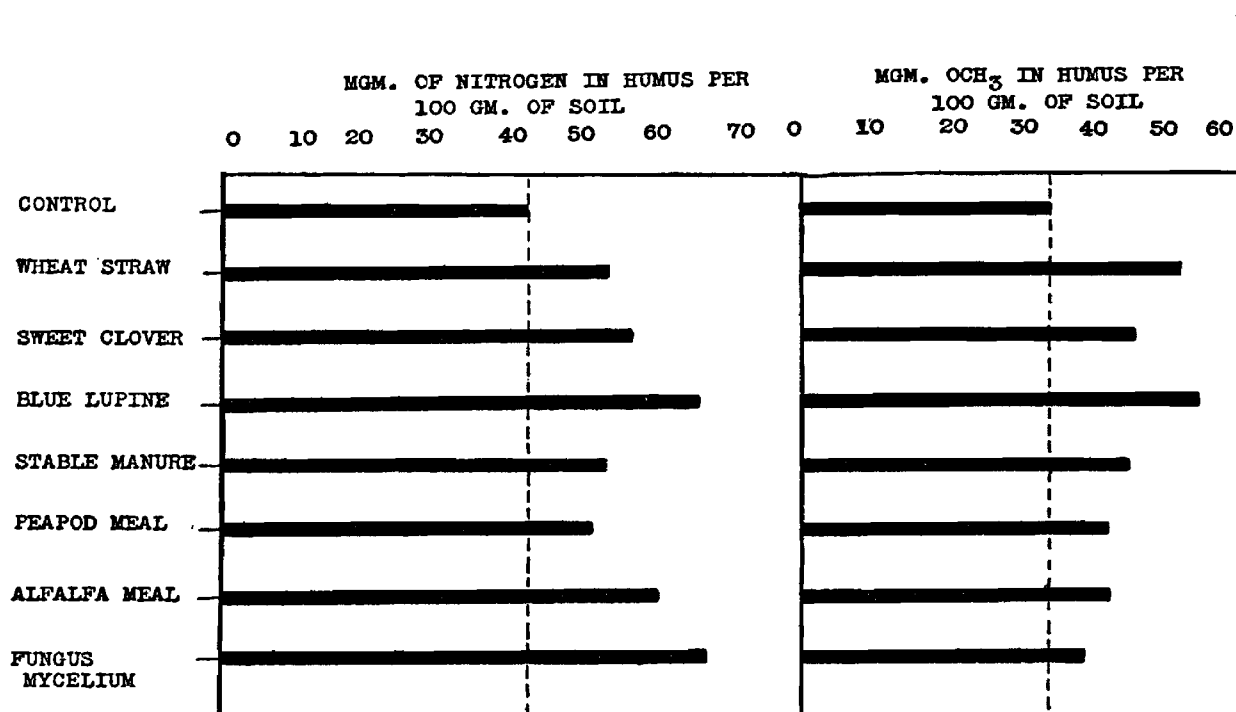


FIG. 9. Accumulation of nitrogen and methoxyl in soil humus as a result of addition of materials of varying C/N ratio; see Fig. 5 (Jensen).

lignin in forest soils has also been demonstrated by a different method of procedure (372).

Lignins and lignin-like complexes occur also in field and garden soils. The results given in table 19 show that 35 to 55 per cent of the humus in such soils is made up of this group of substances. The same is true of the humus in lake bottoms, in river bottoms, and in marine muds.

RATIO OF CARBON TO NITROGEN IN HUMUS

Among the numerous puzzling phenomena concerned with the origin and chemical nature of humus is the more or less definite ratio existing between the carbon and nitrogen in certain forms of humus, especially

in the humus in field and garden soils and in marine muds. Although humus is highly complex in chemical composition and although it contains a great number of definite organic compounds, it does not represent a mere bewildering variety of substances without any special cause or system; one need not, therefore, suspect that every soil or marine bottom formation has a special type of humus of specific chemical composition. On the contrary, humus as a whole is characterized by certain specific physical, chemical, and biological properties that distinguish it from other forms of organic matter in nature, even if certain qualitative and quantitative differences are found between humus types formed under different conditions.

The fats, waxes, and resins of the soil; the carbohydrates and the proteins; the lignins and the lignin-like complexes,—all have their counterparts in plant material, although the corresponding groups may not be identical in chemical composition. This variation is associated with the transformations of the complexes of plant origin in the soil through the activities of microorganisms; some of the plant constituents become completely decomposed, others are modified to a greater or less extent, and still others are only slightly attacked; these processes are also accompanied by the synthesis of new complexes (fats, carbohydrates, proteins, and even lignin-like compounds) by the microorganisms.

One of the most important and characteristic properties of humus is its nitrogen content, a property almost entirely overlooked by many of the students of humus chemistry. As long as it was considered that humus was composed of a few simple "humic acids" and as long as the latter, according to the various hypothetical formulae, were believed to contain only carbon, hydrogen, and oxygen, the nitrogen in the humus received little, if any, attention. In most instances, the nitrogen was looked upon as an impurity; however, as soon as its occurrence in humus was shown to be a characteristic property of the latter, its origin and relation to the other elements received greater consideration. The most important discovery made in this connection was the fact that there exists a more or less definite relation between the carbon and nitrogen contents of humus in field and garden soils. According to Dehérain (211), Boussingault demonstrated that the carbon-nitrogen ratio of cultivated soils varied from 8.0:1 to 12.2:1, with an average of 9.5:1; a pasture soil gave a ratio of 7.9:1. Dehérain himself found that this ratio varies from soil to soil, depending upon soil treatment; in the case of the experimental plots at Grignon, the well-manured soil

had a C:N ratio of 7.5:1 to 8.9:1 and the unmanured plot had a ratio of 4.3:1. A much wider ratio was obtained by Warington (1252) for the Rothamsted soils: the one receiving ammonium salts had a C:N ratio of 10.4:1–10.6:1; the plot receiving stable manure, a ratio of 11.5:1; and the plot in permanent pasture, a ratio of 13.0:1.

Stewart (1095) found that the C:N ratio of certain brown silt loam soils of Illinois was 12.1:1 for the surface layer, 11.5:1 for the sub-surface layer, and 8.9:1 for the subsoil; in the case of black clay loam soils, the corresponding ratios were 11.7:1, 11.9:1, and 9:1. The conclusion was reached that the carbon-nitrogen ratio of the soil tends to become narrower as the age of the humus increases. The nitrogen-phosphorus ratio also varied in the two soils, being 13.5:1 for the silt loam and 11.4:1 for the black clay loam. Both of these observations point definitely to differences in the chemical nature of the humus in different soils.

These results were substantiated by a number of investigators. The C:N ratio for the surface layer of Texas soils was found (309) to be 9.2:1 and for the subsoil 8.3:1. This ratio was reported (1026) to be influenced not only by depth of soil but also by the amount of precipitation. An average of eight soils in the northwestern part of the United States gave a C:N ratio of 12.5:1 in the surface 6-inch layer, 9.6:1 in the soil layer taken at a depth of 12 to 14 inches, 8.9:1 at a depth of 24–36 inches, and 9.1:1 at 36–48 inches below the surface. Soil with a precipitation of 15 inches of rainfall or more had a C:N ratio of 13.1:1, while with a rainfall of 10 inches or less, the ratio was 11.1:1. The treatment of the soil was also of importance. The C:N ratio of soils in arid regions was 11:1, although the first foot contained 2.24 per cent humus and the second foot 1.62 per cent (510). Similar results were obtained for a number of other soils in different regions of the world (474, 156, 481, 690, 1136), as brought out in figure 10.

It was soon shown, however, that the ratio of carbon to nitrogen in humus is not a constant quantity. The range of variation for fifty British soils was shown (691) to be 6.5:1 to 13.5:1, with an average approximating 10.0:1. The high ratio for the surface soil layers was believed to be due to the presence of undecomposed plant remains. Leighty and Shorey (617) found that although the C:N ratio of a large number of soils varied from 3.5:1 to 35.1:1, the common ratios fell between 7:1 and 15:1. The ratios were widest in the surface soils, becoming narrower at lower levels. A wide C:N ratio, such as 20:1, indicates that the organic matter has not undergone extensive decom-

position and that a fair supply of organic matter is available for rapid development of microorganisms, whereas a narrower ratio, such as 10:1 or less, tends to show that the humus is in an advanced stage of decomposition and is only slowly available for further microbial decomposition. A knowledge of the C:N of plant residues, as well as

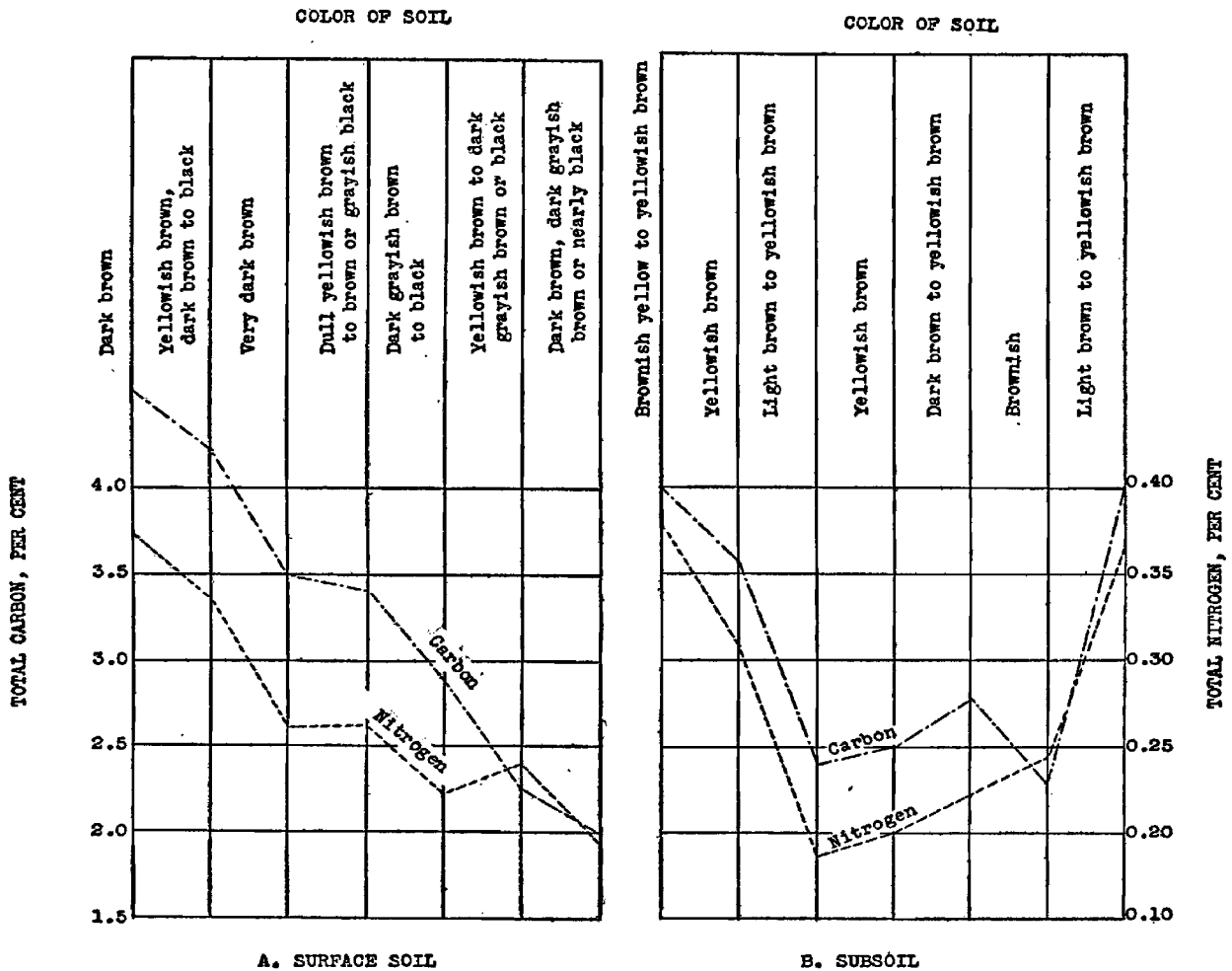


FIG. 10. Carbon and nitrogen content (per cent) of soils and subsoils in the Carrington silt loam series; A. surface soils; B. subsoils (Brown and O'Neil).

of soil humus, is essential to enable one to predict the rate of liberation of nutrients in forms available to higher plants (1027, 935).

Jenny (488) calculated that a definite correlation exists between the mean annual temperature of a given region and the average total nitrogen content of the soil, provided the rainfall-evaporation ratio is constant. The logarithm of the nitrogen content varies inversely with the temperature, every 10°C. decline in mean annual temperature bringing about a two- or three-fold increase in the average nitrogen content.

Jenny (490) has further shown that the C:N ratio of the soil humus becomes narrower with increasing temperature (fig. 11). Although the total nitrogen content of the soil was found, in the case of grasslands, to increase logarithmically with the humidity factor, the C:N ratio, which was about 11.3:1 in the temperate region, was not affected. The nitrogen content of the soil was thus shown (489) to be a function of

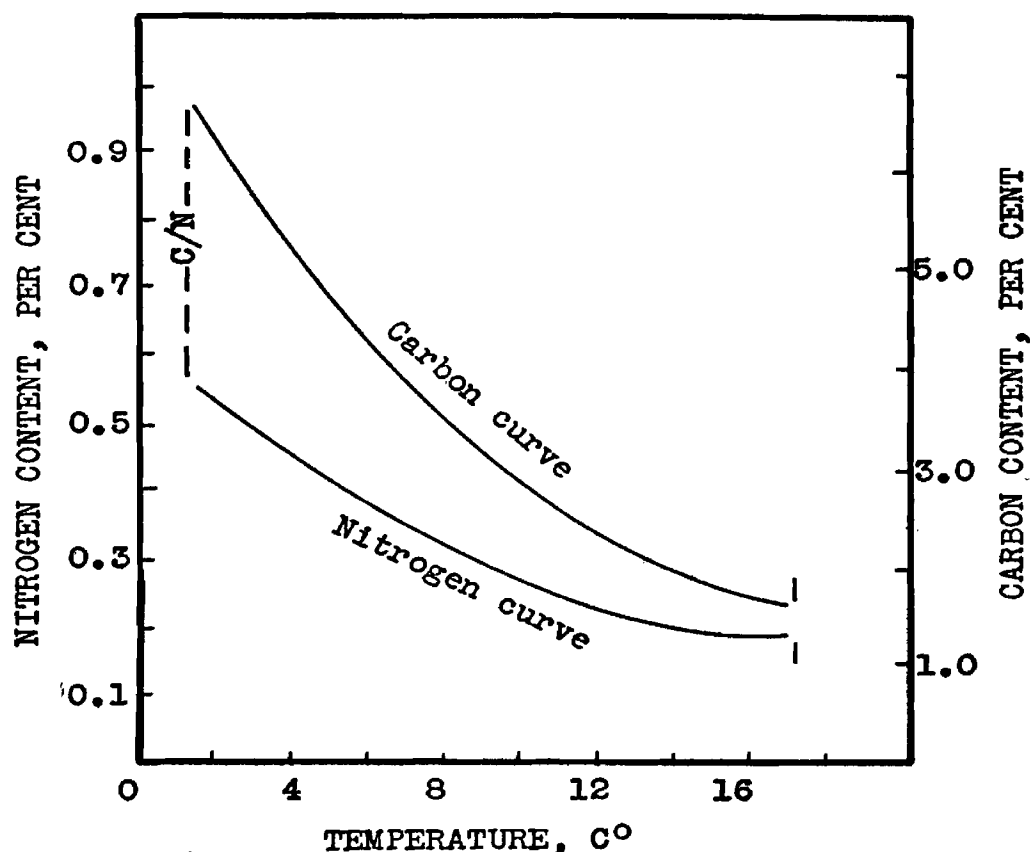


FIG. 11. Schematic representation of the widening C/N ratio of soil humus with decreasing temperature (Jenny).

climate, temperature, precipitation, and evaporation; it was expressed by the following equation:

$$N = t(T, H)$$

N being the total nitrogen of the soil, t the time, T the air temperature, and H the humidity factor.

The carbon-nitrogen ratio of humus can also be calculated from data giving the amounts of the various compounds in the humus. The humus of mineral soils was shown (1223) to consist, on the average, of

45 per cent lignin-like complexes, 35 per cent protein complexes, 11 per cent carbohydrates, and 3 per cent fats, waxes, and resins. From calculations using the known carbon contents for these complexes and assuming 50 per cent carbon for the remaining 6 per cent of the unknown complexes, the following amounts of carbon and nitrogen can be shown to occur in soil humus:

Carbon data

COMPLEX	CONCENTRATION OF COMPLEX		CARBON IN COMPLEX	TOTAL CARBON
	<i>per cent</i>		<i>per cent</i>	<i>per cent</i>
Lignin.....	45	×	64	= 28.80
Protein.....	35	×	50	= 17.50
Carbohydrate.....	11	×	44	= 4.84
Fats, etc.....	3	×	70	= 2.10
Unknown.....	6	×	50	= 3.00
	100			56.24

Nitrogen data

COMPLEX	CONCENTRATION OF PROTEIN		NITROGEN IN PROTEIN	TOTAL NITROGEN
	<i>per cent</i>		<i>per cent</i>	<i>per cent</i>
Protein.....	35	×	16	= 5.6

The average theoretical carbon content of the soil humus is thus found to be 56.24 per cent, and the average nitrogen content, 5.6 per cent. This gives a theoretical ratio of carbon to nitrogen of $\frac{56.24}{5.6}$ or 10.04 per cent; this ratio is very close to the one commonly found in soils. These calculations also show that the common assumption that the humus in mineral soils contains 58 per cent carbon is not far from correct.

Since the relative abundance of the various organic constituents of humus is influenced by a number of factors, including climatic and soil conditions; one would expect that both the chemical composition of humus and the C:N ratio would be different where these factors were different (463a). It has already been pointed out that with an increase in depth of soil the carbon-nitrogen ratio of the humus becomes narrower. This is particularly marked in forest soils, where the nitrogen

content of the humus has been found to be much greater in the deeper horizons (1265) :

NATURE OF SOIL LAYER	RAW HUMUS + LEACHED SAND	HARDPAN	LAYER UNDER HARDPAN	SUBSOIL
Horizon.....	A ₁ -A ₂	A ₃ -B ₁	B ₂	C
Nitrogen content of humus, per cent.	2.08	2.24	3.99	8.44

A detailed discussion of these relationships and further information on the C:N ratios of different types of humus will be presented later, in connection with the discussion of specific humus types.

Humus as a whole. A critical examination of the available information concerning the chemical composition of humus leads one to conclude that the chemistry of humus resolves itself into a study of the chemistry of the various constituent groups of humus. Our knowledge of the chemical composition of plant and animal substances has progressed from the idea of a vital force and the function of earth, fire, water, and air to an accumulated knowledge of the various chemical elements and compounds which compose these complex organisms, depending upon their specific nature and conditions of nutrition. Similarly, in the study of humus, one must advance beyond the hypothetical "humic acids" to investigations of the numerous organic constituents of humus. This involves a study of the fatty and waxy constituents of humus; of the resinous substances; of the various carbohydrates, especially the uronic acid compounds and other hemicelluloses; of the lignins and modified lignin complexes; of the proteins and various other nitrogenous substances; as well as of the numerous other chemical compounds found in humus.

Humus complexes formed from different plant and animal residues, under different conditions and by different groups of microorganisms, vary considerably from one another in chemical composition. One cannot assume identity in composition of the humus of composts, of forest soils, of highmoor peats, of lowmoor and sedimentary peats, and of coal, with the humus of field and garden soils or with that of river or marine bottoms. The chemical composition of the humus formations of the same type of peat or forest soil, but produced in different environments and from different plant associations, may also be dissimilar. Even the humus materials found in different horizons of the same peat bog or forest soil will show considerable differences in compo-

sition because of differences in extent of decomposition and weathering associated with age. Some of these facts are illustrated further in table 26, where the relation between the chemical composition of humus is compared with that of the plant residues from which the humus originated.

Certain fundamental questions still remain to be answered. What is the chemical nature of humus in its final stages of decomposition? Does this also show marked variation in composition or does it come to a certain chemical equilibrium? These questions can only be answered after an examination of the results of the composition of humus in field and garden soils, in marine bottoms, and in lowmoor peats. Such

TABLE 26

Chemical composition of plant residues, manures and soil humus (822a)
Per cent of total organic matter

CONSTITUENTS	CEREAL STRAW	ARTIFICIAL MANURES		HORSE MANURE FOR MUSH- ROOMS	HUMUS IN PEAT	HUMUS IN MINERAL SOIL
		1	2			
Fatty substances.....	1.90	0.73	0.91	0.14	1.12	12.00
Resins.....	4.48	1.95	4.83	3.93	2.24	0.44
Pentosans.....	28.40	23.57	11.26	11.47	4.72	3.44
Hexosans.....	5.05	10.81	4.80	3.48
Cellulose.....	37.35	29.66	19.59	13.17	2.77	2.98
Lignin.....	14.35	20.76	15.54	29.60	16.42	13.65
Soluble "humic acids".....	3.56	16.62	19.25	26.98	27.46
"Humins".....	4.25	5.50	3.50	16.95	6.21
Nitrogen.....	0.41	0.56	1.36	2.42	3.37	2.15

humus is characterized by a low cellulose content and a high protein content, which points to considerable synthesis of microbial cell substance. The high content of lignin, which is usually present in the form of lignin derivatives, is usually designated as "humic substances," "humic acids," or "pure humus," but more correctly as "lignin-humus" or "humus-lignin." This type of humus is further characterized by a dark color. An examination of the results presented in tables 17, 19, and 26 reveals the fact that the protein and lignin account for 70 to 80 per cent of the total organic constituents of the humus in mineral soils and lowmoor peats. This makes the chemical composition of humus quite distinct from that of either plant or animal residues, since most of the plant residues are characterized by high carbohydrate and

low protein contents, while the animal residues have high protein and low lignin contents.

The chemical constituents of humus, exclusive of inorganic constituents, can be divided into two major groups: 1. the proteins and lignin-like complexes, which account for the major portion of the organic matter in humus, and 2. the carbohydrates, fats, waxes, organic acids, alcohols, and other carbon compounds, which account for a smaller part of the organic matter. The organic complexes of humus were similarly divided by the use of the older methods of approach to the chemistry of humus. The adherents of the "humic acid" theory separated humus into "humic acids," chiefly characterized by their solubility in alkali solutions, and into "humins" and "crenic acids" or "fulvic acid"; this corresponds fairly well to the foregoing system of separation, but not quantitatively, however. The separation of humus into "humic matter" or "humus fraction" and "non-humic matter" or "non-humus fraction" (801, 1012) had a similar basis.

By comparing the processes involved in the transformation of the individual plant and animal constituents in the formation of humus with the results presented here on the chemical nature of humus, a concrete system can be proposed to explain the origin and the chemistry of humus. The following facts may be considered as having been definitely established: Humus is a product of decomposition of plant and animal residues, through the agency of microorganisms. The chemical composition of humus is determined by the nature of the residues from which it is formed, by the conditions of its decomposition, and by the extent to which it is decomposed. Chemically, humus consists of numerous organic complexes, the major group of which consists of lignins and lignin derivatives and of proteins; a minor group contains carbohydrates, fats, organic acids, alcohols, and other carbon compounds. The formation and mutual interrelations of these two groups of substances hold the key to the facts explaining the chemistry of humus.

Hébert (408) and Dehérain (211) were the first to suggest the conception of humus as a mixture of lignin and protein, the former being the resistant part of the plant residues, and the latter, a product synthesized by the bacteria which decomposed the plant residues. Since plant, animal, and microbial proteins existing in a free state are readily attacked by bacteria, one cannot be dealing with an ordinary mechanical mixture of lignin and protein in the case of humus; it seems necessary to postulate the existence of chemical or adsorption compounds.

According to Hobson and Page (451), the nitrogen in humus is associated with "humic matter" in some manner which does not allow its removal by methods which ordinarily remove physically bound nitrogenous impurities. This nitrogen passes through the ultra-filter and is not salted out by saturated sodium chloride. The nitrogen in artificially prepared ligno-protein complexes behaves in a similar manner; the proteins in the natural and artificial preparations of humus are acted upon by proteolytic enzymes, such as pepsin and trypsin, only to a very limited extent. On hydrolysis with hydrochloric acid, half of the nitrogen of the "humic acid" was found in the form of amino nitrogen. This led to the conclusion that "humic acid" isolated from soil contains proteins or protein derivatives as the principal nitrogenous constituent. It was suggested that a "salt" is formed between the acidic, negatively charged, non-nitrogenous humic colloid and the basic, positively charged protein, this salt being similar to that formed between tannin and protein (247). A salt-like complex of this type, however, would be broken up in an alkaline solution into its two component parts and the protein would be subject to hydrolysis by trypsin; the lack of such hydrolysis was explained by the shielding action of the "humic acid." The association between the non-nitrogenous complex and the protein would appear to be more intimate than mere "salt" formation obtained by the mutual precipitation, in acid solution, of the "humic acid" and protein. When alkali solutions of lignin and albumin were mixed and precipitated together by an acid, the lignins protected the proteins against bacterial attack; the amino nitrogen distribution (by the Van Slyke procedure) in this complex was found to be identical with that of the "humic acid" isolated from the soil.

Jensen (494) also mixed alkali solutions of lignin and casein and precipitated the mixture with hydrochloric acid. The preparations, containing 3.9 to 4.1 per cent of nitrogen, were added to mineral nutrient solutions, inoculated with soil suspensions and incubated for 3 weeks; only traces of ammonia were produced, whereas in the control solution, containing a corresponding amount of nitrogen as casein, 75-80 per cent of the nitrogen was changed to ammonia. When the preparation was added to soil, its resistance to microbial attack was not so marked, and after 45 days only an insignificant part of the nitrogen was recovered as humus. The conclusion was reached that it did not seem probable that lignin forms resistant adsorption compounds with every protein.

Demolon and Brigando (216, 217) found that the humus of cultivated

soils is able to fix dissolved proteins brought in contact with it. One hundred grams of humus fixed up to 70 gm. of serum albumin and even larger amounts of gelatin. However, when the nitrification in soil of humus obtained from manure (3.37 per cent nitrogen) and that of the humus-protein complex (6.63 per cent nitrogen) were compared with that of an equivalent amount of the serum albumin, humus was found not to increase the amount of nitrate formed in the soil, whereas the albumin fixed by the colloidal humus nitrified as well as the free albumin. It was suggested that the stability of humic nitrogen in soil is due to its specific chemical constitution; the nitrogen in humus is not comparable to that of proteins but is directly linked to carbon in the molecule as in a nitrogen ring compound.

The results of the investigations of Page and his associates (247-8, 450-2), on the one hand, and of Demolon, on the other, would lead one to conclude that although lignin is able to bind proteins and prevent their active decomposition, humus can combine with proteins but does not form an intimate union and does not protect the protein from microbial attack; even the first process seems to take place only under certain specific conditions.

A series of ligno-protein complexes were prepared by Waksman and Iyer (1232) as follows: alkali solutions of lignin and protein were mixed, in the ratio of 3:1 to 6:1, and the mixtures precipitated either by a mineral acid at pH 4.8, or by such salts as CaCl_2 , MgCl_2 , FeCl_3 , or AlCl_3 , at pH 7.0. The preparations were filtered, washed, and dried at temperatures not exceeding 65°C . A series of complexes were obtained which behaved in most respects, such as color, solubility in water and in alkalies, chemical reactivity, and resistance to attack by microorganisms, like the typical "humic acid," "humic matter," or α -fraction of humus. It was suggested that, in order to distinguish these complexes from those found in natural humus, on the one hand, and the artificial "humus preparations" obtained from sugar, on the other, they should be designated as the "humus nucleus." The suggestion was also made that similar complexes, or modified forms, constitute the major portion of humus in soils, peats, and composts.

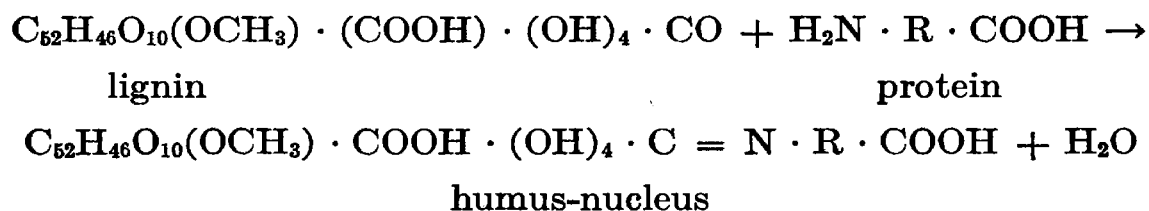
The physical, chemical, and biological properties of the synthesized ligno-protein complex and of natural humus are compared in the following summary:

<i>Property</i>	<i>"Humic matter" (α-humus) in soils or peats</i>	<i>Humus-nucleus or ligno- proteinates</i>
Nitrogen content	2-3 per cent	2-3 per cent
Combination with bases	Combines readily <i>Exp. Conf.</i>	Combines readily <i>Equip. W.T.</i>
Solubility in water	Insoluble	Insoluble
Solubility in dilute alkali solutions	Soluble	Soluble
Solubility in mineral acids	Insoluble	Insoluble
Oxidation by H_2O_2	Readily oxidized	Readily oxidized
Oxidation by acetyl bromide	Only slightly oxidized	Not fully oxidized
Decomposition by micro-organisms	Attacked with difficulty	Attacked with difficulty
Influence on microbial processes	Favorable	Favorable

The major group of constituents of humus already referred to (p. 183) may be considered as equivalent to the ligno-protein complexes synthesized in the laboratory or to modifications of these; their formation in nature is a result of decomposition of plant and animal residues. Since lignins of different origins are not identical in chemical composition, as shown by the variation in methoxyl content (1237), since there are considerable differences in the composition of proteins of different origin, since the types of microorganisms active in the decomposition processes are unlike under different conditions, and since numerous other factors, such as the chemical composition of the residues undergoing decomposition, influence the process of humus formation, it is quite natural to expect that the nature of the "humus-nucleus" and the composition of humus as a whole should not be the same under all conditions.

As to the chemistry of the reaction of condensation between the protein and the lignin, there are several possibilities. These are based upon the fact that lignin is known to possess carboxyl groups, hydroxyl groups, carbonyl groups, and methoxyl groups, in addition to the cyclic rings or the ring skeleton (326). If one assumes that the COOH group of the lignin molecule interacts with the NH_2 group of the protein molecule, a salt will result, even in an alkaline solution; the process of tanning is a reaction of this type. The possibility of interaction between a phenolic OH group of the lignin and the NH_2 group of the protein would meet with the objection that, aside from the improbability of the occurrence of such a reaction, the complex itself could be readily hydrolyzed. The assumption of a reaction between the NH_2 group

and a carbonyl group, of a ketonic or an aldehydic nature, to form a compound of the nature of a Schiff's base, offers a fair degree of probability:



This complex would be quite stable and would possess a high base exchange capacity, a phenomenon characteristic of the humus-nucleus, as will be shown later. The protein in this complex or group of complexes is very resistant to microbial attack. There is no definite relation between the amounts of protein and lignin in the complex. However, the excess of protein beyond a certain concentration is susceptible to rapid decomposition by microorganisms. The same is true for the α -humus of the soil and for free proteins with which it may be allowed to interact, which explains the results of Demolon previously referred to. Once humus is saturated with protein, further protein which may be introduced becomes loosely bound and can easily be attacked by microorganisms.

One need not imagine that the ligno-protein complexes, or modified forms of these, exist in the soil independent of the other humus constituents. They are probably combined in the humus not only with various bases, but also with other organic and inorganic compounds.

It is as unreasonable to look upon humus as a simple chemical compound as it is to consider a plant or an animal as such an elementary system. Humus is extremely complex in composition. It consists of certain major groups of constituents and of a number of minor groups. The physical, chemical, and biological properties of the humus constituents are of particular importance in their relationships to soil processes and plant nutrition.

CHAPTER VIII

HUMUS FORMATION IN COMPOSTS, ANIMAL MANURES, AND GREEN MANURES

“The most proper soyle for Gardens are your Sheep-dung, your Hen muck, and Pidgeons dung, with your well rotted Horse muck, especially for cold Land; or else the rich moulds, or any good Manure that is growne to Mould, is as good and Naturall as any of the aforesaid Soyles, provided you lay good store of it thereon. . . . The Leaves of Trees laid together, or cast into some High-way, or Water-flows, or mingled with other Soyles, will make very good Compost also.”—The English Improver, or a Survey of Husbandry, by Walter Blith (London, 1649).

The processes involved in the formation of humus from stable manures and composts of plant residues are quite different from those in the formation of humus in mineral soils and in forest soils, in peat bogs, and in marine bottoms. In the case of stable manures and other animal manures, one is dealing with plant and animal products which have undergone previous digestion during their passage through the animal digestive tract, intermixed with certain plant materials used as bedding. The materials ingested as food have been modified in composition not only through the action of the animal digestive agencies but also by various bacteria and protozoa inhabiting the digestive system. When these excreta, with or without the admixture of fresh plant materials used as bedding, are placed in a compost or are added to the soil, they undergo immediate decomposition by a number of microorganisms, typical of soils and of composts, which gradually transform the heterogeneous constituents of the manure into a homogeneous mass of humus. When composts of green or mature plant materials are prepared, with or without the addition of inorganic nutrient salts, the processes of decomposition are similar to those of composts of stable manure, although the rate of decomposition may be different. The same general type of humus will be produced in all cases, and the products will vary more in relative abundance of the different chemical constituents than in the specific nature of these constituents.

Humus in stable manures and in composts. The chemical composi-

tion of the animal excreta differs markedly from that of the original foodstuffs fed to the animal. Stable manure consists of certain undigested constituents of the foodstuffs; of certain transformation products of the original constituents of the foodstuffs; of various waste products of animal metabolism; of numerous cells of bacteria and protozoa, which inhabit the animal digestive tract and multiply there extensively; of the animal urine; and finally of the bedding used in the stable. The various foodstuffs consumed by the animal are not digested alike; some constituents are attacked more readily than others and therefore will not contribute in the same proportion to the excreta (1283a). Different plant materials and even the same plant at different stages of growth vary considerably in chemical composition and

TABLE 27
Chemical composition of various fresh manures, litter free (1228)
On per cent basis of dry material

CHEMICAL CONSTITUENTS	SHEEP MANURE*	HORSE MANURE†	COW MANURE*
Ether-soluble substances.....	2.83	1.89	2.77
Cold water-soluble organic matter.....	19.19	3.19	5.02
Hot water-soluble organic matter.....	5.73	2.39	5.32
Hemicelluloses.....	18.46	23.52	18.57
Cellulose.....	18.72	27.46	25.23
Lignin.....	20.68	14.23	20.21
Total nitrogen.....	4.08	1.09	2.38
Ash.....	17.21	9.11	12.95

* Solid and liquid excreta.

† Solid excreta only.

also in their digestibility by the animal; it is, therefore, quite natural to find that the excreta produced from different foodstuffs, even when consumed by the same animal, are not the same in chemical composition. The higher the lignin content of the plant material, the less readily is the latter digested (567). The cellulose, hemicelluloses, fats, and proteins are most readily utilized, while the lignins are acted upon to a limited extent; as a result, the animal excreta are considerably richer in lignin than are the plant substances fed to the animal.

It is well to emphasize further the fact that different animals do not digest the same foodstuffs in a like manner, which explains the difference in chemical composition of the excreta of different animals, as shown in table 27. The various forms of bedding also differ in chemical

composition. These factors are largely responsible for the chemical variation in composition of stable manures obtained from different sources and under different conditions. The composition of the manure influences not only the mechanism and rapidity of its decomposition but also the nature of the humus formed. An understanding of the chemical nature of humus produced from stable manures requires a knowledge of the composition of the original constituents of the manure and of the processes of decomposition.

Most of the available information concerning the chemical composition of stable manures is limited to the inorganic constituents, especially the elements phosphorus and potassium, and to the total nitrogen content (457, 925). An analyses of 284 samples of stable manure (941) gave, on the average, 78.6 per cent water, 0.430 per cent nitrogen, 0.201 per cent P_2O_5 , and 0.606 per cent K_2O . The individual samples varied considerably, the water from 73 to 83 per cent (65–85 per cent), the nitrogen from 0.25 to 0.65 per cent (0.25–1.00), the P_2O_5 from 0.10 to 0.40 per cent (0.10–0.60) and the K_2O from 0.30 to 1.10 per cent (0.10–1.7), respectively.

Comparatively few analyses of the organic complexes present in animal excreta and stable manures have been made. Further, since the methods used for these organic analyses differed considerably, it is frequently difficult to interpret the various results so as to make them comparable. It may be sufficient to call attention to the marked variation in the methods used for the determination of cellulose, hemicelluloses, and lignins, the three major constituents of manures; it is hardly necessary to emphasize the fact that cellulose obtained by one method of analysis may not be the same chemical substance as the cellulose determined by another method; the same is true of the other two groups of organic complexes. It is always essential, therefore, to know the method used in making the specific determinations.

When stable manure is placed in a compost, which is kept under conditions of favorable moisture and aeration, the various organic constituents become attacked by a great variety of microorganisms, including fungi and bacteria, both aerobic and anaerobic. These organisms do not attack all of the chemical constituents of the manure at the same rate. The nature and rapidity of decomposition of the compost as a whole and of its specific organic constituents, depend to a large extent upon the nature and chemical composition of the manure, as modified by its various constituents, and upon the conditions under which the decomposition of the manure takes place (fig. 12). Falck (278, 281)

has shown that in composts of stable manure containing cereal straw, thermophilic bacteria bring about the destruction of a large part of the pentosan and of the cellulose, but not of the lignin; the concentration of the latter in the residual compost gradually increases, and gives rise to dark brown humus substances, which are transformed only by the "corrosive" action of certain basidiomycetous fungi. The humus thus produced was spoken of as "mild humus." When the manure is first allowed to undergo aerobic decomposition, for a period of a few days, so as to allow a rapid rise in temperature, and is then compressed in order to produce anaerobic conditions, a compost is formed which

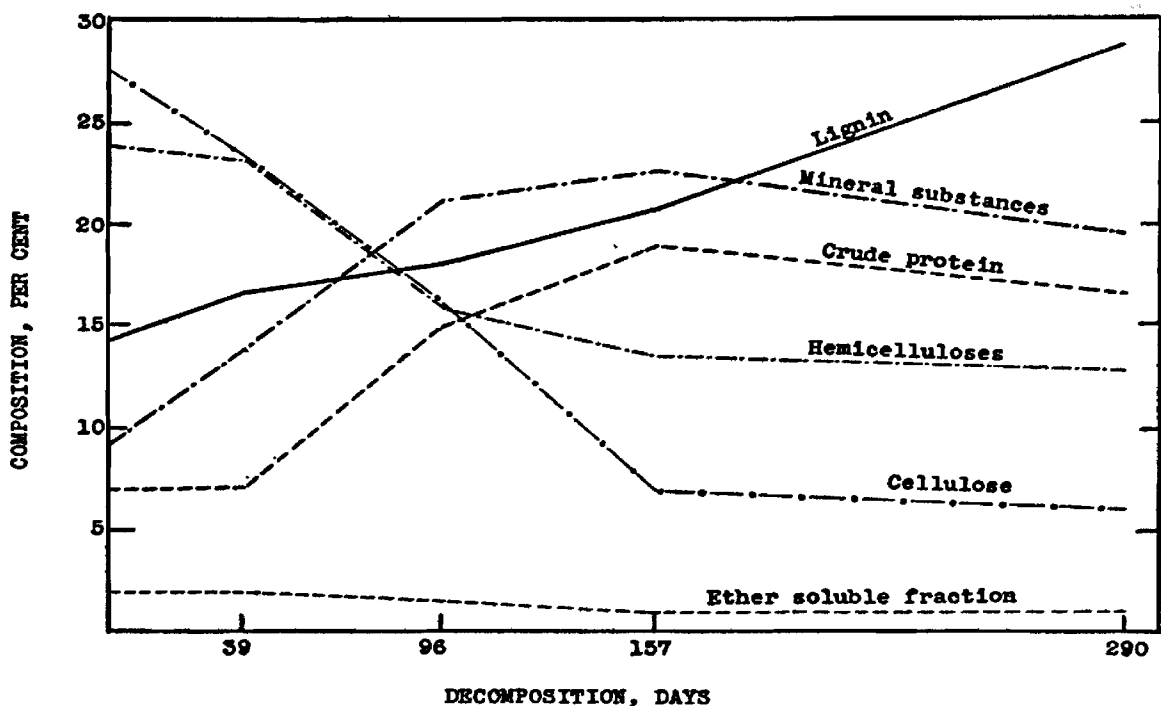


FIG. 12. Changes in the chemical composition of horse manure compost during different stages of decomposition (Waksman and Diehm).

behaves differently from the commonly composted manure; this process was spoken of as the "hot fermentation process" (584a, 651).

König (564, 566) found that while horse manure lost, during a certain period of composting, 51.7 per cent of its pentosan, cow manure lost, in the same period of time, only 19.5 per cent of this carbohydrate. The influence of moisture and aeration upon the decomposition of the pentosan and cellulose in horse manure, at 35–37°C., is shown in table 28. Some reduction in the amount of the nitrogenous constituents of the manure was also found to take place during the process of decomposition; however, this reduction was very much less than that of the

carbohydrates. This is due to the fact that the microorganisms attacking the carbohydrates in the manure synthesize considerable cell substance, thus storing away in the form of microbial proteins a large part of the nitrogen, which is liberated in the decomposition of the urea and other readily decomposable nitrogenous constituents of the manure. This is chiefly responsible for the increase in the protein content of the manure in the process of composting. Egorov (254) calculated that 50 to 66 per cent of the total nitrogen in the solid animal excreta was in the form of microbial cells. During the process of composting of the manure, the water-soluble forms of nitrogen are gradually transformed into cell proteins by the microorganisms active in the

TABLE 28

Loss of dry matter and carbohydrates in manure as a result of composting under different conditions (254)

	PER CENT OF DRY MATERIAL LOST AS A RESULT OF DECOMPOSITION				
	Aerobic			Anaerobic	
	Moisture content, 30 per cent	Moisture content, 50 per cent	Moisture content, 75 per cent	Water saturated	CO ₂ atmosphere
Total dry matter.....	38.5	48.2	47.8	35.7	36.3
Pentosan.....	71.0	82.6	78.2	55.8	61.1
Cellulose.....	53.2	61.8	64.6	41.1	47.3

decomposition processes, thus augmenting the proteins of microbial origin in the manure.

A proximate chemical analysis of fresh horse manure and of the same manure at different periods of decomposition is given in table 29. Composting took place in the autumn, under cover. In order to illustrate the changes in the total concentration of the various organic constituents of the manure, the results were calculated for the beginning of the decomposition and for the 27-day period on the basis of an original 450 kg. of fresh manure containing 134 kg. of dry matter (1228, 1233).

These results prove definitely that when stable manure undergoes decomposition and is transformed into humus, there is a gradual increase in the lignin complexes, in the organic nitrogenous compounds, and in the mineral substances. This is accompanied by a darkening in color and an increase in alkali-soluble substances. The humus thus

produced tends to become more uniform in chemical composition, and is found to consist largely of lignins or lignin-like complexes and of organic nitrogenous substances. This phenomenon was already well recognized by Thénard (1149) and especially by Hébert (408) and Dehérain (209); the latter stated that the "black matter" of manure consists primarily of "vasculose" (lignin) and of proteins, the first being left as a result of the decomposition of the plant residues and the second being formed from the soluble nitrogenous compounds of the manure.

It was at first believed that the availability of different manures depends largely upon the speed of their "humification." The fact that

TABLE 29

Chemical changes produced in the decomposition of horse manure in compost (1233)

CHEMICAL CONSTITUENTS	AT START		27 DAYS		63 DAYS
	Relative concentration	Total weight	Relative concentration	Total weight	Relative concentration
	<i>per cent</i>	<i>gm.</i>	<i>per cent</i>	<i>gm.</i>	<i>per cent</i>
Ether-soluble fraction.....	2.87	3,870	1.36	1,395	1.10
Cold water-soluble organic matter..	3.64	4,860	4.72	4,770	3.31
Hot water-soluble organic matter...	1.48	1,980	5.00	5,040	3.89
Hemicelluloses.....	17.78	23,850	15.40	15,525	13.02
Cellulose.....	28.35	38,025	26.32	26,550	15.59
Lignin.....	15.64	20,870	20.44	20,610	27.02
Water insoluble protein.....	7.81	10,485	11.56	11,655	13.13
Total nitrogen.....	1.44	1,935	1.92	1,935	2.35
Ash content.....	13.48	18,090	14.50	14,625	15.49
Total dry material.....		134,100		100,800	

horse manure is less readily available than cow, sheep, pig, or chicken manure was explained (172) by the fact that the former humifies more slowly. With the advance of our knowledge of the chemical composition of the manure and the processes of decomposition, it was found that the availability of the manure is controlled by its composition. When fresh stable manure is added to the soil, only the water-soluble forms of nitrogen become readily available for the growth of higher plants (515, 69, 412), while the complex organic nitrogenous compounds, which comprise about a half of the total nitrogen in fresh manure, are not available (fig. 13). This is due primarily to two factors: 1. the nitrogen of the organic complexes becomes liberated

slowly and is immediately consumed again by the microorganisms that use the carbohydrates in the manure as sources of energy; 2. at least part of the organic nitrogen compounds are prevented from becoming readily available, through processes of interaction with the lignin complexes in the manure. Only after stable manure has undergone rather extensive decomposition, resulting in the destruction of the excess of cellulose and hemicelluloses, do the organic nitrogenous compounds of

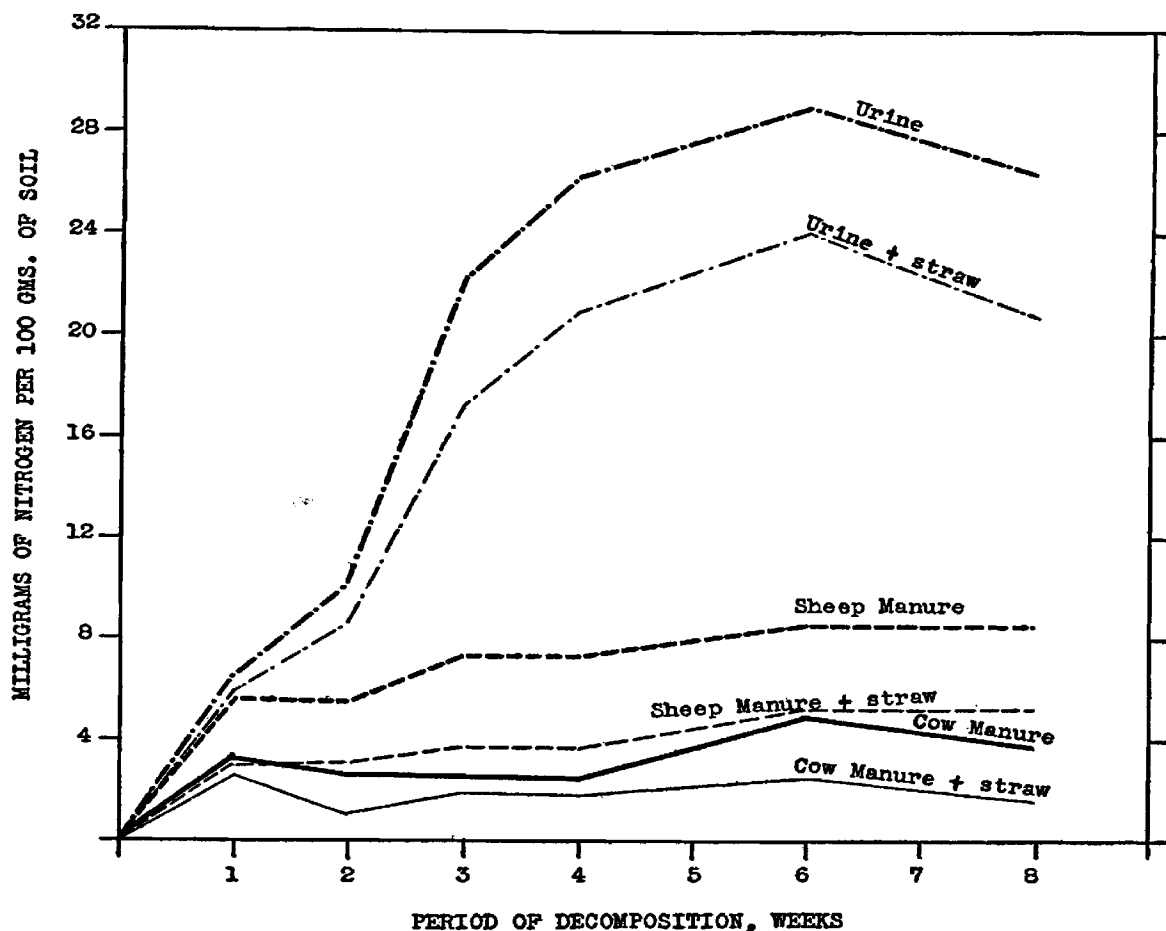


FIG. 13. Influence of straw upon the liberation of nitrogen as nitrate from urine, cow and sheep manure, in the process of decomposition (Joshi).

the manure become partly available for crop growth. This can best be determined by changes in the C:N ratio of the decomposing manure, which becomes gradually narrower, or by the increasing content of organic nitrogen. Lemmermann (622, 625) has shown that when the C:N ratio of composted straw reaches 20:1, the nitrogen content on the basis of dry material has increased to about 2 per cent, the pentosan content has diminished to 12 per cent, and the total decomposition is about 50 per cent. At this stage, the compost has no longer a tendency

to bring about a reduction in the soluble nitrogen when applied to soil. When this compost undergoes still further decomposition, sufficient nitrogen is liberated from the proteins to provide for the needs of the microorganisms attacking the carbohydrates in the compost. Still further decomposition leads to the liberation of nitrogen in excess over the needs of the microorganisms and finally results in the accumulation of nitrogenous materials, which are available to higher plants (271).

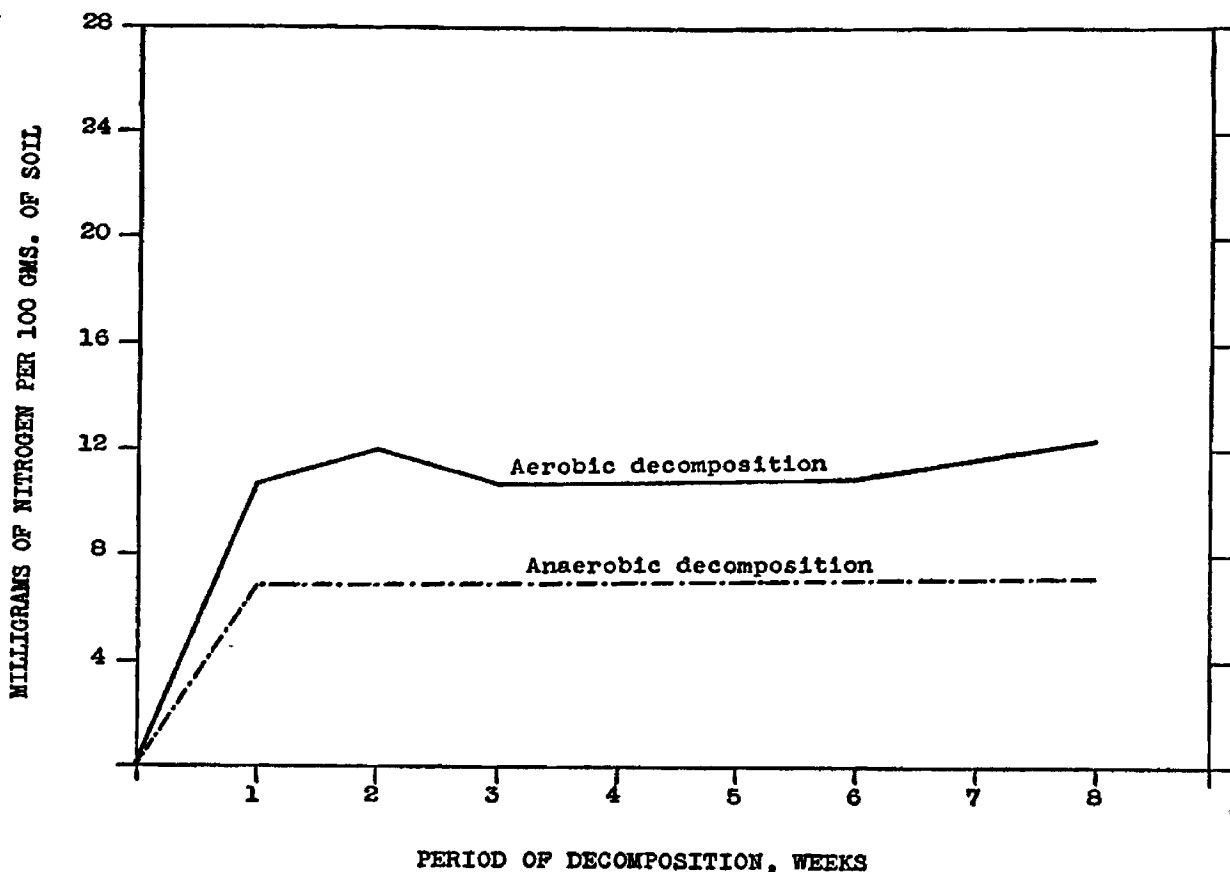


FIG. 14. Decomposition of sheep manure under aerobic and anaerobic conditions, as measured by nitrogen liberation (Joshi).

Barthel (70) explained the slow nitrification in soil of the organic nitrogen in stable manure by the fact that this nitrogen is present in the manure largely in the form of microbial bodies. These bodies, as in the case of *Azotobacter* cells, decompose only slowly, and very little nitrogen is liberated as NH_3 . This is contrary, however, to the results of other investigators (1091, 410), who demonstrated, by measurements of the evolution of CO_2 , that microbial cell substance decomposes very readily. The nitrogen present in *Azotobacter* cells was

actually found (272) to nitrify rapidly, whether introduced into the soil in the form of preformed cells (dry or wet) or allowed to be formed there subsequent to the addition of mannitol. When microbial cell substance undergoes decomposition in soil, only a part of the nitrogen is transformed to nitrate, while another part persists in the soil in the form of certain resistant residues, largely humus-like in nature; even after 90 days of decomposition in sand media, 25 to 64 per cent of the nitrogen in microbial cell substance was still left in the residue (496).

Humus formation in the decomposition of stable manures in composts or in soils is very much similar to the general processes of humus formation; because of the specific nature of the substances undergoing decomposition and the conditions under which this usually takes place, certain special problems may be involved (191, 344, 355, 368, 483, 847, 1217). Among these, may be mentioned problems concerned with conservation of the nitrogen, the hygienic treatment of human excreta and the maximum production of humus (465, 861). The conclusion is frequently reached that, because equal amounts of nutrient elements in the form of mineral fertilizers and stable manures give equal effects upon plants, the latter is not superior or perhaps even inferior to the former. The fact that manure frequently has an insufficient concentration of available nitrogen and especially the importance of the residual effect of manure in soil in building up its humus content are thereby overlooked (625).

There is no doubt that the phosphorus and potassium compounds in the manure are about as readily available as those in artificial fertilizers. However, the nitrogen in the manures is only about one-third to one-half as available as that of inorganic fertilizer; this has been indicated by numerous field tests as well as by nitrification experiments. There is little justification, therefore, for comparing the availability of the nitrogen in organic manures and in fertilizers, without considering the accumulative effects of the manure on the fertility of the soil and its physical condition; this error has been frequently made in fertilizer trials, where only the given crop yields were measured. Stable manures were found to give particularly significant results, as compared with inorganic fertilizers, in dry years and on light soils. The changes in the humus content of the soil as a result of treatment with fertilizers and manures are clearly indicated in the classical experiments of Rothamsted (925a):

Loss of soil organic matter after 50 years treatment

CROP		ORIGINAL SOIL IN 1876	SOIL ANALYSIS AFTER FIFTY YEARS (1926)		
			No fertilizer or manure	Com- plete fertilizer	Stable manure
Barley	Nitrogen content of the soil, per cent..	0.156	0.094	0.109	0.151
Barley	Loss of nitrogen, per cent.....	40	30	3
Barley	Carbon content of the soil, per cent..	1.49	0.90	1.07	1.50
Barley	Loss of carbon, per cent.....	40	28	0
Wheat	Nitrogen content of the soil, per cent.	0.156	0.109	0.104	0.145
Wheat	Loss of nitrogen, per cent.....	30	33	7
Wheat	Carbon content of the soil, per cent..	1.49	1.23	1.07	1.52
Wheat	Loss of carbon, per cent.....	17.5	28	0

Humus formation in the preparation of "artificial manures." Under the term "artificial" or "synthetic" manure, one commonly includes composts prepared from plant residues, of a wide C:N ratio, to which some inorganic fertilizers may have been added. When kept at conditions of favorable moisture content, aeration, and reaction, the plant materials in the compost decompose rapidly. The most important constituent element of the fertilizer added to the compost is nitrogen in an available form; phosphorus and calcium are next in importance. The plant residues that are commonly used in the preparation of composts, such as straw, corn stalks, plant stubble, and leaves, are low in nitrogen and high in complex carbohydrates, namely, cellulose and hemicelluloses. The decomposition of these carbohydrates makes available considerable energy for the growth of microorganisms; this is characterized by the synthesis of microbial cell substance, for which available nitrogen and phosphorus are required by the fungi and bacteria active in the decomposition processes. Because limited amounts of nitrogen are generally present in the plant residues used for the preparation of the composts, the nitrogen and phosphorus required by the microorganisms, as well as some lime and potash, have to be supplied from other sources, in order to insure rapid decomposition. The inorganic nitrogen can be added to the composts in the form of ammonium salts, nitrates, urea, or cyanamide; it is then readily assimilated by the microorganisms during the process of decomposition of the easily decomposable constituents of the plant material and is transformed into organic compounds. As a result of the decomposition the compost is reduced in dry weight, darkens in color, and is gradually

transformed into humus; the C:N ratio of the compost becomes narrower, as a result of the rapid decomposition of the carbohydrates and the synthesis of the organic nitrogenous complexes.

The rapidity of decomposition of the plant constituents in the compost and their transformation into humus depend upon the nature of these residues, their chemical composition, the amount and nature of the inorganic nutrients added, especially the nitrogen, the moisture

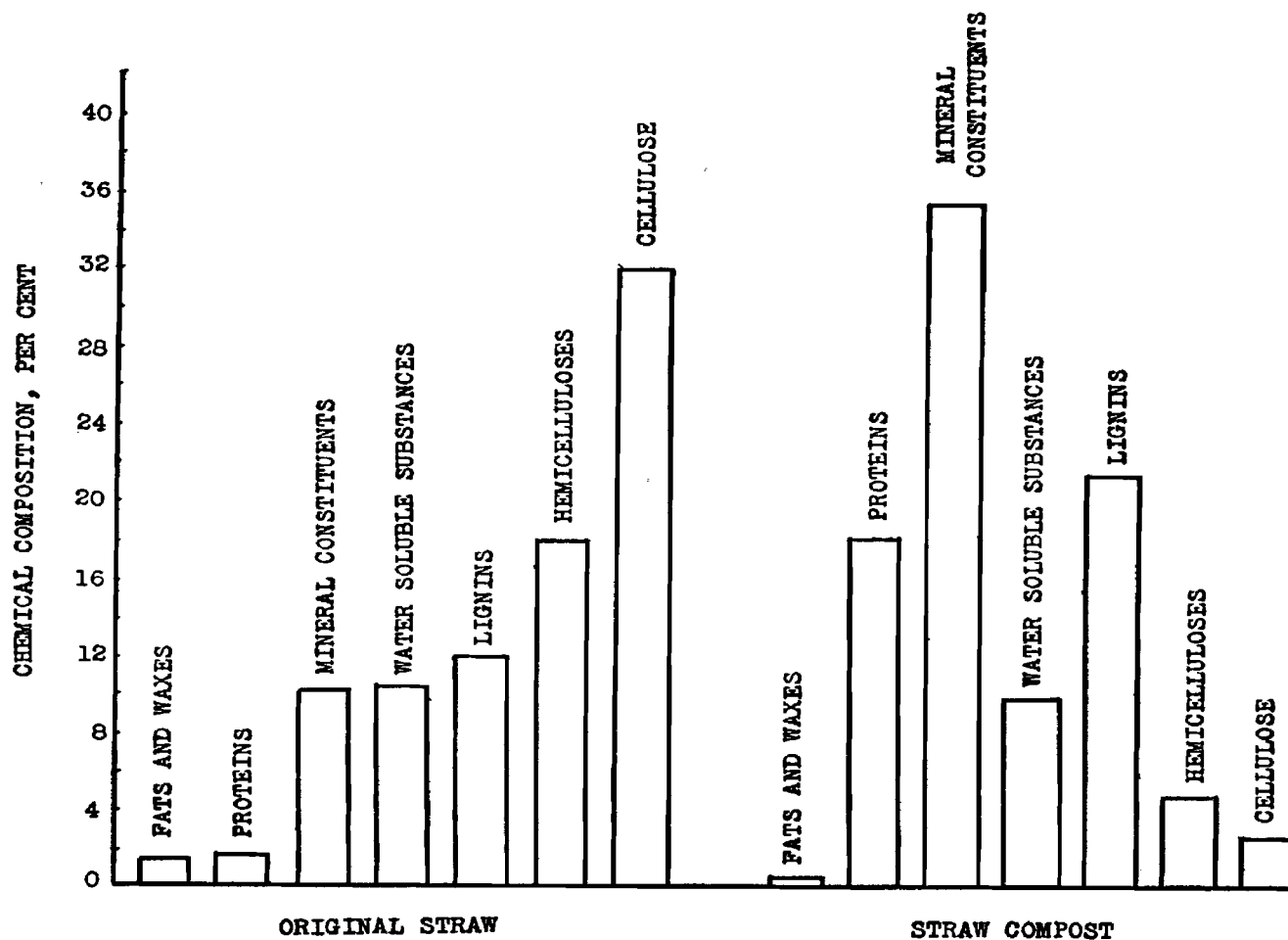


FIG. 15. Comparative chemical composition of oat straw and of a compost prepared from it (Waksman and Gerretsen).

content of the compost, its proper aeration, and the temperature control (472, 1046, 303, 215a). The chemical nature of the humus produced as a result of the composting and its effect upon soil processes will also depend upon the nature of the plant residues and upon the conditions and extent of their decomposition. The humus of a compost produced from cereal straw will, therefore, vary from that formed from oak leaves, from pine needles, or from soybean stover.

A detailed discussion of the changes taking place in the formation of humus in the decomposition of plant residues was presented previously (p. 119). Figure 15 shows the relative composition of "artificial manure," as compared with that of the original plant material from which it was prepared. Oat straw was allowed to decompose for 273 days, at 37°C., in the presence of added inorganic nutrient salts. As a result of the decomposition, the cellulose has disappeared almost completely; the hemicelluloses and fats have been markedly reduced; the lignin has increased appreciably in relation to the other constituents, while the relative amount of ash and protein have increased to an even larger extent. The increase in the relative ash content is due to its accumulation as a result of the destruction of some of the organic complexes. The increase in the protein content is not only relative to the total constituents but is also absolute, largely as a result of the synthesis of microbial proteins from the inorganic nitrogen added to the compost. The lignin has increased because it is more resistant to microbial decomposition than are the other plant constituents. Temperature and moisture have an important influence upon the rapidity of decomposition of straw in composts and upon the formation of humus (1229). A comparison of the chemical composition of composts of "artificial manure" with that of composts of horse manure is found in table 26.

Instead of using a highly carbonaceous and low nitrogen containing material, such as straw, for the preparation of composts, which necessitates the addition of inorganic salts of nitrogen, one may employ a mixture of two organic residues, one low in nitrogen and another high in nitrogen. A mixture of this nature was first used (1234a) for the preparation of composts for mushroom production. Scheffer and Karapurkar (944a) found that a mixture of alfalfa and straw, in a ratio of 1:3, with a nitrogen content of 1.363 per cent and a C:N ratio of 26.4-30.8:1, contained a proper balance between carbon and nitrogen, in respect to decomposition. A higher concentration of alfalfa led to nitrogen liberation, and a lower, to a lack of nitrogen. In general, if the C:N ratio of the organic substances added to the soil was above 20:1, nitrification was repressed; below 20:1, active nitrification set in soon after the active processes of decomposition had passed. The chemical composition of the materials, the rapidity of decomposition, and the nature of the microorganisms were found to be of importance in this connection. Similar results were obtained (465) in the composting of plant residues with stable wastes, under aerobic conditions (651).

In the presence of a certain amount of moisture, animal manures and plant residues, such as hay and peat, kept in heaps, may undergo a process of anaerobic decomposition, resulting in the formation of certain volatile substances which, on coming in contact with air, ignite spontaneously. The large heap acts as an insulator, preventing radiation of heat from the inside and preventing penetration of oxygen from the outside. The lack of an excess of moisture in the case of the hot fermentation of manure, prevents the absorption of the heat. The moisture, temperature, and lack of oxygen penetration create conditions which are favorable for spontaneous heating (157).

Humus formation in the decomposition of green manures. The study of the decomposition of green manures and of their transformation into humus is concerned with two distinct problems; namely, the liberation of the nitrogen in the plant material in an available form, and an increase of the supply of humus in soil. Green manures are utilized for several very distinct purposes in farm practice: 1. to increase the supply of total and available nitrogen in the soil: to this end, various leguminous plants are grown, the nature of the legume depending largely on such factors as the region, the season of the year, the nature of the soil, and the rotation system; 2. to conserve the nutrient elements of the soil, especially the nitrates, from being leached out during the part of the year when no cultivated crops are being grown on the soil; 3. to increase the supply of organic matter in soil.

In most of the investigations dealing with the subject of green manures, chief attention has been directed, not to the nature of the organic constituents of the green manure plants or to the processes of their decomposition or to their decomposition products, but to the influences that these organic constituents exert upon crop production. However, in order to understand the nature of the processes involved in the decomposition of the plants used for green manuring purposes and their transformation into humus, it is essential to know the chemical composition of those plants. A plant changes in chemical composition during growth (1242, 171), hence during decomposition of plant materials representing different stages of development there will be differences in the nature of the processes, in the rapidity of decomposition, and in the transformation of the nutrient elements into available forms. Table 30 shows the results of decomposition of a typical green manure plant (rye), harvested at different stages of growth. When the plants are young, they decompose rapidly, as shown by the rapidity of CO₂ evolution; a large part of the nitrogen found in the plants is lib-

erated as ammonia. When the plants are mature, they decompose much more slowly; their low nitrogen and high carbohydrate contents are responsible for the fact that not only is there no nitrogen liberated, but some of the nitrogen is actually removed from the surrounding medium by the microorganisms active in the decomposition processes.

In the decomposition of green manures in soil, the plant materials containing a balanced proportion of available carbohydrate compounds to available nitrogen compounds decompose rapidly (640); those containing an excess of nitrogen compounds decompose more rapidly; and those containing an excess of carbohydrates decompose less rapidly. This is true of both legumes and non-legumes. When comparatively young plant materials are used as a green manure, there is danger of a loss of nitrogen through volatilization as ammonia, the loss depend-

TABLE 30

Rapidity of decomposition of rye plants at different stages of growth (1242)

Two grams of dry material decomposed for 27 days

STAGE OF GROWTH	CO ₂ GIVEN OFF	NITROGEN LIBERATED AS AMMONIA	NITROGEN CONSUMED FROM THE MEDIUM
	<i>mgm. C</i>	<i>mgm. N</i>	<i>mgm. N</i>
Plants only 25-35 cm. high.....	286.8	22.2	0
Just before heads begin to form.....	280.4	3.0	0
Just before bloom.....	199.5	0	7.5
Plants nearly mature.....	187.9	0	8.9

ing upon the amount of total and available nitrogen that the green manure contains (203).

The carbon-nitrogen ratio of the decomposing plant material becomes narrower with the advance in decomposition and tends to approach 10:1, namely, that of normal soil humus (1311). The transformation of the different organic constituents of plants used for green manuring purposes at different stages of growth is brought out in table 31. The young plants, low in lignin and in cellulose but high in water-soluble substances and in nitrogen, decompose much more rapidly than the mature plants; they leave a much smaller residue (humus), and only a small part of the original nitrogen is stored away in the humus. These results confirm the general considerations presented previously in connection with the discussion of the origin of humus. A considerably larger amount of humus is left in the soil as a result of decompo-

sition of more mature plants because of their slower decomposition and their higher lignin concentration; a smaller amount of the plant nutrients is liberated from the plants in the more mature state. Frequently a considerable period of time may elapse before these nutrients, especially the nitrogen, are liberated. The age of the plant at the time it is used for green manuring purposes is thus found to exert an important influ-

TABLE 31

Formation of humus during decomposition of rye plants at different stages of development (1242)

STAGE OF GROWTH	CHEMICAL CONSTITUENTS	AT BEGINNING OF DECOMPOSITION†	AT THE END OF DECOMPOSITION PERIOD*	
		mgm.	mgm.	per cent of original
Just before heads begin to form	Total water-insoluble organic matter	7,465	2,015	27.0
Just before heads begin to form	Pentosans	2,050	380	18.5
Just before heads begin to form	Cellulose	2,610	610	23.4
Just before heads begin to form	Lignin	1,180	750	63.6
Just before heads begin to form	Protein insoluble in water	816	253	31.0
Plants nearly mature	Total water-insoluble organic matter	15,114	8,770	58.0
Plants nearly mature	Pentosans	3,928	1,553	39.5
Plants nearly mature	Cellulose	6,262	2,766	44.2
Plants nearly mature	Lignin	3,403	3,019	88.7
Plants nearly mature	Protein insoluble in water	181	519	286.7

* 30 days for young plants and 60 days for mature plants.

† 10 gm. material (on dry basis) used for young plants and 20 gm. for old plants.

ence upon the amount and rapidity of liberation of the nutrient elements in an available form and upon the chemical nature and abundance of the humus produced. One can thus control to a considerable extent either the liberation of the nutrients or the amount of humus to be produced from a green manure crop.

When one compares different plant materials which are commonly

used for green manuring purposes, especially legumes with non-legumes, even more striking results are obtained (63, 634). Since legumes are higher in nitrogen and decompose more rapidly than non-legumes, the rate of liberation of the nitrogen in an available form and the nature and abundance of humus produced will be different with each type of plant material. Even legume residues, such as cowpea roots and stems (516) and soybean residues (1189), when plowed under, may exert a depressing effect upon the crop immediately following. This is due to the wide carbon-nitrogen ratio of the material, especially the roots. This injurious effect, however, is not so great as that following the application of a non-legume in a mature state or when it is low in nitrogen (1290). This phenomenon can best be measured by the effect of plant materials upon the formation of nitrate in the soil; sorghum roots cause a more rapid disappearance of the nitrate than do corn roots (1290, 1278, 334), whereas an application of clover leads to a more rapid reappearance of nitrate than does an addition of timothy.

The humus left from the decomposition of green manures does not completely replace the humus lost from the soil as a result of cultivation. Mooers (723) has shown, for example, that when cowpeas were grown on a soil and the whole crop was turned under annually, there was a loss of 0.11 per cent humus, calculated from the total carbon content of the soil, or a total of 2,200 pounds of humus per acre during the 20-year period. When the cowpea crop was removed and only the stubble turned under, the loss of humus from the soil was considerably greater; at the end of the 20 years, there was a total loss of 0.24 per cent humus, or 4,800 pounds per acre. As a result of the turning under of 20 annual crops of cowpea hay containing about 20 tons of dry matter, there was left in the soil only 2,600 pounds of humus, i.e. only 6.5 per cent of the total plant material was left in the soil as humus. In the case of the same soil receiving stable manure, at the rate of 4 tons per acre, for a period of 20 years, a gain of 0.11 per cent of humus took place. On measuring the "black matter" of the soil, referred to as "active" or "colloidal" humus and extracted with dilute ammonium hydroxide solution, a loss of 0.07 per cent was found, after 10 years, in those plots in which the cowpea crop was removed; when the cowpeas were plowed under, the loss was 0.05 per cent; however, the soil receiving stable manure showed a gain of 0.03 per cent.

The nature of the soil must also be considered in the utilization of specific plants for green manuring purposes. In the case of soils in a good tillable condition, the acidity of the soil does not affect the

decomposition of the green manures (1156). In the case of arid lands (1151), certain anomalies have been observed. Under dry land cultivation soils were found to respond to phosphorus applications but not to nitrogen or potassium. Under irrigation, however, the soils respond well to nitrogen, but less well to phosphorus and potassium.

Stable manure has a beneficial effect, but not green manure, under dry land agriculture. Under irrigation, green manures are efficacious. The same is true of the high rainfall sections. It was suggested that the important effect of green manure is exerted upon the soil solution and upon the soil colloidal complex. This effect is not sought, therefore, in an increase in humus as such, but in its ability to replenish a depleted soil solution. It is effective only on soils in which the soil solution is subject to consistent leaching, so that the bases left in the absorbing complex are held too tenaciously to maintain a satisfactory concentration in the liquid phase under the influence of CO_2 alone. Green manures also exert an important influence upon the activities of microorganisms (1047), especially nitrate formation (662, 652, 678, 1278) and ammonia liberation. Under still other conditions, such as paddy lands (498) or soils of the tropics (1066), the use of green manures opens special problems for consideration. In China and in Japan, the green manure cover crop is frequently allowed to decompose in composts, before it is plowed into the soil (470).

The effect of a green manure crop upon the soil thus depends upon: (a) the nature of the plant and its age, which influence its chemical composition and the rapidity and nature of its decomposition, (b) the type of soil, (c) the method of soil treatment, and (d) the system of crop rotation (825, 1294, 203). The use of leguminous plants usually favors the growth of good subsequent crops (346a). This is also true in orchards, especially during the early growth of the trees (184). In some instances, it has been found that it made little or no difference whether the green manure crop was buried young or at a mature stage, fresh or desiccated, or even whether the tops were burned so long as the ashes were retained; a stable system of farming based on green manuring could thus be maintained (282).

Humus in mushroom composts. The successful commercial production of cultivated mushrooms is at present dependent chiefly upon the supply of available horse manure as a source of material suitable as a medium for growth; this manure is composted for a certain length of time with the result that it is transformed into a dark colored humus. This process is usually carried out by placing the manure in heaps and

allowing it to decompose under aerobic conditions; to bring this about, the compost is turned at frequent intervals. Water is supplied to keep the compost at about 70–80 per cent moisture so as to make the conditions favorable for the growth of the microorganisms decomposing the constituents of the manure. Under these conditions, the manure undergoes rapid decomposition, as shown by the abundance of heat evolved; the compost is turned three or four times and mixed thoroughly. Within four to eight weeks, depending upon the nature of the manure, especially the relative amount and nature of the bedding, the abundance of liquid urine, or the presence of soluble nitrogenous substances, the season of year, and other conditions, a dark brown to black compost will result which serves as a favorable medium for the growth of the mushroom (603).

The resulting compost has a chemical composition which is quite different from that of the original manure. This is due to the fact that during the process of composting, a number of changes take place in the various chemical constituents of the manure. These changes can be briefly summarized as follows: There is an appreciable decrease in the water-soluble substances, the fats, cellulose, and hemicelluloses; a relative increase in the concentration of the lignins; a large increase in the protein content; and an increase in ash running parallel to the decrease in total dry material in the compost. In this dark colored mass of humus the ligno-proteins predominate, associated, however, with a considerable amount of cellulose and hemicelluloses, as shown in table 29.

A similar compost can be prepared from plant residues alone, such as straw or other material, without the use of animal excreta. In such a case it is essential to supply the necessary elements required by the microorganisms for the rapid decomposition of the plant materials; a compost will then result which is similar in chemical composition to the compost resulting from horse manure (215a). By employing a mixture of straw and a green material, such as clover, alfalfa, young rye plants, or tobacco stems, one can prepare a compost which will be inexpensive and meet the same needs as the manure compost (1234a).

The compost prepared in the foregoing manner, either from manure or from plant material plus inorganic fertilizer, is placed in beds and allowed to come to a uniform temperature and moisture. The beds are then "spawned" or inoculated with the mycelium of the cultivated fungus, *Psalliota (Agaricus) campestris*; the mycelium of this organism begins to develop rapidly, growing throughout the mass of the compost.

This fungus does not attack the humus in the compost as a whole but feeds primarily upon certain of the humus constituents. The chemical changes produced by the mushroom mycelium in the compost are characterized primarily by the decomposition of the proteins and the lignins in the compost and by an increase in the water-soluble constituents, including nitrogenous substances. The hemicelluloses and the cellulose are also attacked by the fungus, frequently to a considerable extent; this points to the ability of the organism to utilize these plant constituents.

In the process of composting of horse manure or the mixture of plant residues, chemical changes were brought about by the microbiological population of the manure and compost which made it a favorable medium for the growth of the mushroom fungus. Among these changes, the increase in protein and lignin content is of special importance. The proteins are produced by the microorganisms in the compost at the expense of the ammonia or other soluble forms of nitrogen originally present in manure, while the polysaccharides are used as sources of energy. The accumulation of the lignin is due to its resistance to decomposition by the common fungus and bacterial population of the compost. These two groups of complexes are of decided importance in the growth of the cultivated mushroom, since they serve as the nutrients most essential for its development. The process of composting can be carried out too far, in which case the material becomes again a poor medium for mushroom production. Whether the complete removal of the cellulose renders the lignin or the resulting ligno-proteins resistant to attack by the mushroom or whether the physical condition of such a compost makes it difficult for the development of the mycelium, still remains to be determined.

The development of microorganisms which bring about the decomposition of the carbohydrates in the composts results in the evolution of considerable heat; this would also be injurious to the growth of the mushroom. In the preliminary composting of the manure or the plant material for a period of 4 to 8 weeks, the compost gradually becomes a poor medium for the growth of the common fungi and bacteria. The mushroom mycelium grows at the expense of those complexes in the compost which are not decomposed readily by the common organisms or which are synthesized in the process of decomposition of the compost; namely, the lignins, the organic nitrogenous complexes, and, to some extent, the cellulose.

Répin (881) believed that the mushroom fungus feeds exclusively

upon the cellulosic materials in the compost; the soluble substances play thereby only a negligible part, serving to bring about the dissolution of the agglutinant substances present in the straw, which result in the liberation of the cellulose; the minerals and the nitrogen com-

TABLE 32
Chemical composition of manure and residue after mushroom growth (409)
Per cent of dry material

CONSTITUENTS	FRESH MANURE	COMPOSTED MANURE	SPENT MUSHROOM MANURE
Mineral substance.....	13.00	31.25	40.00
Fats.....	4.00	0.70	0.60
Cellulose.....	35.20	24.25	13.60
Xylans, etc.....	24.83	10.86	12.70
Vasculose (lignin).....	9.60	15.00	13.40
Gums, tannins, organic acids.....	5.25	2.19	6.27
Protein.....	8.12	15.75	13.43
Ammonia nitrogen.....	0.290	0.005	0.032

TABLE 33
Decomposition of the organic constituents of composted horse manure by Psalliota campestris (1233)
Period of decomposition, 215 days

CHEMICAL CONSTITUENTS	CONTROL	BROWN STRAIN OF AGARICUS	WHITE STRAIN OF AGARICUS
Total weight*.....	100	82.4	85.0
Ether-soluble portion.....	1.26	0.48	0.43
Water-soluble organic matter.....	3.24	18.70	25.05
Hemicelluloses.....	6.80	2.64	2.02
Cellulose.....	12.51	7.51	6.66
Lignin.....	22.91	7.77	6.31
Ash.....	45.20	56.90	61.50
Total nitrogen.....	1.560	1.770	1.790
Water-soluble nitrogen.....	0.142	0.884	1.172
NH ₃ -N.....	0.041	0.283	0.465

* Residual weight is calculated to 100 gm. of original material; all other results are calculated on per cent basis of dry material.

pounds were not considered as playing any part in the nutrition process. Hébert and Heim (409) reasoned, with justification, that the minerals and the nitrogenous substances present in the mushroom must be derived from the compost. Manure was even found to be short of calcium and potassium, as compared with phosphorus, to supply the

mineral needs of the organism. A careful study of the chemical changes produced in the organic constituents as a result of composting brought out the fact that during this process there are a diminution in the ammonia content, in the fats, and especially in the cellulose and xylan and a proportional increase in the organic nitrogenous substances and in the vasculose (lignose), as shown in table 32. These transformations were similar to those obtained by Hébert (408) for the decomposition of manure on the farm in general.

A detailed analysis of the processes involved in the growth of mushrooms upon composted manure is brought out further in table 33, which confirms the general observations discussed previously. The composts used in this experiment were washed free from water-soluble substances, sterilized, and inoculated with pure strains of *Psalliota campestris*. Although the actual amount of reduction of the total organic matter by the growth of the fungus is comparatively small, the transformation of certain organic constituents in the compost is very marked. The residue, usually known as "spent mushroom soil," is much lighter in color than the original compost, is richer in ash and in water-soluble substances, and is poorer in lignin and in cellulose, hence it can decompose much more readily than the compost itself when added to the soil (1227).

Organic fertilizers as sources of humus. In addition to stable manures, composts of animal manures and of plant residues, and green manures, a number of organic fertilizers of animal and plant origin are frequently added to the soil. These include various types of peat, the chemical nature of which is discussed later; guano (836); dried blood; bone meal; tankage; fish meal; leather meal; hoof meal; cottonseed meal; linseed meal; and others. Most of these materials are applied to the soil primarily because of their high content of nitrogen and phosphorus. However, before these elements become liberated in a form available for plant growth, they must be decomposed. The decomposition is never complete, since some of the organic constituents give rise to humus. The formation of humus is indicated by an incomplete liberation of the nitrogen in an available form, as a result of decomposition by microorganisms, and by the chemical changes which the organic nitrogenous complexes undergo in the soil. Lathrop (612) has shown that in the decomposition of dried blood in soil, a part of the nitrogen is transformed into a protein which is characteristic of the organic matter of the soil. The lower the nitrogen content of the organic fertilizers, the slower is the liberation of the nitrogen in an available form and the greater is the amount of humus produced.

CHAPTER IX

HUMUS IN FOREST AND HEATH SOILS

“Le terreau forestier comprend l’humus du sol et l’humus de la couverture.”—HENRY.

Nomenclature of forest humus. No other phase of humus investigation, with the possible exception of the “humic acid” conception, has been so much confused as that of the humus in forest soils. A number of causes are responsible for this confusion; namely, the variation in nature and chemical composition of the residues of the forest vegetation, the relation of these residues to the soil proper, and their decomposition as influenced by the specific nature of the mineral portion of the soil. The tendency to confuse local distinctions of soil type, which result from minor variations in structure and chemical nature of soil, with the broad natural systems of classification has further contributed to the confusion.

The yearly contributions of the surface forest vegetation to the soil, in the form of needles, leaves, cones, pollen, branches, and twigs, remain, for a shorter or longer period of time, upon the surface of the soil, gradually decomposing and becoming, sooner or later, a part of the soil. The nature and speed of decomposition of these residues depend upon a number of factors: 1. The nature of the higher vegetation: the needles of evergreens vary markedly in chemical composition from the leaves of deciduous trees; this difference in composition exerts a marked influence upon the rapidity of the decomposition processes and the type of decomposition. 2. The nature of the microorganisms active in the disintegration of the plant residues: when fungi are predominant, a type of humus will result which is different from that produced by a population consisting largely of bacteria and invertebrates. 3. The nature of the soil, particularly its structure, which affects the penetration of the water, and its chemical composition, especially the reaction and abundance of basic materials. 4. Environmental and climatic conditions, including rainfall and temperature. The aerobic or anaerobic nature of the decomposition processes, the preferential development of fungi or bacteria, and the speed of decomposition are considerably influenced by the environment.

The type of forest floor which is formed will depend upon the particular combination of the aforementioned factors. These will control, not only the speed of decomposition of the plant residues, the amount of humus formed, and the chemical nature of this humus, but also its influence upon soil processes and forest growth. Climate and vegetation are the two most important controlling factors determining the type of forest humus produced. Since these factors differ greatly in character in different parts of the world, attempts made by investigators in various countries to construct systems of classification based upon local conditions, which may not have parallels elsewhere, have frequently resulted in nomenclatures which are only of local importance and which are unsuited for universal application without considerable modification.

Practical foresters and agricultural chemists have classified certain types of forest soil, on the basis of the forest vegetation, in order to develop a specific forest policy. In some instances, as in the case of the system developed by P. E. Müller (737), a definite useful end was accomplished; attention was thereby called to the fact that different types of forest soil are produced as the result of specific soil and environmental conditions, leading to specific processes of decomposition brought about by the activities of definite soil microbial populations. In many other instances, however, attempts made to attach permanent labels to forest soil types were less successful, since local differences were usually confused with important fundamental soil processes; many of the distinctions suggested for the various forest soil types were based largely upon the appearance of the forest vegetation or of the surface soil layer rather than upon the fundamental causes underlying the formations of the specific soils (21, 274, 372).

As a result, numerous labels were attached to forest soil types. Frequently different designations were applied to the same general type of forest humus, because of local distinctions. It is sufficient to cite such terms as "humus layer," "humus cover," "raw humus," "surface humus" (Auflagehumus), "mor," "dry peat" (Trockentorf), "moor peat" (Moortorf), "forest moss peat," "moder," "surface moder," "duff,"—all of which have been used and are still being used for the same general type of humus accumulation on the surface of certain types of forest soil. This indiscriminate terminology, especially when employed by different workers using different languages, was the principal cause of the resulting confusion. When some of the foregoing names were used to designate, on the one hand, specific soil types as a

whole and, on the other hand, only certain layers of the forest soil profile, the confusion became chaos. Because of the varying conditions of decomposition of forest residues and of soil formation, a specific soil type may differ from other similar types in minor characteristics, but still possess the same general features.

Confusion in the nomenclature of forest humus types became even more aggravated as a result of the fact that most of the pedologists who attempted to define soil types, altogether disregarded the surface humus layer of forest soils: they considered this layer not as a part of the soil proper, but as something extraneous, merely covering the surface of the soil. In making this assumption, one neglects the fact that the humus layer gives to the forest soil some of its most important characteristics and contributes materially, if not largely, to the development of the individuality of the soil. The humus layer of the soil should, therefore, be considered as a part of the soil itself (606).

No attempt will be made here to suggest any new system of classification of forest soils or to evaluate old systems; emphasis will be placed only on the processes involved in the transformation of the organic matter in forest soils and upon the types of humus resulting. The term "humus" will of course be applied here, as throughout this book, to all the plant and animal residues brought upon or into the soil and undergoing decomposition.

General types of forest humus. As early as 1826, Sprengel (1075) recognized the existence of a number of humus types which are formed during the decomposition of plant residues under different conditions. Emeis (269) pointed out, in 1875, that humus formations in different forests possess certain distinct characteristics. He distinguished three general types of humus: in one, the organic matter is more or less mixed with the inorganic part of the surface soil layer, and the nitrogen may be expected to accumulate as nitrate; in two others, the organic residues accumulate principally on the surface of the soil. In 1878, P. E. Müller (737) submitted evidence to prove that the nature of the humus layer modifies the type of forest soil formed; this humus layer depends on climate, vegetation, moisture content, and biological activities in the soil. Müller separated the forest humus into two general types; namely, *mull* (muld in Danish) and *mor*. The mull was considered to represent an intimate mixture of the humus with the mineral soil, in the form of a loose friable mass with a crumbly structure; the humus content of the mixture was found to be rather low, usually less than 10 per cent; this type of soil is inhabited by large earthworms and

supports an abundant vegetation of geophytes. In the case of the mor soil, a humus layer very high in organic matter is formed on the surface of the mineral soil, in the form of a dense carpet; large earthworms are missing in this type of soil; the predominant vegetation is different from that of the mull soil, consisting largely of ericaceae and mosses. In addition to these two general types of forest soil, Müller recognized certain transitional phases, such as "mull-like mor" or "insect mull," "alpine humus," etc.

Frank (307) emphasized the fact that forest humus is not merely a mass of residues of individual plant constituents, but is a living system in which numerous fungous hyphae penetrate the humus in all directions and frequently make up a considerable part of the total organic matter in the humus.

These early conceptions of forest humus, which seemed to lay a definite foundation for further study of forest soil types, were unfortunately either completely disregarded by subsequent investigators or were restricted in their application. Ramann (859) confined the term "mull" to the designation of only that part of the soil which consists of animal excrements, whereas the term "mull soil" was applied to any soil which has a friable, crumbly structure. Albert (21) attempted to limit the term "mull" to only that type of humus which has been brought into the soil in solution, whereas the term "moder" was used to designate humus which has been brought into the soil mechanically. The designation "raw humus" became generally accepted for the same soil type called "mor" by Müller; frequently, however, the terms "peat" or "dry peat" were also applied indiscriminately to the same type of soil; more recently the term "surface peat" has been utilized (1203-5). This misuse of the term "peat" is rather unfortunate, since it confuses a typical forest soil type with that of a peat; the latter is a humus formation of a distinctly anaerobic environment and has little in common with forest soils, except that certain types of peat originate from forest growth. The confusion has become especially marked in the case of forest soil formations which are designated as "moder," "dry peat," and "surface peat."

Frequently, various other types of humus have been recognized, based, not upon fundamental differences in chemical composition, or the processes of formation, or the nature of the decomposition processes, but upon mere superficial characteristics. Among the terms are found "primary humus" or "secondary humus," "mild humus" or "strong humus," humus of "fibrous" or "crumbly" structure or "structureless"

humus. It is sufficient to call attention, by way of illustration, to the classification of Erdmann (274), who recognized nine types of forest soil, including, in addition to "mull," "moder," and "dry peat," also "moder soil humus," "peat soil humus," "field soil humus," "black soil humus," etc. Heuell (433) soon afterward remarked that only the first three types are of importance and, of these, the second and third are preferably combined into one group, namely, the "raw humus" formations, which brings us back to the original classification of P. E. Müller. An attempt to distinguish between "surface humus" and "soil humus" is also unjustified, unless these distinctions are based upon a difference in the chemical nature of the two forms of humus.

Without going into a detailed discussion of the various systems proposed for the classification of forest soils, most of which are only of local significance, it can be concluded that the early conception of Müller, in a somewhat modified form, can fully answer the present needs. All forest soils would thus be grouped into two general classes; namely, *mull* and *mor* or *raw humus*; these can be subdivided into several sub-types, depending on local conditions. Juncker (518), for example, recognized three types of humus in the spruce plantations in Denmark: "poorly humified," "amorphous," and "fibrous" types. Bornebusch (129) suggested that the soil types be divided on the basis of morphological characters, which can be observed directly in nature with the naked eye. Romell and Heiberg (913) proposed the substitution of the word "duff" for "raw-humus." They recognized several types of duff, depending on the structure of the humus; namely, "root duff," "leaf duff," "greasy duff," and "fibrous duff"; the mull type was also subdivided into "crumb mull," "grain mull," "twin mull," and "detritus mull." Various other modifications of this general system have been suggested, as in the case of the following grouping (660):

1. podsol type (equivalent to raw humus, with a definite leached layer),
2. raw-humus type (no gray podsolized layer or only a very thin one),
3. humus type, 4. mild-humus type, 5. mull type.

Humus formation as a basis of classification of forest soils. Several points of view should be considered in any attempt to develop a useful system of classification of forest soils, on the basis of humus formation, namely:

1. The biological point of view, first expressed by P. E. Müller, later by various other Scandinavian investigators, and more recently by Vater (1205), Romell (911), and others; the biological factors, especially the higher vegetation, have been considered as contributing

materially to the differences in the forest soil types and to the characterization of the forest soil humus. Müller emphasized the fact that the various types of humus produced in different forests are a result of the visible and invisible "microcosm" composing the living part of the humus layer.

2. The chemical point of view, as expressed by Ramann, who paid particular attention to the influence of the chemical composition of the inorganic soil layer, especially the colloids and bases, on the nature of the forest soil humus.

3. The genetic point of view (regional soil science) as developed by the Russian pedologists, who considered climate as the all-important factor in determining soil types and soil characteristics.

4. The microbiological point of view, as expressed by Hesselman, Falck, and others. The influence of trees in modifying the type of forest soil was considered to be (430-2) merely a result of differences in the chemical composition of the litters. Different humus formations are produced as a result of differences in rates of decomposition, these rates being governed partly by the supply of bases and by their loss due to leaching.

P. E. Müller looked upon the formation of raw humus or mor in forest soils as a more or less anaerobic process, similar to that which takes place in the formation of peat; the word "Torf" was actually used to designate this type of humus in the German translation of his work. According to Ramann (859), mull soils are poor in humus because in these soils the organic matter decomposes rapidly; it was believed that the humus accumulates in raw humus soils, by reason of the fact that conditions are unfavorable for decomposition. A difference was believed to exist, not only in the rate of decomposition, but also in the nature of the decomposition processes in these two soil types; the term "decay" was, therefore, used to designate the process of decomposition of organic residues in mull soils, while "putrefaction" was used to designate the decomposition processes which take place in raw humus soils. This explanation of the differences in the nature of the humus in the two types of forest soils has been universally accepted in soil literature. Ramann stated that, in mull soils, an equilibrium is established between the production of litter and the rapidity of humus decomposition, whereas in raw humus soils, an abnormal progressive accumulation of humus takes place.

The mull soil is usually covered with a layer of litter not more than one year old; the upper soil horizon, just below the litter, has a low

organic matter content, frequently 10 per cent or less; this type of soil is characterized by an active fauna of earthworms and myriapods, as

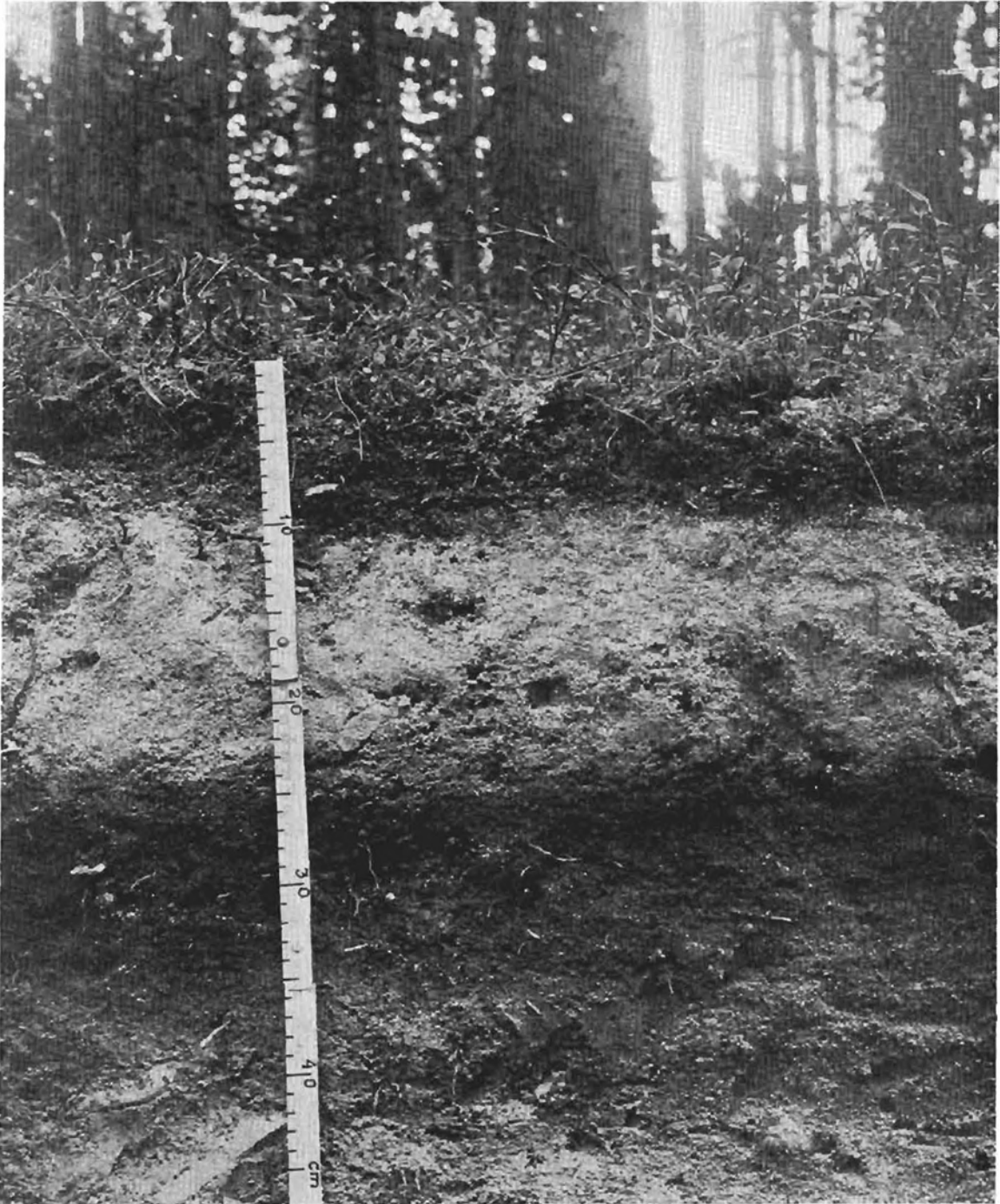


FIG. 16. Humus podsol on ground moraine in North Sweden (Tamm)

well as by an active type of bacterial decomposition, while the fungous flora is kept down (534, 737, 280, 912, 605). It is frequently (129)

subdivided into, (a) true mull, where the humus is largely and conspicuously mixed with the mineral soil, the transition to the latter not being distinct; (b) superficial mull, when the mixture with the mineral soil is not conspicuous and the transition distinct.

The litter of raw humus soil includes several years' accumulation of plant residues; the upper soil horizon, just below the litter, contains 80 to 90 per cent organic matter. The Russian school of pedologists included the surface humus layer of forest soils, when considered at all, in horizon A together with the bleached layer. Ramann demonstrated that two different strata can be distinguished in the unincorporated humus layer; namely, an upper stratum in which the plant residues have retained more or less of their structure, and a lower stratum which is dark colored and in which only few discernible plant fragments remain.

Although most workers agree as to the nature of the mull type of soil and the relationships of humus to its formation, considerable confusion still prevails concerning the raw humus formations. The very function of humus in the formation and chemical composition of the profile in this type of forest soil is still a matter of speculation. The conception prevailing among the German investigators can best be illustrated by the following outline (21, 667, 585):

Raw-humus soil profile

SOIL	NATURE OF ORGANIC RESIDUES
1. Litter	Leaves, needles, branches, twigs, cones, freshly fallen to the ground and little decomposed.
2. Surface humus (moder, surface peat) or raw humus	Homogeneous mass, dark, structureless, formed by rapid decomposition; plant structure still recognized; peat-like in character.
3. Soil humus	Decomposed organic matter incorporated with the inorganic part of the soil.

American workers (28) recognized the following distinct layers in the raw humus profile:

1. *Litter*, comprising the upper, slightly decomposed portion of the forest floor.

2. *Duff*, the intermediate layer, or the more or less decomposed organic matter, just below the litter.

3. *Leafmold* or *humus*, comprising that portion of the profile in which the decomposition of the litter is so far advanced that its original form is no longer distinguishable.



FIG. 17. Mull soil profile exhibiting almost no horizon differentiation (Lunt)

These three layers of the raw humus forest floor have been designated by Hesselman (432) as follows:

1. Surface layer or litter (Förna).
2. F-layer, just below the litter, in which the organic matter is undergoing active decomposition; this has, therefore, been spoken of as the decomposing or "fermentation" layer, to use an English equivalent for the Swedish word.

3. H-layer, in which the original structure of the plant residues can no longer be recognized; this can be referred to as the "humus" layer. This layer is recognized (129) as existing in three different forms: (a) fine humus, (b) fibrous humus, and (c) greasy humus.

This system of separation of the humus horizon (A_0) of the forest soil profile seems to cover the present needs for characterizing the raw humus type of soil in broad terms. Other forms of humus are found in the A_1 - A_2 , or the "bleached" horizon; in the B, or the "accumulation" horizon; as well as in the C horizon, or the original parent material. The humus present in these horizons is not the same chemically,

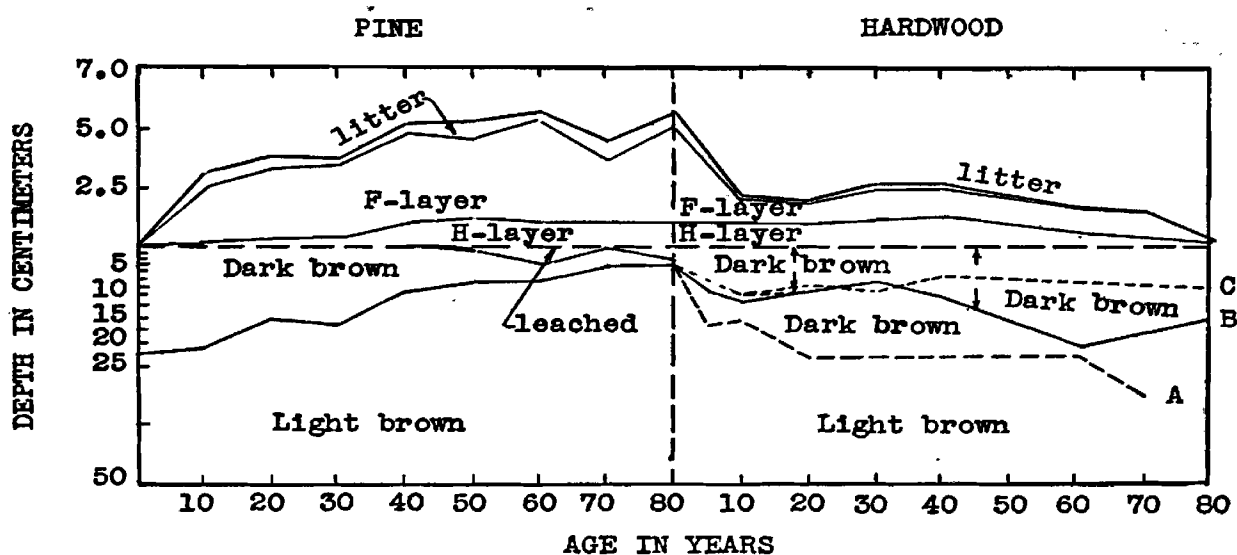


FIG. 18. Development of forest soil profiles under pine and succeeding hardwood vegetation; A, B, C, designate different plots of hardwoods (Griffith, Hartwell and Shaw).

as will be shown later. A typical raw humus profile is illustrated in figure 16 and a mull profile in figure 17.

A change in forest vegetation gradually leads to a change in the nature of the soil and especially in the type of humus formation (fig. 18), as shown by Fisher (299). Frequent forest fires also modify the nature of the soil humus by giving rise to a soil which is less acid in reaction and which contains a greater concentration of nitrogen, total organic matter, and replaceable calcium (436).

Abundance of humus in the forest soil profile. The total carbon content of the organic matter in all the forest soils and in the forest trees of the globe has been calculated (989) to be equivalent to 1,060,000,000,000 kg. of carbon dioxide; this represents about one-half as much carbon dioxide as is present in the entire atmosphere. Two-thirds of

the total amount of carbon dioxide consumed yearly by the surface vegetation of the globe (40,000,000,000 kg. of CO₂) is utilized by the forest vegetation; nearly one-half of this returns to the soil in the form of tree residues. These facts supply sufficient reason for attaching great importance to the transformation of the organic matter in forest soils, both from the point of view of forest economy and for a better understanding of the cycle of nutrient elements in nature. The yearly tree residues left either on the surface of the soil or in the soil itself thus contain nearly 1 per cent of the total carbon dioxide present in the atmosphere. To keep the most essential element, carbon, in circulation, these residues must undergo rapid decomposition.

TABLE 34
Distribution of humus in various forest soil profiles (725)
Pounds of organic matter per acre

FOREST PROFILE	THICKNESS OF LAYER	DEEP RAW HUMUS SOIL	SHALLOW RAW HUMUS SOIL	RICH MULL SOIL	MULL SOIL
	<i>cm.</i>				
Litter.....	0.63- 1.88	13,664	3,774
F-layer.....	1.25- 2.5	18,674	6,173
H-layer.....	5.0 - 7.5	138,254	60,768
Horizon A.....	2.5 -17.5	17,404	11,766	336,773	136,871
Horizon B.....	20.0 -30.0	315,698	173,631	131,757	50,830
Horizon C.....	10.0 -20.0	64,422	18,743	33,037	11,152
Total organic matter.....		554,450	271,081	515,231	202,627

Henry (419) calculated that the yearly fall of tree residues, as leaves, needles, twigs, and bark, per hectare of land ranges from 3,000 to 5,000 kg. Ebermeyer (250) found that the average annual fall of tree residues per hectare ranges from 1,860 to 5,340 kg. of dry litter, with an average of 3,036 kg. There is considerable variation from year to year, depending on the fertility of the soil, the nature of the vegetation, and the climate. The nitrogen content of the litter varies from 0.8 to 1.0 per cent. Alway and Zon (33) reported the yearly fall of pine litter in America as 1,798 to 2,464 pounds per acre, with the following concentration, in pounds, of the important mineral constituents: 41.6-105.0 ash, 8.4-17.7 nitrogen, 8.6-21.3 CaO, 2.2-3.5 P₂O₅, 2.4-4.3 K₂O, and 2.3-6.7 SO₃. The total forest floor, or the surface humus-layer, was found to contain per acre an average of 28,142 pounds of material

(16,553–33,987 pounds), with 28.05 per cent ash, 0.98 per cent nitrogen, 0.86 per cent CaO, 0.17 per cent P₂O₅, 0.15 per cent K₂O, and 0.22 per cent SO₃. Morgan and Lunt (725) found that a 27-year-old plantation of pine trees gave 2,000 to 3,000 pounds of annual residues per acre, not including the dead roots. According to Falck (280), the amount of organic matter in the residues exceeds that of the annual wood growth; the ratio of the total nitrogen in the leaves to that of the wood is 1:1 for a birch forest, and about 2.5:1 for spruce forests. The birches removed 10.4 kg. of nitrogen from one hectare of soil. The birch residues decompose much more rapidly than the spruce residues.

It was at first believed that the total amount of humus in forest soils is determined largely by the soil type and the surface vegetation; however, more recently evidence has been submitted (1132, 725, 911) which points to the fact that the actual organic matter content of both mull and raw-humus soils is, on a dry weight basis, of the same order of magnitude. Tamm (1132, 911) calculated the organic matter in two profiles, representing the two major types of forest soil.

DEPTH	LAYER	TOTAL VOLUME	TOTAL WEIGHT	HUMUS	TOTAL HUMUS
1. Mull or brown forest soil profile					
		<i>liters</i>	<i>kg.</i>	<i>per cent</i>	<i>kg.</i>
Surface to 11 cm.	Crumb mull	110	88	9.7	8.5
12–28 cm.	Upper brown soil	170	170	4.0	6.8
29–56 cm.	Lower brown soil	280	340	2.0	6.8
57–100 cm.	Subsoil	440	660	1.0	6.6
Total humus in 1 square meter of soil, to a depth of 1 meter.....					28.7
2. Raw humus profile					
Surface to 4 cm.	Surface humus	40	...	0.15 kg. per liter	6.0
1–8 cm.	Leached horizon	80	120	2.2	2.6
9–18 cm.	Rust brown layer	100	150	3.0	4.5
19–100 cm.	Subsoil	820	1,230	1.2	14.8
Total humus in 1 square meter of soil, to a depth of 1 meter.....					27.9

The organic matter in the litter, 1–3 cm., in depth, should be added to the above figures in the two profiles.

Morgan and Lunt (table 34) determined the humus content of four

characteristic forest soil profiles, to a depth of 40 inches, in kilograms per square meter of surface, as follows:

SOIL TYPE	HUMUS CONTENT
	<i>kg. per liter</i>
Deep raw humus soil.....	62.1
Shallow raw humus soil.....	30.4
Rich mull.....	57.8
Mull.....	24.9

These results led Romell to the conclusion that there is no consistent difference in the organic matter content of the humus layer or in the entire profile between mull soils and pronounced forms of raw-humus or duff soils. Morgan and Lunt further calculated that the total amount of organic matter in forest soils is of the same order of magnitude as that of prairie soils. However, the nature of the organic matter in the two soil formations is quite different, as can easily be demonstrated by a lower total nitrogen content and by a wider carbon-nitrogen ratio of the organic matter in forest soils.

The C:N ratio of the organic matter in the forest floor and in the underlying 6 inches of soil was calculated (28) for three Minnesota forests and found to be 19:1 and 18.4:1, 24.1:1 and 13.1:1, 12.3:1 and 13.5:1, respectively. In most instances, it was found (659) that the C:N ratio decreases with the depth of profile. The wider C:N ratios in the humus of forest soils than in field and garden soils is due to several factors: 1. a difference in the extent of decomposition, as shown especially by the F-layer, which is high in cellulose and hemicelluloses, while the humus in grasslands is low in carbohydrates; 2. a difference in the mechanism of decomposition, as can be demonstrated by a difference in the microbiological populations; fungi predominate in forest soils, especially those of the raw-humus type, while bacteria and actinomyces are most abundant in grassland soils; 3. the specific nutrition of the forest vegetation, which frequently depends upon the activities of mycorrhiza fungi. When the B horizon is reached, the C:N ratio may become wider or narrower, depending entirely on the rate of mobility of the nitrogenous and non-nitrogenous humus constituents from the surface layers.

The wider carbon-nitrogen ratio of the humus in forest soils has an important bearing upon the method of its determination and calculation. The determination of the loss-on-ignition as a measure of the

humus content of the soil may be justified only for the litter and F-layer, since the inorganic fraction in these formations is very small. When the content of inorganic matter in the soil layer is greater than 10 per cent, as usually occurs below the F-layer, a large error is introduced in the determination. It is more logical, therefore, to calculate the amount of humus from the content of organic carbon found in the

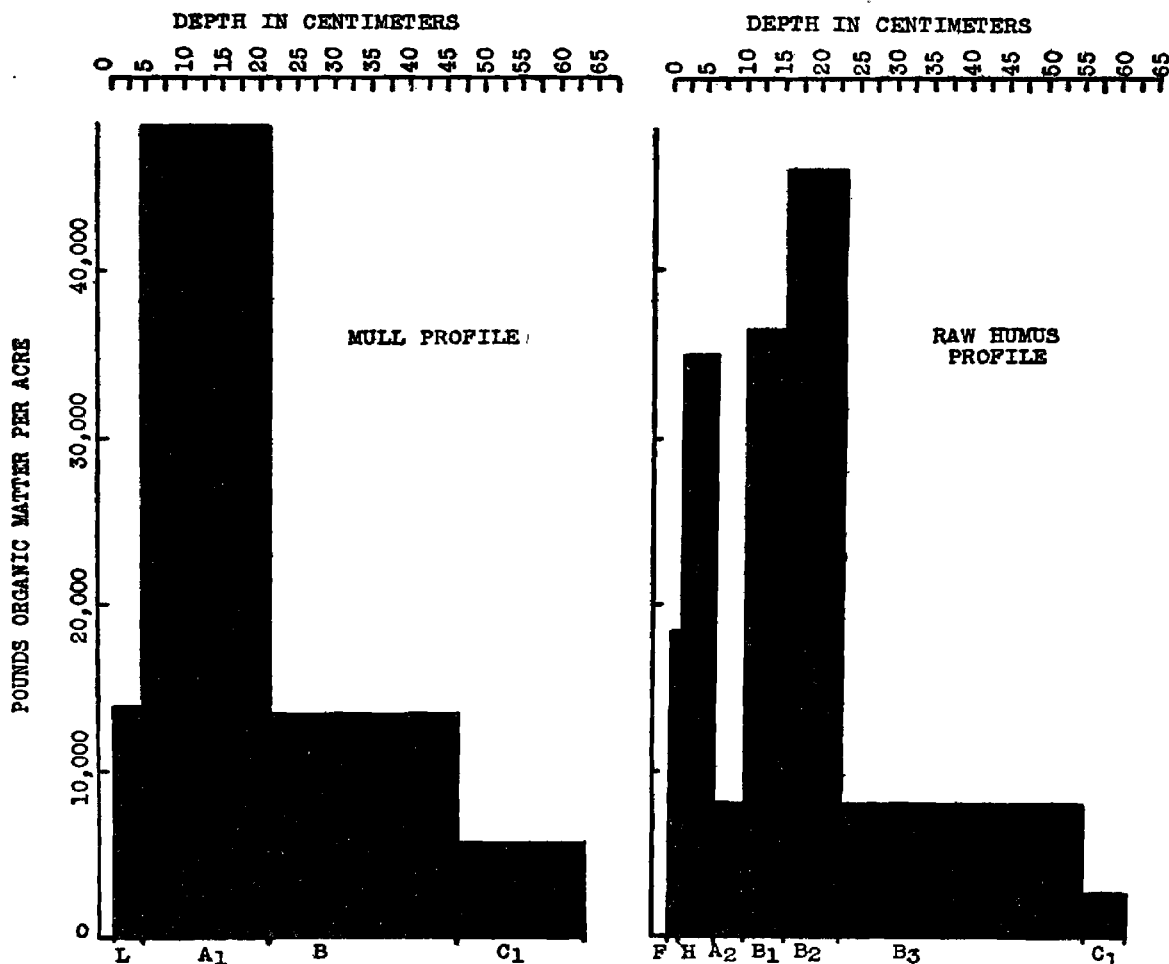


FIG. 19. Organic matter distribution in two typical forest profiles; the quantities are given in pounds per acre-inch. The total organic matter content of the two 24 inch profiles per acre was 404,651 lbs. for the raw-humus and 520,736 lbs. for the mull (Lunt).

particular soil. However, the factor 1.724, which is commonly used, with a certain amount of justification, for calculating the humus content of field and garden soils, is unsuited for application to forest soils; criticism of its use in this connection is fully justified because of the wider C:N ratio of the forest humus. Forest humus, especially in the F- and H-layers, is high in cellulose and in hemicelluloses and has,

therefore, a carbon content much lower than 58 per cent. Lunt (659) suggested that different factors should be used for different layers; namely, 1.89 for the litter, 1.85 for the F-layer, and 1.80 for the H-layer. This suggestion would be justified, if it were known that humus in all forest soils originates from the same vegetation, under the same conditions, and by the action of the same microorganisms. But since this is not the case, different factors would have to be used for each forest. For the present, it is sufficient to determine the humus content of the litter and F-layer by loss on ignition and in all the other layers by the total organic carbon, using the conventional factor 1.724 (p. 243).

Chemical composition of forest litter and of forest soil humus. The chemical nature of the humus in forest soils varies considerably, because of the variation in the composition of the tree residues and of the lower vegetation and differences in the nature of the microorganisms active in the processes of decomposition. Different plants and even the residues of the same plant grown under different conditions vary considerably in chemical composition. The leaves of deciduous trees contain 4–10 per cent ash, with a high content of calcium and magnesium, while the needles of conifers contain 1–10 per cent ash, usually not more than 4 per cent, and are generally poorer in bases. The dry matter of young leaves of deciduous trees contains the greatest amount of nitrogen, phosphorus, and potassium, while mature leaves are highest in total ash and especially in silica and calcium; the water content of the leaves also decreases with the advance of the growing season (689). Rissmüller (891) observed pronounced changes in the composition of beech leaves during growth. The cellulose content (crude fiber) increased from 14.46 per cent in May to 25.52 per cent in November, on a dry basis; the fats and waxes also increased, while the proteins decreased from 28.25 per cent in May to 7.81 per cent in November; the total ash increased from 4.67 to 11.42 per cent, largely as calcium, magnesium, and silicate, with a gradual decrease in phosphate and potassium.

The organic complexes of the litter have commonly been considered under four analytical divisions: 1. The ether- and alcohol-soluble substances, including oils, fats, waxes, sterols, resins, organic acids, phosphatides; spruce and pine needles may contain 7 to 16 per cent of ether-soluble substances and 25 to 31 per cent of alcohol-benzol-soluble material (1205, 549, 574). 2. The non-nitrogenous extractives, including sugars, dextrans, starches, pentosans. 3. Nitrogenous bodies, such as proteins and their derivatives. 4. The so-called crude fiber, con-

modified only to a limited extent, while the minerals and the proteins accumulate. Side by side with these decomposition processes there occurs synthesis of new organic complexes in the soil, through the

TABLE 36

Proximate chemical composition of plant residues and humus produced in a pine forest floor (372)

Per cent of total dry material, free from ash and ether- and alcohol-soluble substances

NATURE OF MATERIAL	PENTOSAN	CELLULOSE	LIGNIN*	"PURE HUMUS"
Green needles.....	12.2	26.3	37.6
Forest litter.....	8.8	21.9	22.0	29.3
"Moder".....	6.0	19.5	20.8	39.1
"Surface peat".....	5.3	14.0	14.2	41.6
"Forest-sphagnum peat".....	3.1	2.4	9.1	59.6

* The transformation of the lignin into "humus" is discussed in detail elsewhere.

TABLE 37

*Chemical nature of humus in a forest soil profile (1223)**

HORIZON	pH	TOTAL ORGANIC MATTER, PER CENT OF DRY MATERIAL				CHEMICAL NATURE OF ORGANIC MATTER, PER CENT OF TOTAL DRY MATERIAL†						
		Loss on ignition	Total C	Total N	C/N	Ether-soluble	Hot water-soluble	Alcohol-soluble	Hemicelluloses	Cellulose	Lignin	Protein
Litter.....	4.49	96.00	50.99	1.01	50.5	6.38	4.06	2.57	18.23	15.72	38.38	6.31
F-layer.....	4.23	82.04	43.63	1.60	27.0	4.86	6.73	4.16	11.94	8.24	44.24	10.00
H-layer.....	3.79	75.20	41.45	1.56	26.6	4.25	3.31	3.54	9.49	4.75	50.13	9.75
A ₁	3.96	18.95	10.36	0.42	24.6	3.21	1.88	2.25	8.00	14.18
A ₂ (bleached).....	4.00	5.80	2.45	0.12	20.4	3.12	4.10	2.42	10.30	17.50
B ₁	4.24	11.75	4.74	0.24	19.8	1.54	2.38	1.08	8.70	17.94
B ₂ (passing into C).....	4.26	9.90	3.27	0.10	32.7	1.00	1.03	0.98	6.22	10.50

* White pine-hemlock, raw humus soil, located at Keene, New Hampshire.

† In case of samples from A₁, A₂, B₁, B₂, results are based on organic matter calculated from total carbon content.

agency of fungi, bacteria, protozoa, worms, and insects; these complexes account for most of the increase in the protein content of the humus and for the formation of new hemicelluloses, especially polyuronides.

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		Loss on ignition	Total C	Total N	C/N	Ether-soluble	Hot water-soluble	Alcohol-soluble	Hemicelluloses	Cellulose	Lignin	Protein
Litter.....	4.49	96.00	50.99	1.01	50.5	6.38	4.06	2.57	18.23	15.72	38.38	6.31
F-layer.....	4.23	82.04	43.63	1.60	27.0	4.86	6.73	4.16	11.94	8.24	44.24	10.00
H-layer.....	3.79	75.20	41.45	1.56	26.6	4.25	3.31	3.54	9.49	4.75	50.13	9.75
A ₁	3.96	18.95	10.36	0.42	24.6	3.21	1.88	2.25	8.00	14.18
A ₂ (bleached).....	4.00	5.80	2.45	0.12	20.4	3.12	4.10	2.42	10.30	17.50
B ₁	4.24	11.75	4.74	0.24	19.8	1.54	2.38	1.08	8.70	17.94
B ₂ (passing into C).....	4.26	9.90	3.27	0.10	32.7	1.00	1.03	0.98	6.22	10.50

* White pine-hemlock, raw humus soil, located at Keene, New Hampshire.

† In case of samples from A₁, A₂, B₁, B₂, results are based on organic matter calculated from total carbon content.

agency of fungi, bacteria, protozoa, worms, and insects; these complexes account for most of the increase in the protein content of the humus and for the formation of new hemicelluloses, especially polyuronides.

On comparing the chemical nature of the humus in the surface organic horizons of the forest soil profile with that of the lower inorganic horizons, certain important differences are obtained, as shown in table 37. The humus of the inorganic soil horizons approaches in chemical composition the humus of a normal field soil. With an increase in soil depth, there is an increase in the nitrogen content of the humus (756, 1053). This is due to the fact that with an increase in depth there is an increase in the stage of decomposition of the humus, which is characterized by an increase in the protein content; a factor which probably contributes even more to this condition is the more rapid movement of the nitrogenous fractions of the surface organic layers and of the bleached horizon than of the non-nitrogenous complexes.

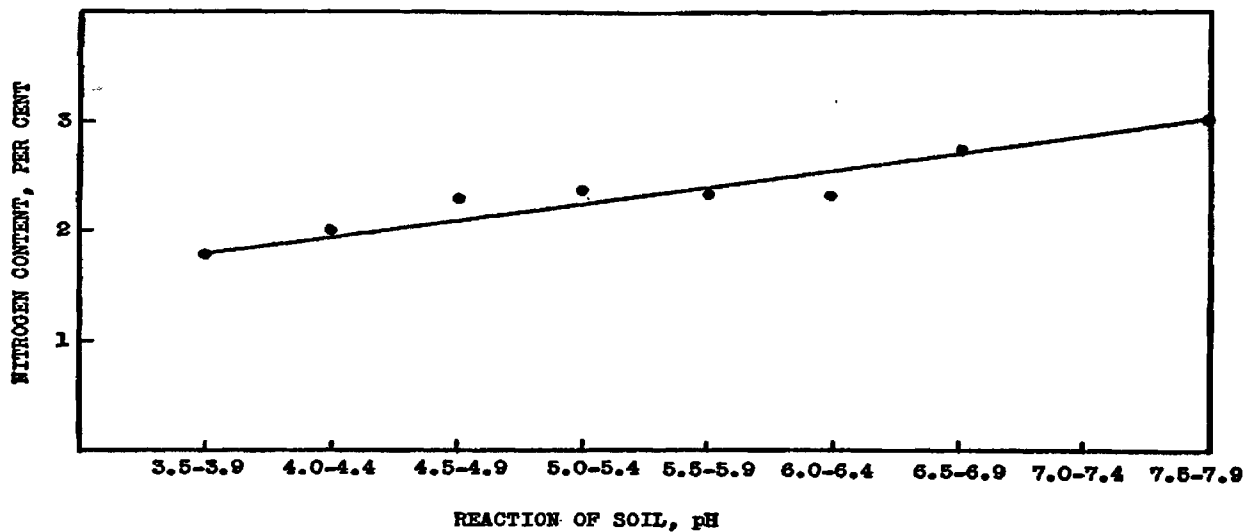


FIG. 20. Relation between nitrogen content of humus and the reaction (pH) of humus cover (Hesselman).

Even more striking results were reported by Weis (1265) for heath podsoles; the nitrogen content of the humus in the accumulation horizon was found to increase to 8 per cent or more, and in some cases, even to 22 per cent.

A definite relation has also been demonstrated between the nitrogen content of the humus and its reaction (fig. 20). This is probably due largely to the fact that an increase in the base content of the plant residues is favorable to an increase in the rate of decomposition, as a result of which a humus is produced which is higher in nitrogen and less acid in reaction (see 386, 848).

Various attempts have been made to distinguish certain humus types from one another on the basis of definite physical and chemical char-

acteristics. W. von Schütze (991) suggested the possibility of measuring the degree of decomposition of the humus by the color produced when it is suspended in ammonia. P. E. Müller differentiated the various types of forest soil by their total organic matter content: true mull soil was considered to contain less than 10 per cent of humus; "mull-like peat," 30–60 per cent; and true "peat" or raw-humus soil, over 60 per cent humus. Meinecke (694) suggested that humus types be distinguished by the rapidity of their decomposition, as measured by the course of CO_2 evolution. The measurement of the rate of liberation of nitrogen as ammonia or nitrate, for characterizing forest soil types, was also suggested (p. 341). Nemec (750) believed that various forest soil types could be distinguished by measuring the degree of oxidation of their humus by means of H_2O_2 . Günther (382) proposed a method of classifying humus forms in forest soils on the basis of their catalytic action. The distinctions obtained by these methods are mostly of relative significance, but they give valuable information in the hands of some investigators. They cannot find universal application for distinguishing forest soil types, however, except where certain specific information is wanted, such as the rate of humus decomposition, the rapidity of liberation of nitrogen, the formation of ammonia or of nitrate. Humus types can be separated only on the basis of the chemical composition of the different horizons in the profile, as pointed out previously.

Presence of specific chemical complexes in forest humus. Of the various groups of organic constituents of the forest litter and humus, the carbohydrates, especially the pentosans, have been studied most extensively. This is due primarily to the ease of determining the pentosan content by the furfuraldehyde method; however, as pointed out previously, when organic materials are boiled with 12 per cent HCl , not only pentosans, but also uronic acid complexes and other pentose-yielding groups, such as nucleic acids, will yield furfuraldehyde.

According to Czapek (198), the wood of the pine tree contains 6.16–6.97 per cent pentosan, the bark contains 10.32–11.0 per cent, and the needles contain 4.4–6.7 per cent; the corresponding figures for beech trees are 19.95–23.57, 15.84–16.98, and 15.18–20.50 (leaves) per cent; the oak tree contains 15.40–20.42, 11.56–14.89, and 8.70–10.43 per cent pentosan respectively. Pentosans are also present in the dead portions of mosses, as well as in lichens and ferns, to the extent of 2.6–12.7 per cent. Young leaves contain less pentosan than old leaves, young oak leaves having 13.35 per cent on a dry, ash-free basis, and

old autumn leaves, 17.88 per cent (549). In the case of evergreens, the spring needles contain 9.36 per cent pentosan; fall needles, 9.28 per cent; and needles several years old, 8.60 per cent, thus showing a slight decrease in pentosan content with age.

In the process of decomposition of the tree residues and formation of humus the pentosans are attacked rapidly. This is shown by the

TABLE 38
Pentosan content of tree products and of forest soil humus (549)

TYPE OF VEGETATION	NATURE OF RESIDUE OR HUMUS	PER CENT OF DRY MATERIAL		
		In total air-dry substance		In water, ash and extractive-free substance
		Pentosan	Benzol-alcohol soluble material	Pentosan
Beech.....	Dead leaves	14.06	11.63	16.62
	First layer of humus	13.13	6.65	15.26
	Second layer	9.96	4.05	12.24
	Third layer	6.23	4.76	7.78
	Fourth layer	3.44	3.03	5.70
Oak-forest.....	Leaves	13.93	12.19	15.12
	Litter	10.40	5.30	13.01
	Raw-humus	4.59	2.57	9.61
Spruce forest.....	Needles, many years old	7.28	22.13	8.60
	Raw humus, 1st layer	6.99	7.53	8.42
	Raw humus, 2nd layer	5.29	5.15	7.45
	Raw humus, 3rd layer	3.39	2.73	7.20
Pine forest.....	Needles, many years old	8.72	25.47	9.67
	Raw humus, 1st layer	7.10	12.68	8.41
	Raw humus, 2nd layer	6.80	9.7	8.09
	Raw humus, 3rd layer	2.99	5.03	5.52

distribution of pentosans or furfural-yielding constituents in the humus of different horizons of various types of forest soil, as compared with that in tree residues (table 38). In evergreen forests, Nemec (754) found that humus which was decomposed only to a limited extent contained 5.47-9.11 per cent pentosan; humus in a state of medium decomposition contained 4.59-5.78 per cent pentosan; and humus that

had undergone the greatest amount of decomposition contained only 1.58–5.78 per cent. No such relation was observed in the case of humus in deciduous forests.

The disappearance of cellulose during the process of humus formation is similar to that of the pentosan, being even more rapid. The lignin, on the other hand, may accumulate, especially in the raw humus forests. In the process of the decomposition of the plant residues, the lignin is partly transformed and partly left unaltered in the humus. The transformed complex is found to be lower in methoxyl content, is readily soluble in alkalis, is insoluble in acetyl bromide, and is dark in color; it shows, therefore, the characteristics typical of "humus" or "humic acid" (148, 372).

The abundance of extractives in forest litter and humus is usually determined by extraction with ether and alcohol or with benzol-alcohol, thus giving the fats, waxes, and resins. Kleberg (549) found that benzol-alcohol extracts 14.15 per cent of the dry ash-free material from green leaves, from old leaves—13.65, from spring needles—27.49, from autumn needles—29.71, and from needles many years old—28.02 per cent. The higher content of resins in needles may account for their slower decomposition. The following amounts of extractives were obtained (754) from various types of forest humus, with the same reagent:

DEGREE OF DECOMPOSITION OF HUMUS	CONCENTRATION OF EXTRACTIVES, PER CENT OF DRY HUMUS		
	Pine humus	Spruce humus	Beech humus
<i>per cent</i>			
54	13.91	9.97	4.68
61	12.94	7.29	5.02
69	6.74	5.22
74	3.48	2.91
80	2.24	2.17

The amount of extractives present in forest humus was found to have an important influence upon the process of nitrate formation. A concentration of about 5 per cent of extractives, on the basis of dry, ash-free material, was shown (751) to be the toxic limit; the injurious effect of higher concentrations is due largely to the resinous materials present in the extract. Some investigators (1208), however, have definitely demonstrated that the injurious effect of wood products upon plant growth is due to the consumption of the available nitrogen by the microorganisms attacking the wood; this was demonstrated by the

fact that while uninoculated clover was injured by increasing amounts of wood, inoculated plants, which did not depend for their nitrogen upon the available supply in the soil, were not affected.

Formation and transformation of forest humus. In a normal actively developing forest, the decomposition of the soil humus must keep pace with the addition of fresh residues from the forest vegetation. Should the first process become slower than the second and the humus accumulate on the surface of the soil, a condition will be brought about which is frequently referred to as "forest soil sickness" and which tends to diminish the rate of tree growth (785, 1116, 160, 161, 416, 570, 786).

Soil humus in general and forest soil humus in particular are not in a stable condition; they undergo continuous modification, the nature and degree of which depend upon numerous conditions. In the process of formation of humus, as a result of the decomposition of the plant residues, a gradual disappearance of the cellulose and hemicelluloses and an accumulation of the lignins, the proteins, and the mineral constituents take place. The chemical nature of the humus formed in different forest soils varies, since the rate and nature of the processes of decomposition depend on the chemical composition of the plant residues, on the nature of the microorganisms active in the decomposition processes, and on the nature of the inorganic portion of the soil, especially base content, mechanical composition, water table, etc. (6a, 752, 753).

Falck (279, 282) distinguished two processes of decomposition of plant residues in forest soils: (a) *corrosion*, where both the cellulose and the lignin are equally decomposed, and (b) *destruction*, where the cellulose is nearly completely decomposed, while the lignin is not attacked and is allowed to accumulate. Corrosion leads to a more or less complete decomposition of the tree residues and is characteristic of mull soils; in destruction, the lignin-rich complexes accumulate, as characterized by the raw-humus formations. The corrosive fungus *Agaricus nebularis*, an inhabitant of birch forest litter, attacks the pentosans, both in broad leaves and in needles, but to a much greater extent in the former. The ratio of the lignin to the cellulose does not change appreciably from that in the original residues. There is no appreciable increase in carbon content as a result of this type of decomposition, since the cellulose content of the humus produced is not very different from that of the original residues. The fungus *Coniophora cerebella*, however, brings about a typical process of destruction: it attacks only the cellulose and the hemicelluloses in the residues, while

the lignin is preserved quantitatively; this is accompanied by an increase in the carbon content of the humus and in its alkali solubility. The humus formed by the latter process is very resistant to decomposition. The coniferous forest soils contain few lignin-decomposing fungi; this explains the predominance of the latter process in these soils. This type of humus formation is similar to that which takes place in the formation of peat, with the principal difference that, in forest soils, fungi are largely concerned with the decomposition of the cellulose, whereas, in peat bogs, bacteria bring about this process. This may partly explain the frequent reference to the type of humus produced under these conditions as "peat humus," "forest peat," and "dry peat." Deciduous forest soils contain an extensive flora of Basidiomycetes, of which *A. nebularis* is a type; these bring about active decomposition of the lignins. In mixed forests, the lignin-decomposing fungi are also present.

When humus produced from broad leaves or needles, by the fungus *Coniophora*, was sterilized and inoculated with the fungus *A. nebularis*, little or no decomposition of the lignin took place. However, when the tree residues were decomposed first by *A. nebularis* and the product was sterilized and inoculated with *Coniophora*, active growth and decomposition of the organic matter took place. This led Falck to conclude that the cellulose-decomposing fungi liberate the lignin in a form (humus) in which it can no longer be attacked rapidly even by lignin-decomposing organisms; he believed that this explains the formation and resistance of humus in raw-humus forest soils.

As a result of the activities of the two types of organisms mentioned, either humus destruction or humus accumulation may occur; the humus formed in the first process is comparable to the so-called "mild humus," since it is less acid in reaction, it decomposes more readily, and the nitrogen is liberated in the form of nitrates. The humus formed by the second process is known as "acid humus"; it decomposes with difficulty and the nitrogen appears as ammonia or nitrate only in small amounts; hence this type of soil has been called "sick."

The anaerobic processes of decomposition of forest tree residues result in destruction of the cellulose and accumulation of the lignin. With the advance in the decomposition of the wood, whether by pure or by mixed cultures of microorganisms, there is a gradual increase in the alkali-soluble material (166); this is principally a result of the modification of the lignin molecule and is to some extent associated with the transformation of the protein, both of which yield the characteristic

soil humus. A summary of the processes taking place in the decomposition of tree residues and in the formation of humus is presented in figure 21; the fraction designated by "humus" has been separated from the "lignin" fraction by the insolubility of the former in acetyl bromide.

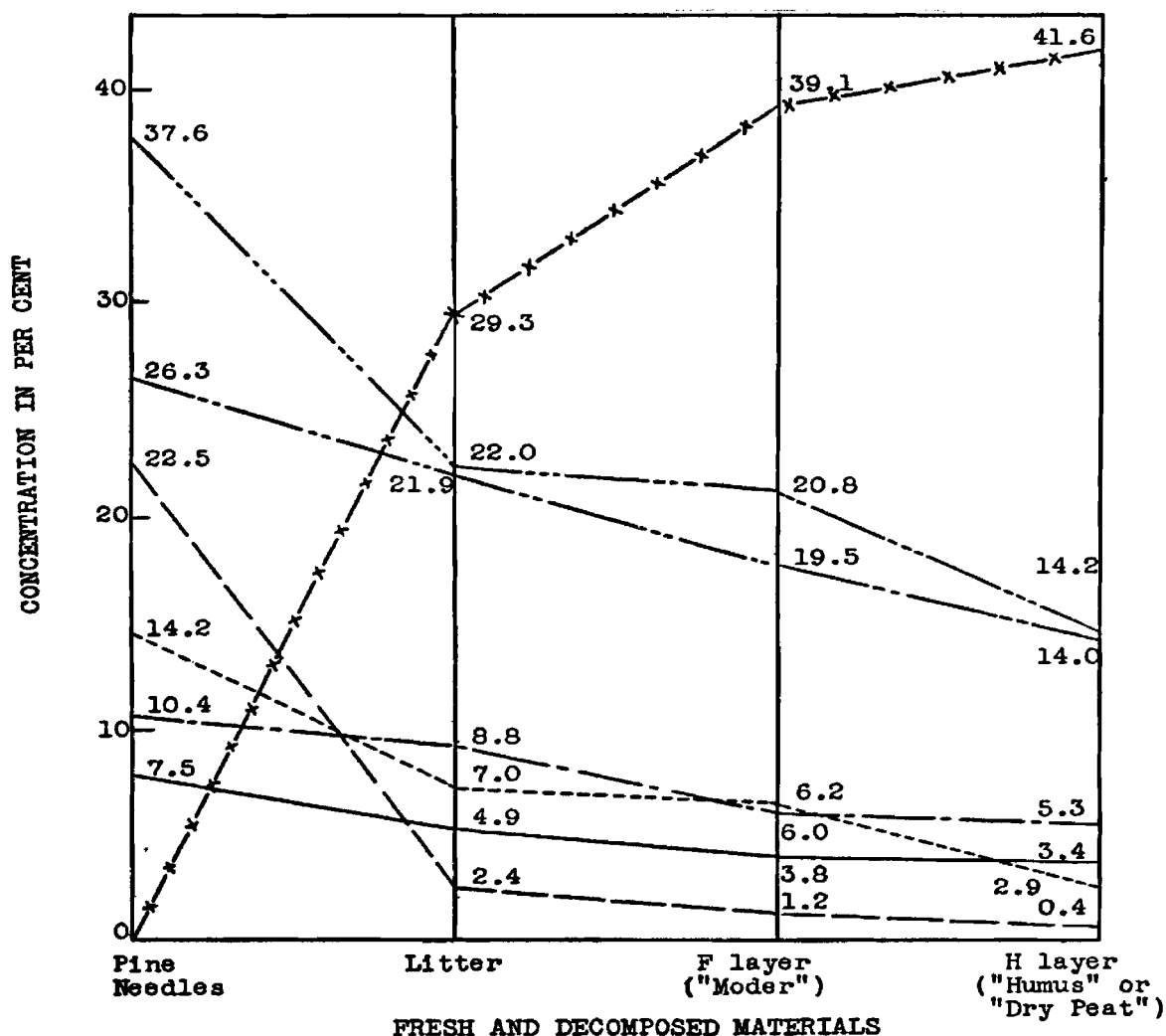


FIG. 21. Decomposition of the various constituents of plant residues in the transformation of organic matter in forest soil. Ether soluble material ———, alcohol soluble material ———, water soluble material — — —, pentosans ———, cellulose ———, lignin ———, humus — X — (from Groszkopf).

The rapidity and course of decomposition of different forms of forest humus can be readily estimated either from the rate of evolution of carbon dioxide from a given quantity of humus or from the rate of liberation of the nitrogen in an inorganic form, namely, as ammonia or nitrate. When the course of CO₂ evolution was used for measuring

the rate of organic matter decomposition, the litter was found (697) to decompose most rapidly, followed by the humus of the F-horizon, and finally by the humus of the H-horizon; the difference in the rapidity of decomposition of the humus in the F- and H-layers may be very marked. The forest vegetation is of considerable importance in this connection (755): forest soils with a vegetation of *Hypnum schreberi*, *Polytrichum formosum*, *Vaccinium myrtillus*, and *Molinia coerulea* tend to form a type of humus which is fairly resistant to decomposition, while the organic matter in mull soils undergoes more active decomposition. Lundegårdh (656) has also shown that true mull soils respire much more actively than raw humus soils, although the latter may give considerable amounts of CO₂ (251, 696, 911).

When the liberation of nitrogen is used as an index of humus decomposition, totally different results are obtained: the highest amount of mineralized nitrogen is usually produced in the F- and H- layers, and the lowest, in the litter. This is due primarily to the fact that the C:N ratio of the litter is still too wide for any of the nitrogen to become liberated in an available form. Hesselmann (432) divided the forest soils into nitrifying brown soils and non-nitrifying podsol soils; in the former, the humus is intermixed with the mineral layer, whereas in the latter, the humus is largely of the mor or raw-humus type. A parallelism has been shown (2, 3) to exist between the rates of liberation of the nitrogen as ammonia and nitrate and the productivity of the forest soils. Table 39 brings out the influence of forest type upon the rapidity of liberation of nitrogen in an available form.

The relationship of humus to the nutrition of forest trees has been a subject for much discussion. Ehrenberg and Bahr (259) found that forest humus, without the addition of lime, exerted an injurious effect upon the growth of agricultural crops but, subsequent to liming and composting, it became somewhat more effective as a result of the liberation of nitrogen in available forms; they concluded that the value of humus in forest soil has been greatly overestimated. More recently, Süchting (1116-7) stated emphatically that "only that forest humus is the best which is never formed," because forest humus contains a large part of its nitrogen in organic undecomposable compounds. Möller and Hausendorf (720), on the other hand, demonstrated that humus has a favorable effect upon forest trees, brought about through the supply of a continuous stream of available nitrogen; pine, spruce, and oak trees provided with raw humus grew far better than when supplied with artificial nitrogenous fertilizers. They came to the conclusion

that the abundance of nitrogen and humus determines the fertility of the soil. It has been suggested also that the mycorrhiza in forest soils are concerned in rendering nitrogen available to the trees (695).

A close connection between nitrification in soil and rejuvenation of coniferous forests has been established. In the case of raw-humus formations, where the liberation of nitrogen does not proceed farther than the ammonia stage, rejuvenation is limited (432). Nitrogen transformation in forest soils depends upon a number of factors (351): 1. Reaction; when the humus is at a pH 3.5 to 5.0, ammonia is the principal form of mineralized nitrogen; very little nitrate is formed at pH 3.9 or less, but appears only at pH 4.0 or higher (fig. 22). 2. Nature and accumulation of the organic matter; ammonia formation is prac-

TABLE 39

Liberation of nitrogen in the decomposition of humus from different forest soils (2)

SOIL TYPE	pH OF HUMUS	TOTAL NITROGEN IN HUMUS	AMMONIA LIBERATION, MILLIGRAMS PER KILOGRAM OF HUMUS		NITRATE FORMATION, MILLIGRAMS PER KILOGRAM OF HUMUS		NITROGEN MOBILIZED, PER CENT OF TOTAL NITROGEN
			At start	After 2 months incubation	At start	After 2 months incubation	
		<i>per cent</i>					Incubation, 2 months
Calluna type.....	4.2	1.495	32	159	0.9	1.4	1.074
Vaccinium type.....	4.6	1.666	55	200	1.3	1.3	1.207
Myrtillus type.....	4.8	1.796	68	325	1.6	1.7	1.819
Oxalis-myrtillus type.....	5.2	2.234	107	636	1.2	4.6	2.868
Oxalis-majanthemum type.	5.0	2.795	135	698	11.4	568.1	4.425

tically independent of humus accumulation, while very little nitrate is formed in soils containing over 70 per cent organic matter; humus poor in nitrogen undergoes decomposition without the liberation of very much of the nitrogen in an available form; only after considerable decomposition has taken place will the nitrogen be first liberated as ammonia, and then changed to nitrate. 3. Nature of the mineral soil, especially its physical and chemical properties. 4. Topography. 5. Abundance of lime and minerals. 6. Specific nature of the plant vegetation. The treatment of forest soils, such as liming, cultivation, and removal of trees, has an important influence in modifying the processes of liberation of the nitrogen in an available form (619).

Humus formation in alpine regions. Although the nature of humus

formation at high altitudes is distinctly different from that in forest soils, because of differences in vegetation and primarily because of the specific conditions under which decomposition is taking place, this type of humus has nearly always been associated with forest humus. In his review of P. E. Müller's book, Ebermeyer spoke of alpine humus as a dark, powdery soil, consisting only of plant residues and containing no excrements of rainworms or chitinous particles of insects; this humus formation was a meter or more in thickness.

The accumulation of humus at high altitudes is largely due to the fact that the prevailing low temperatures are less injurious to growth

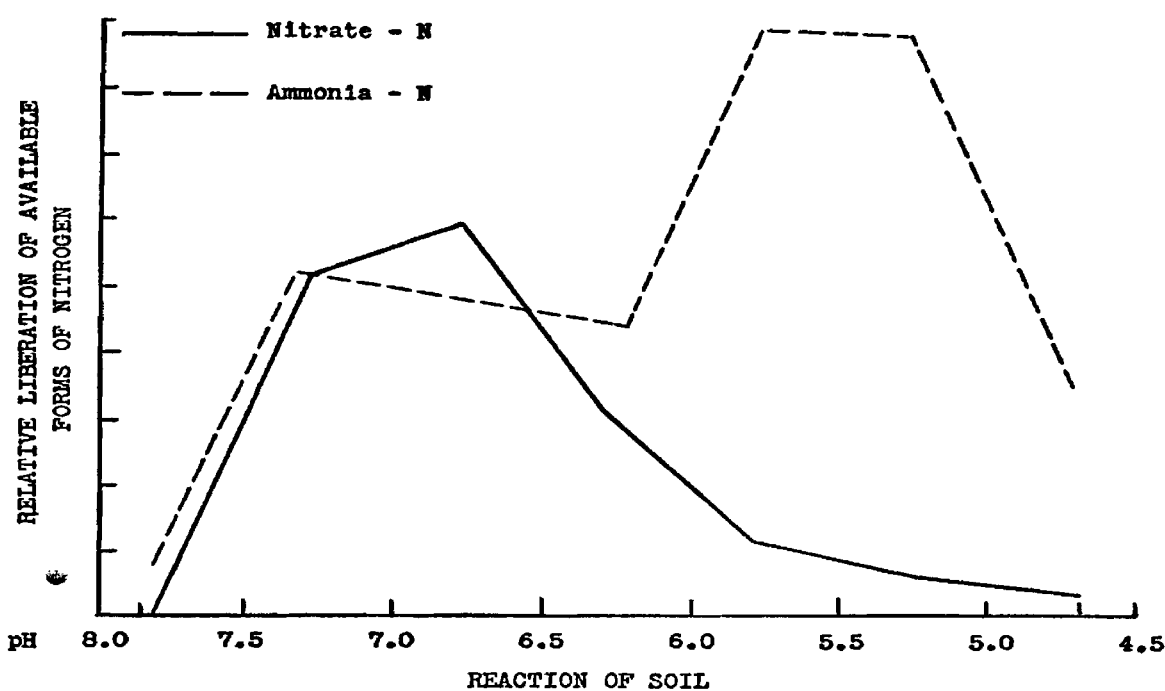


FIG. 22. Influence of reaction upon the nitrate and ammonia nitrogen liberation in forest soil (Aaltonen).

of the higher vegetation than to the activities of the microorganisms that are concerned with the decomposition of the plant residues. As regards accumulation of organic matter, alpine humus is similar to raw-humus formations in forest soils. This type of humus has mostly been formed on limestones (618). The A-horizon, which consists chiefly of plant residues and dust particles, predominates over the other horizons. Very few chemical analyses of alpine humus have so far been reported. A sample obtained from Pike's Peak, at a height of 4,600 meters (1241), was found to be high in hemicelluloses, cellulose, and proteins, and comparatively low in lignin. Under favorable conditions

of temperature and reaction, this form of humus could undergo active decomposition.

In the case of humus formed on limestone, loss on ignition was found to range between 86.7 and 95.6 per cent, while the nitrogen content was between 1.46 and 2.29 per cent; in the case of humus formed on silicate rocks, the loss on ignition was 40.0 to 91.8 per cent and the nitrogen content 1.37 to 2.0 per cent (618, 1187, 620). The following summary (834) shows the distribution of humus in a profile of an alpine podsol soil:

HORIZON	DEPTH	HUMUS
	<i>cm.</i>	<i>per cent</i>
A ₁	5-15	34.9
A ₂	15-20	2.1
B	20-25	16.7
BC	25-35	10.9
C	60-70	4.1

The meager information available concerning the distribution of alpine humus (487) points to a parallelism between the humus content and the acidity of the soil, as shown by the following summary:

REACTION	HUMUS CONTENT
<i>pH</i>	<i>per cent</i>
5.4	11-62
5.1	12-42
4.7	24-59
4.4	25-69

Similar results were obtained by Wasowicz (1254). The high acidity of the soil (that of Pinetum association being pH 3.7-3.9) and the low annual temperature were believed to be largely responsible for the wide C:N ratios of the alpine soils, which ranged from 9.7:1 to 34:1 (that of Pinetum being, on the average, 29.4:1). The factor calculated for the humus-carbon relationship was 1.84. The humus of the mountain soils was characterized by a high content of hemicelluloses and a low content of cellulose, as distinguished from the composition of fresh plant residues, where cellulose was more abundant than hemicelluloses (1121). This was believed to be due to the occurrence in the humus of an abundance of microbial cell substance which is rich in hemicelluloses. The general conclusion was reached that climate, rather than

plant association, exerts the controlling effect upon the formation of humus in soil.

Humus in heath lands. Heath soils are also characterized by raw-humus formations resulting from a vegetation of *Calluna vulgaris* and various other plants, including species of *Erica*, *Nardus*, *Vaccinium*, *Lycopodium* and *Polytrichum*, and lichens. The humus content of a typical heath soil profile is shown in table 40. In this, as well as in a number of other profiles, Weis (1265) found that the nitrogen content in the humus increases with an increase in depth; in the case of some profiles, it was found to be 2.08 per cent for the raw humus in the leached sand horizon (A₁-A₂), 2.24 per cent for the humus in the hardpan (A₃-B₁), 3.99 per cent for the layer under the hardpan (B₂), and

TABLE 40
Abundance and nature of humus in a heath podsol profile (1265)

HORIZON	DESCRIPTION OF HORIZON	THICKNESS OF HORIZON	pH	HUMUS CONTENT	NITROGEN CONTENT	NITROGEN IN HUMUS
		<i>cm.</i>		<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
A ₁	Raw humus	8.9	3.6	27.03	0.49	1.81
A ₁ -A ₂	Transition to bleached sand	3.8
A ₂	Pure bleached sand	7.0	3.9	1.78	0.03	1.68
A ₃	Humus hardpan	7.4	4.1	12.65	0.29	2.29
B ₁	Iron hardpan	6.2	4.5	2.65	0.06	2.30
B ₂	Transition between iron hardpan and parent material	34.4
C	Parent material begins at a depth of	67.8	4.8	0.24	0.005	2.08

8.44 per cent for the humus in the subsoil (C). Weis further substantiated these results by showing that in heath podsoils the organic colloidal constituents which contain the highest amounts of nitrogen move downward most readily; consequently, the nitrogen content of the organic matter increases with depth. The organic nitrogen in the heath soils, especially in the raw-humus horizon, was found to be readily mineralized and liberated, as soon as the soil was limed and cultivated.

Some of the heathlands approach in nature certain peat formations; they will, therefore, be discussed elsewhere (p. 266). Further details on the occurrence of humus in podsol profiles and its rôle in soil formation and profile development are given elsewhere (p. 379).

Summary. The specific problems connected with the study of forest

soil humus, as distinct from that of humus in field and garden soils, in peats, and in composts, can be summarized as follows: 1. This type of humus is characteristic and varies in chemical composition under different conditions, depending primarily upon the surface vegetation, climate, soil structure, and microbial activities. 2. Humus of different horizons in the forest profile differs considerably in chemical composition, which permits a distinct separation of the various soil horizons; humus is found in forest soils in all stages of decomposition, from undecomposed tree residues on the surface (litter) to forms of humus well decomposed in the B- or accumulation horizon. 3. Forest humus is characterized by a specific microbial population, belonging both to the animal and plant kingdoms, which also contribute by their cell substance to the formation of this humus. 4. Forest humus is characterized by specific decomposition processes, which affect the vegetative growth of the forest.

The significance of humus in a forest soil can be determined not so much by its abundance as by the rapidity of its decomposition. The forest literature is full of contradictory statements concerning the importance of humus in tree growth; some investigators claim that humus is highly important in forest soils, because of its physical, chemical, and biological properties, while others go to the other extreme and state that the best humus is the one that is never formed. These two views have developed from observations on two distinct types of humus, one being the incorporated soil humus as found in mull soils, and the other being the little decomposed humus which forms the forest floor of raw-humus soils.

When the interpretation of the relationships of humus to tree growth in forest soil is based primarily upon the nature of its decomposition, the point of view becomes changed. Those tree residues which consist largely of needles and of other products of coniferous forests are attacked largely by fungi, which reduce slowly the cellulose and hemicelluloses, leaving the lignins to accumulate; an organic mat results which is low in bases, is acid in reaction, is low in nitrogen, decomposes only slowly, and undergoes leaching easily. On the other hand, the plant residues which consist largely of broad leaves and other products typical of deciduous forests, are attacked by numerous fungi, bacteria, and invertebrates, which decompose the cellulose, hemicelluloses, and lignins; a type of humus results which is high in bases, is less acid in reaction, and is higher in protein; the humus is bound by the bases in the form of ligno-protein complexes, which are not readily leached. Between these two extremes are found all the gradations of the various types of forest humus.

CHAPTER X

HUMUS IN MINERAL SOILS (FIELD, GRASSLAND, GARDEN AND ORCHARD)

"The accumulation of humus in soil can take place only under those conditions where decomposition of the organic matter is less than its addition; when decomposition equals addition, no accumulation is possible."

—P. KOSTYTSCHEV.

Most of the investigations on the chemical properties and origin of humus have been carried out by the use of peats and coals, and only to a limited extent by the use of humus in soils and in composts. Conclusions drawn from studies of the first two types of humus have frequently been applied, quite indiscriminately, to mineral soils, in an attempt to interpret not only the nature of humus but also its functions in these soils. Such interpretations have not always been justified, since not only does the chemical composition of humus in mineral soils vary considerably from that of peats and coals, but the interrelationships between the organic complexes and the inorganic constituents in such soils are of the greatest importance in their formation and resultant fertility.

Method of quantitative determination of humus in mineral soils. In most of the earlier analyses of the humus content of mineral soils, the loss on ignition was taken as the standard method of measurement. It was soon recognized, however, that when a soil is ignited, certain inorganic constituents also undergo various changes with a marked loss in weight. This is true especially for soils rich in carbonates and hydrated silicates; these complexes lose carbon dioxide and chemically combined water upon ignition, thus tending to give too high humus values (1282).

In view of the fact that humus in mineral soils is largely in an advanced state of decomposition and may, therefore, be considered to be similar in chemical nature in different soil types, it was natural that an attempt should be made to obtain a factor which could be used to calculate the humus content from the determined amount of one of its important constituent elements. It is universally agreed that carbon is the most characteristic element of humus; hence calculations of the amount of

humus in mineral soils have been based frequently upon the concentration of organic carbon. The assumption is thereby made that the carbon content of humus is constant. It has been shown in the discussion of the origin of humus, however, and will be brought out further in considering the relation of humus to soil type, that the chemical composition of humus varies considerably even in mineral soils.

Sprenghel (1074) was the first to report that soil humus contains 58 per cent carbon. Schulze (990) later obtained similar results by another method of calculation. With this figure as a basis, Wolff (1296) suggested that in determining the abundance of humus in mineral soils, the total amount of organic carbon found by combustion should be multiplied by the factor 1.724. Warington (1253) compared the loss on ignition with the amount of humus calculated from the organic carbon, by use of this factor, and found that the former gave results greatly in excess of those calculated by the latter method. He suggested, therefore, that the loss on ignition as a method of humus determination be abandoned and that the humus content of the soil should always be based on the organic carbon found. These results were substantiated by Loges (648) and others. Van Bemmelen (88) made extensive use of the above factor, which came to be known frequently as the "Van Bemmelen factor." From a detailed study of the elemental composition of soil humus, Berthelot and André (109) obtained results showing a slightly lower content of carbon than 58 per cent; namely, C—56.1 per cent, H—4.4 per cent, N—4.9 per cent, and O—34.6 per cent.

The factor, 1.724, has, therefore, come into general use, especially in the work of the Russian pedologists and other students of soils who were more interested in the abundance of humus rather than its nature and functions. Recently (168, 617), however, this method for calculating the humus content of the soil has been subjected to much criticism, based primarily upon the assumption that the carbon content of humus varies considerably. Rather (863) treated the soil, previous to ignition, with a dilute solution of hydrochloric and hydrofluoric acids to remove the carbonates and hydrated silicates or zeolites; the soil was then ignited, and the loss on ignition was believed to represent the true organic matter. Read (868-9) found, by the use of a modification of this method, that the percentage of carbon in the humus of surface soils may vary from 30.20 to 56.27 per cent, with an average of 49.26 per cent. These results led to the conclusion that the factor commonly used is too high; they suggested that it be modified, based

on a carbon content in humus of 50 to 52 per cent. They also recommended that the amount of humus in soil be calculated from the total nitrogen content, using the factor 16; the results thus obtained were believed to be more reliable than those based upon the carbon content.

An examination of the results obtained by the method of Rather reveals the fact that when a peat containing 91.8 per cent organic matter has been previously treated with acids, only 80.8 per cent organic matter was obtained. The hemicelluloses, which frequently form an important group of humus constituents and the concentration of which varies considerably in humus, undergo decarboxylation when treated by dilute mineral acids. These facts tend to throw considerable doubt upon the value of the foregoing method for calculating the amount of humus in mineral soils. Consequently, any recommendation of a new factor based on the results obtained by that method is open to criticism (22). Leighty and Shorey (617), therefore, argued with much justification that, since humus is made up of numerous organic compounds varying in carbon concentration, any calculation based upon a single factor can be considered only as an approximation. This can lead to only one conclusion, namely, that an approximation based on the greatest number of determinations thus far available should receive most consideration.

More recently (1241), the humus content of mineral soils was calculated from the results obtained by the proximate chemical analysis of humus (p. 183); these results led to the conclusion that the factor 1.724 comes as close to representing the actual relation of humus to carbon as can be expected in such a variable natural body as the soil. Although a single factor based on the amount of organic carbon found cannot be applied indiscriminately to forest, heath, and peat soils, or to composts, where the humus contains considerable amounts of undecomposed or readily decomposable plant residues rich in carbohydrates, it may be applied with less hesitation to mineral soils.

Fulmer (333) suggested that the humus content of the soil be calculated on the basis of the amount of total nitrogen and of "humic acid" or "black matter," as determined by the Grandeau method:

$$C = \frac{b \times 55}{a}$$

C is the per cent of nitrogen in the black matter, *b* the per cent of total nitrogen in the soil, and *a* the per cent of humus in the soil. No con-

stant relation was found for various soils. The assumption was made in these calculations that the nitrogen concentration of all humus extracts is always the same, which is far from correct, as pointed out previously.

The determination of the total organic matter in mineral soils on the basis of their nitrogen content, using either the factor 16 or 20, has met with even greater criticism, because of the even wider variation in the nitrogen content of humus, as shown by the carbon-nitrogen ratio. This ratio is not constant and varies considerably in the humus of different soils, as well as of different layers of the same soil (p. 180). Dyer (249) was among the first to point out that the ratio of carbon to nitrogen is higher in the surface layers of soil and becomes narrower with depth, until, at a depth of 45–54 inches, it becomes more or less constant.

Abundance of humus in mineral soils. The humus content of mineral soils varies considerably, depending on soil type, vegetation, and treatment. Knop (551–2) proposed the following classification of soils based on the relative abundance of humus:

HUMUS CONTENT	NATURE OF SOIL
<i>per cent</i>	
0– 2.0	Humus-poor soil
2.0– 5.0	Humus-containing soil
5.0–10.0	Humous soil
10.0–15.0	Humus-rich soil
>15.0	Humus-excess soil

The amount of humus found in ordinary field, garden, and orchard soils, as well as in most pasture lands, may be considered as rather limited. It is controlled by climatic conditions, nature of the vegetation, chemical and physical properties of the inorganic part of the soil, activities of microorganisms, cultural treatment, and fertilizer practice. Most of the humus found in soils of humid regions is concentrated in a thin surface layer, designated as the “surface soil”; below this layer it diminishes rapidly. In soils of arid and semi-arid regions, the content of humus is more or less uniform from the surface to considerable depths.

Humus is found in mineral soils in concentrations varying from 0.5 to 10.0 per cent. The black soils or chernozems are considerably higher in humus than the gray (serozems), brown (chestnut), or red

(krasnozems) soils (tables 41 and 42). The nitrogen content of the humus is more or less constant, especially within each broad soil type,

TABLE 41
Humus content of certain grassland soils in Nebraska (1929)

NATURE OF SOIL	HUMUS CONTENT OF SOILS		NITROGEN CONTENT OF SOILS		HUMUS-NITROGEN RATIO	
	Depth of soil					
	0-15 cm.	16-30 cm.	0-15 cm.	16-30 cm.	0-15 cm.	16-30 cm.
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>		
Moody.....	6.09	4.25	0.296	0.221	20.6	19.2
Carrington.....	4.94-5.85	3.78-4.68	0.245-0.278	0.194-0.223	19.4-21.1	19.1-21.5
Marshall.....	4.67-5.37	2.32-2.76	0.240-0.280	0.173-0.217	19.2-20.3	18.3-19.3
Crete.....	4.81	3.28	0.228	0.171	21.1	19.2
Hoedrege.....	2.88-4.09	2.29-3.28	0.159-0.193	0.108-0.121	18.1-21.2	21.2-21.3
Rosebud.....	2.56-2.93	1.50-1.73	0.130-0.173	0.084-0.107	16.9-19.7	15.7-17.9

TABLE 42
Humus content of some Russian soils (1904)

TYPE OF SOIL	HORIZON	HUMUS	NITROGEN IN SOIL	NITROGEN IN HUMUS
		<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
1. Podsols:				
Strongly podsolized, fine sandy soil, Vologda.....	A ₁	3.64	0.205	5.65
	A ₂	0.37	0.030	8.11
	B ₂	0.10	0.024	8.38
	C ₁	0.22	0.019	8.49
Loamy soil, Smolensk.....	A ₁	3.45	0.186	5.40
Clay soil, Tifis.....	A ₁ + A ₂	2.23	0.130	5.83
2. Chernozems:				
Loamy chernozem, Voronezh.....	A	11.04	0.524	4.70
Clay chernozem, Orenburg.....	A	9.88	0.440	4.48
Clay chernozem, Armenia.....	A	15.64	0.748	4.78
3. Chestnut and brown soils:				
Chestnut soil, Akmolinsk.....	A ₁	2.01	0.117	5.82
	A ₂	1.11
	B	0.84	0.043	5.10
Brown soil, Samara.....	A	1.97	0.12	6.00
	B	1.54	0.11	7.14
	C	0.80	0.04	5.71

the humus-nitrogen ratio varying from 16.9:1 to 21.2:1, for the surface soils, and from 15.6:1 to 21.4:1, for the subsoils.

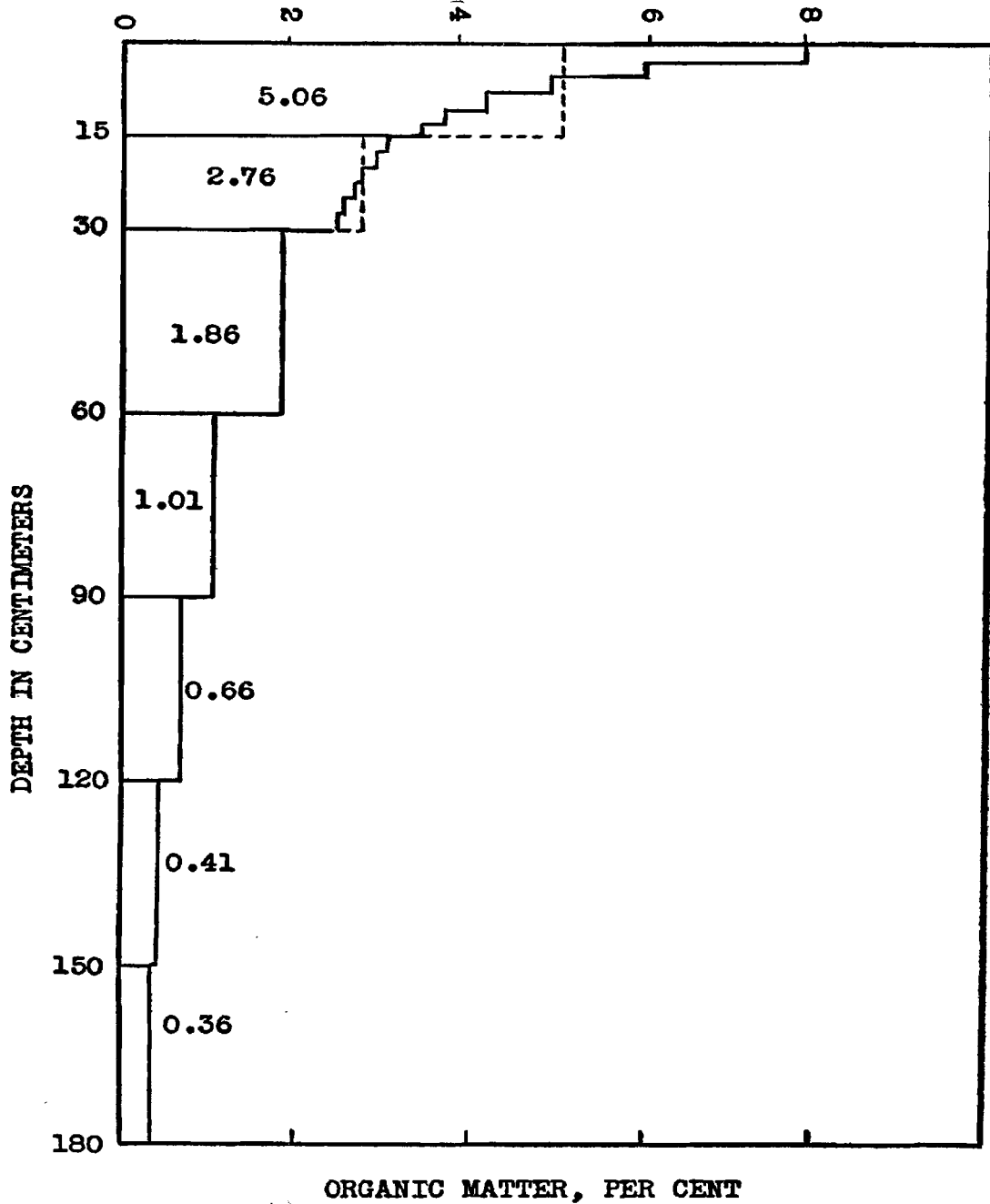


FIG. 23. Humus content at different depths of a Nebraska silt loam (Alway and McDole).

Glinka (349, 350) reported that the chernozem soils of Russia contain about 1,100,000 kg. of humus per hectare of the surface 100-cm. layer, with about 45,000 kg. of nitrogen. Morgan and Lunt (725) found that the humus content of American prairie soils ranges from

275,000 to 550,000 kg. per hectare, with 15,000 to 28,300 kg. of nitrogen; the humus-nitrogen ratio of these soils was found to be about 20:1. Most of the humus is found in the surface 30-cm. layer of soil, but less so in the case of podsol soils than in black and brown soils. Figures 23 and 24 show the distribution of humus in the profiles of two American prairie soils, and figure 25 illustrates the distribution of nitrogen in the upper layers of a soil profile.

The distribution of humus and nitrogen in several profiles of some typical Russian soils is shown in table 42. In the podsol soils, the humus

TABLE 43

Influence of depth upon the humus and nitrogen content of soil (1904)

DEPTH OF SOIL	SOIL TYPE					
	Chernozem (Tula)			Podsol (Vologda)		
	Humus content of soil	Nitrogen content of soil	Total nitrogen per hectare of soil	Humus content of soil	Nitrogen content of soil	Total nitrogen per hectare of soil
<i>cm.</i>	<i>per cent</i>	<i>per cent</i>	<i>kgm.</i>	<i>per cent</i>	<i>per cent</i>	<i>kgm.</i>
0-10	10.05	0.50	6.000	7.92	0.324	3.888
10-20	9.37	0.42	5.040	0.177	2.124
20-30	6.75	0.33	3.960	0.61	0.031	0.372
30-40	5.97	0.26	3.120	0.033	0.396
40-50	4.54	0.21	2.520	0.42	0.035	0.420
50-60	0.16	1.920	0.041	0.492
60-70	0.14	1.680	0.43	0.048	0.576
70-80	0.12	1.320	0.032	0.384
80-90	0.08	0.960	0.027	0.324
90-100	0.08	0.960	0.25	0.017	0.204
Total nitrogen per hectare to a depth of 100 cm., kgm.....			27.480			9.180

content drops rapidly as one proceeds from the A₀- and A₁- to the A₂-horizon, then increases again in the B₁- and diminishes in the C-horizon, because the humus has been washed out from the A₂- and deposited in the B-horizon. The limited evidence points to the probability that the humus as a whole is not leached downward, but that only certain constituents are particularly susceptible to movement. This can be demonstrated by the fact that although the concentration of humus and nitrogen diminishes with depth in the case of podsol soils, the nitrogen content of the humus becomes greater in the lower horizons.

It is of further interest to note that although the amount of humus found in chernozem soils is much higher than in the podsols (except the surface organic layer of the latter) the nitrogen in the humus is lower (25, 29). In the chernozems, humus is more uniform in chemical nature and is distributed to a much greater depth, as is further brought out in table 43 (see also 241, 244, 340, 357, 526, 804, 827, 1055, 1057, 1271).

Chemical nature of humus in field and garden soils. The methods used in studying the chemical nature of humus in mineral soils are

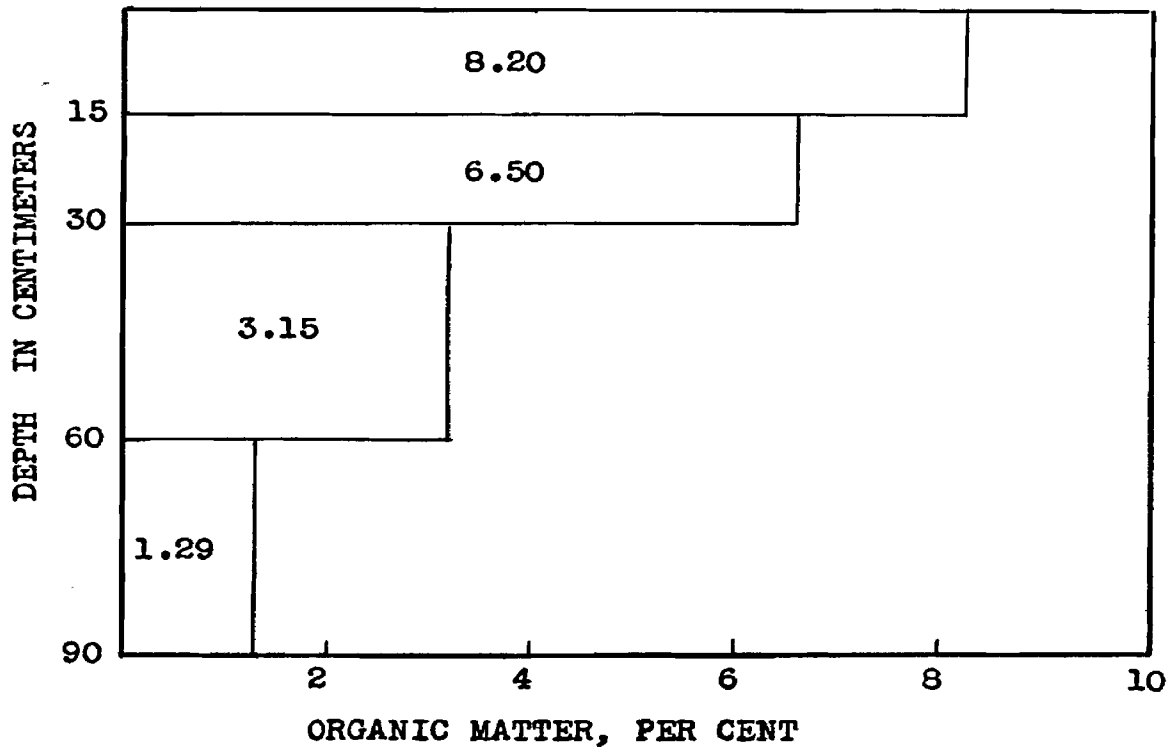


FIG. 24. Humus content at different depths of a Carrington silt loam in Minnesota (after Rost).

even less definite than those employed for humus in peat and in forest soils, largely because of the difficulty of removing the humus in an unchanged state from the former soils in which it occurs only in limited concentration. Further, humus in mineral soils is much more changed in chemical composition from that of the original plant materials than in the case of the other types of humus. As pointed out previously, this humus consists predominantly of lignins or lignin derivatives and proteins, together with some amounts of hemicelluloses, fats, and waxes and small quantities of numerous other complexes; it is not in a static chemical condition, but constantly changes in composition, depending

on soil types (p. 374), treatment, and conditions of environment and climate. The humus in the various horizons of podsol soils differs considerably in chemical composition; this is not true to the same extent for the black and brown soils: it was found (1241), for example, that the chemical nature of humus in horizons A and B of a prairie soil was strikingly similar.

Among the various groups of humus constituents, the nature of the nitrogenous complexes has aroused particular attention. While some investigators (612, 728, 1223) emphasized the protein nature of this nitrogen, others (1080a) claimed that it must be largely in other forms. Recently, the former point of view has again been emphasized by Remezov (876-7). He divided the organic forms of nitrogen in the humus into three fractions: 1. water-soluble (4.30 per cent of total nitrogen), 2. hydrolyzable by acid, 3. non-hydrolyzable. The water-soluble fraction was found to depend on the total nitrogen content of the humus and on the nature of the exchangeable cations; the higher the organic nitrogen content in soil and the greater the concentration of anions, as compared with cations, the greater was this fraction found to be. The amount of the acid hydrolyzable fraction was found to depend on the process of hydrolysis. The use of strong acids was found to result in secondary reactions; hence, 5 per cent HCl, in the autoclave at 200°C., has been recommended as the hydrolyzing agent. Different soil types gave marked differences in their nitrogen distribution. The amide nitrogen content of serozems and podsols was high but not in the case of chernozems; in peats, the mono-amino acids were higher than the di-amino acids. The non-hydrolyzable form of nitrogen was believed to comprise the oldest organic fraction, which did not depend upon the present soil types.

The major effect of humus upon soil is twofold: 1. it improves the soil physically, 2. it modifies its biological and biochemical nature, thus producing conditions which are favorable for plant growth. The nature of the soil protein, for example, was found (876) to modify the colloidal part of the soil, the constancy of the base-exchange complex, and the cation capacity of the soil. In order to study the specific effects of the various humus constituents upon the soil, it is important to determine the relative abundance of these constituents in humus by methods outlined elsewhere (p. 406). Some of these groups were considered to be more readily subject to decomposition or oxidation.

In order to distinguish between the fractions which decompose rapidly and slowly, Tiurin (1168) utilized the method of Waksman for

hydrolyzing the soil humus. The procedure consists in treating the soil with 80 per cent sulfuric acid in the cold, then diluting it with water and heating. The readily hydrolyzable compounds are thereby brought into solution; their concentration can be determined by measuring either the reducing sugar formed (1241), or the total carbon and nitrogen (1168). It has also been suggested (1168) that the consumption of oxygen might be measured by the dissolved organic compounds;

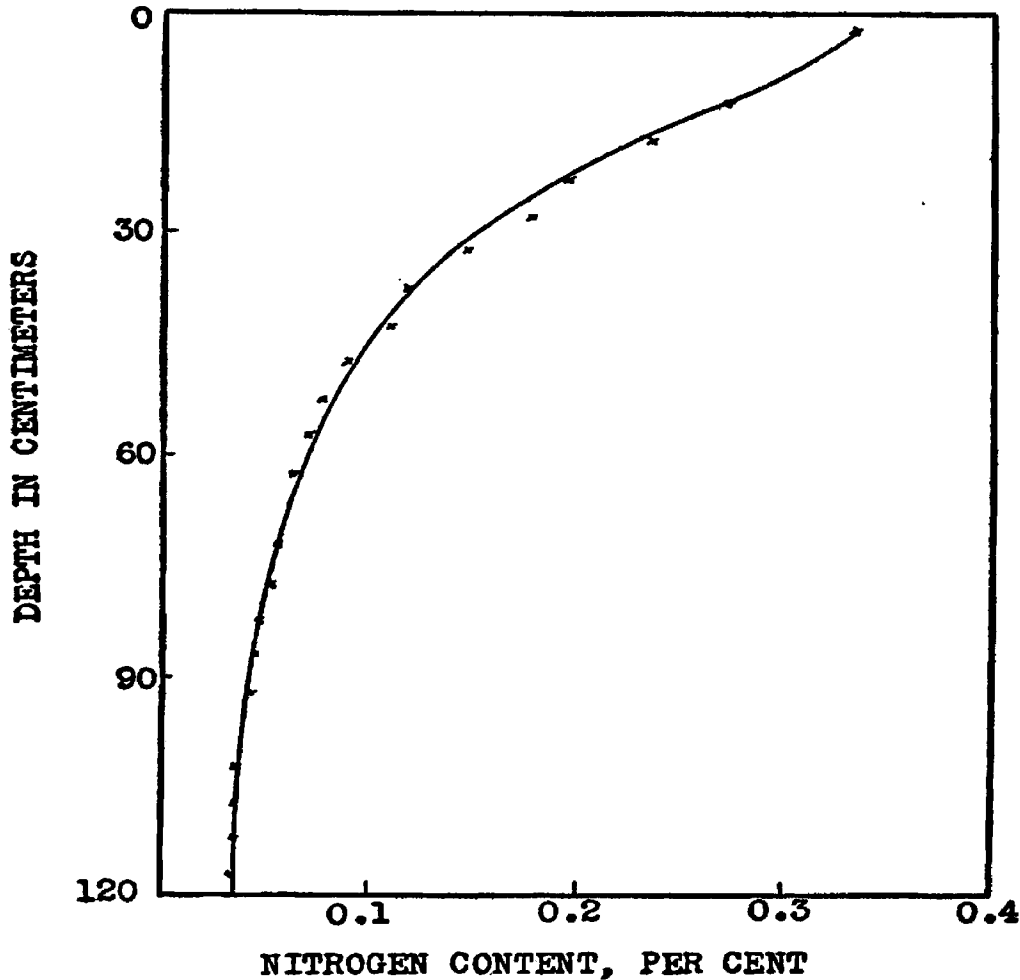


FIG. 25. Nitrogen distribution with depth of a Carrington silt loam, Nebraska (after Russell and Engle).

the sum of oxidation values of the unhydrolyzed matter in the residual soil and of the hydrolyzed fraction was found to be equivalent to the oxidation value of the original soil; about one-third of the organic matter of a chernozem and of a podsol forest soil and about one-half of a brown forest soil were shown to be hydrolyzable.

Humus in orchard soils. Humus has been found to be of great significance in orchard soils. Citrus trees, for example, are highly bene-

fited when at least a part of their nitrogen is supplied in an organic form (1196). In order to maintain healthy development of the trees, cover crops as well as additions of organic manures, are therefore commonly utilized. When manures are replaced by artificial fertilizers, an unhealthy condition develops in the trees. In orchard management, the vigor of the trees was shown to be controlled by the supply of humus in the soil (42); as a result of this, the quality and quantity of the cover crop are considered a fairly good index of the subsequent crop yield. In the case of irrigated lands, the supply of humus regulates the penetration of water and, to a large extent, controls the fertility of the soil as regards tree growth (727). Clean cultivation of orchard soils results in an appreciable reduction of the supply of humus, often to as much as one-half of the original content, in 10–15 years (184). On the other hand, too much organic matter, especially from legumes, may not be very desirable, because it favors excessive vegetative growth of the trees.

According to Lundegårdh (657), 50 per cent of the increased crop yields resulting from manuring and fertilizing may be due to an increase in photosynthesis, because a greater supply of CO_2 is made available through microbial activities.

Influence of cultivation and fertilization upon the abundance and nature of humus in soil. As a result of continuous cultivation of the soil, without a sufficient return of organic matter in the form of manure, composts, and plant residues, the humus content gradually diminishes.

Snyder (1057) found that when a prairie soil is first brought under cultivation, humus decomposition sets in rapidly; this is accompanied by a loss in nitrogen. After the soil has been cultivated for several years, it is found to contain less humus, and the rate of decomposition of the latter is gradually reduced. Summer fallow brings about a rapid destruction of the humus, and the nitrogen is made available at too rapid a rate. Similar results have been reported for gray-desert or serozem soils, where humus decomposition proceeds at an even more rapid rate upon cultivation. Geltzer (346) found that when virgin serozems were first plowed, cultivated, and irrigated, there was a loss in humus content of nearly 50 per cent within three years. Subsequently, the loss became smaller, until a certain equilibrium was established. A large part of the initial rapid decomposition was no doubt due to the presence in soil of undecomposed or partly decomposed plant residues in the form of roots and stems of grasses and other vegetation. Rapid decomposition occurs when a peat bog is drained, or,

in the case of sphagnum peats, drained and limed, and also after a forest floor is cultivated, with or without liming.

Not only the total humus, but its chemical nature as well, as determined by a number of methods, the simplest of which is the C:N ratio, is considerably influenced by fertilizer treatment; this was demonstrated (451) to hold true for the soil in the long-time field experiments at Rothamsted. To establish the influence of soil treatment, other chemical characteristics of soil humus, such as an analysis of its nitrogen distribution, can also be used. It has been shown (238), for example, that by fallowing a soil for thirteen years, without the addition of fertilizer, the total humus and total nitrogen were reduced by 43 per cent. The reduction of the nitrogen was largely at the expense of the di-amino form, the amide nitrogen decreasing only slightly. When the same soil received stable manure annually, there was an increase in amide nitrogen, above the uncultivated soil, even when the increase in total humus and total nitrogen was not quite sufficient to replace the loss due to cultivation.

The modification of the amount and nature of humus by cultivation and fertilization can also be measured by a change in total nitrogen and in the alkali-soluble organic fraction; the ratio of the results obtained by these two methods of measurement varies in different soils but is not affected by treatment of the same soil, as shown in table 44. When dilute alkali solutions, cold or hot, are used to extract a part of the soil humus (the "humic acid" or soluble humus fraction), different soils are found to show certain definite relations. When a 0.2 per cent NaOH solution was used, the extract titrated with standard KMnO_4 solution, according to the method of Demolon (215), soils in a good state of fertility gave the following ratios (513):

$$\frac{\text{soluble humus}}{\text{total nitrogen}} = 3.5, \quad \frac{\text{total humus}}{\text{soluble humus}} = 5.0$$

The use of this relationship was suggested as a method for distinguishing the quality of the humus in different soils and for determining the effect of soil treatment in modifying the nature of its humus.

It should be emphasized that it is the nature of the humus in the soil, rather than its total concentration, that is primarily concerned with soil productivity. In the case of cacao soils (392), for example, good soils were found to have a carbon-nitrogen ratio ranging from 7.0 to 8.3, whereas poor soils had a ratio of 5.7 to 6.8 (463a).

These and other observations lead one to conclude that humus does not decompose in the soil as a whole, but that certain constituents of the humus decompose more readily than others. One may even be tempted to consider the existence of unstable and stable forms of humus, as was done by certain pedologists. Such a classification of humus should be very limited in its application, until more definite information is obtained concerning the chemical differences that may exist between the various forms. The term "stable humus" might be used to designate that type of humus which has undergone extensive decomposition, similar to what has taken place in well-decomposed composts or cultivated mineral soils. It is characterized by an almost

TABLE 44
Total and soluble nitrogen in different soils, as influenced by fertilizer treatment (926)

FORMS OF NITROGEN	SOIL TYPE					
	Old arable land, Rothamsted			Old grass land, Rothamsted		Prairie soil, Manitoba
	Soil treatment					
	No manure since 1839	Artificial fertilizer since 1843	Stable manure since 1843	No manure since 1856	Artificial fertilizer since 1856	No manure
Total nitrogen per cent.....	0.097	0.115	0.217	0.260	0.230	0.618
Soluble nitrogen,* per cent.....	0.050	0.062	0.114	0.173	0.149	0.230
Ratio of soluble to total nitrogen.	51.8	53.8	52.5	66.3	66.3	37.2

* Soluble in dilute alkali solutions.

complete disappearance of the cellulose and hemicelluloses; by a considerable increase in the percentage of the lignin-like complexes, especially the proteins; and by a narrowing of the C:N ratio to about 10:1 or less. The term "unstable humus" might be applied to those forms of humus which still undergo rapid decomposition when placed under favorable conditions, as by correcting the reaction, by proper aeration (drainage), by a more favorable temperature, or by the addition of mineral nutrients or available nitrogen essential for the activities of microorganisms; the carbon-nitrogen ratio in this form of humus is much wider, varying from 20:1 to 30:1 in composts and in the forest floor, to as high as 80:1 in highmoor peats. The second form of humus may also originate by a special type of decomposition, whereby the

microorganisms attack not only the cellulose and hemicelluloses, but also the lignin; an unstable form of humus may thus result; "spent mushroom soil" and certain types of forest soil are illustrations of such processes. The "stable" form of humus is found predominantly in mineral soils, below the very surface layer, in the A₂- and B-horizons of forest soils, in lowmoor peats, and in well-drained peat soils; the "unstable" form of humus is found in decomposing composts, in undrained peat bogs, and in the forest floor. The difference between the two is more of degree than of kind; the second type of humus has either been less decomposed under the particular conditions, or has undergone a special type of decomposition.

At a time when confusion still existed between the total organic matter of the soil and the fraction soluble in dilute alkalis, frequently designated as "humus," statements were often made in which results obtained from the study of the latter were applied to soil humus as a whole. Weir (1264), for example, came to the conclusion that the removal of soluble humus from the soil had no effect in diminishing the productiveness of the soil, although the particular soil responded readily to nitrogen applications; the fact was not sufficiently emphasized that the "soluble humus" referred to the alkali-soluble fraction, and no sufficient distinction was made between this fraction and humus as a whole.

As a result of continuous cultivation, losses, not only of total humus, but also of the nitrogen content of humus have been observed repeatedly (31, 32). This is especially true of soils receiving applications of lime (723, 646, 338, 77), which led to the general conclusion that lime hastens the rate of decomposition of humus; this loss of organic matter is partly offset by the production of larger crops due to the use of lime, with the result that larger quantities of plant residues reach the soil and are converted into humus (846). The numerous frequently conflicting theories concerning the effect of lime upon the transformation of humus in soil may be placed in two general groups:

1. Wolff (1298-9) was among the first to observe that the presence of calcium in soil reduced the rate of decomposition of manure in soil and favored the accumulation of humus. This increase in humus, due to the presence of calcium, was explained by Slezkin (1045) as a result of the transformation of the soluble and colloiddally dispersed humus into an insoluble form, which results in the fixation of the humus.

2. On the other hand, definite evidence has been submitted (77)

that the addition of lime to soil hastens the loss of humus. The nature of the soil is of considerable importance. Soils rich in lime but present in the non-chernozem region were found to lose their fertility very rapidly on cultivation (1062). Lemmermann (624) also reported that an increase in the amount of lime added to the soil leads to an increase in the destruction of the organic matter in the soil.

Soils kept in grass (pasture) usually show an increase of both humus and total nitrogen (170). Sievers (1027) found that as a result of 30 years' cultivation, unlimed soils contained 1.279 per cent organic carbon and 0.104 per cent nitrogen and had a C:N ratio of 12.39 to

TABLE 45

Influence of manuring and cultivation upon the chemical composition of humus in mineral soils (822a)

Per cent of dry materials

CONSTITUENTS	FIELD SOIL				ORCHARD SOIL				PEATY SOIL
	Unmanured		Manured		Unmanured		Manured		
	Total soil	Soil humus	Total soil	Soil humus	Total soil	Soil humus	Total soil	Soil humus	
Fats and resins.....	0.48	11.40	0.75	13.61	0.79	11.42	0.69	9.94	12.52
Pentosans.....	0.14	3.32	0.72	13.07	0.37	5.35	0.25	3.61	4.46
Cellulose.....	0.33	7.84	0.39	7.08	0.58	8.40	0.55	7.93	6.89
Lignin.....	0.40	9.50	0.49	8.90	0.56	8.11	0.43	6.06	4.17
"Humic acid".....	1.84	43.70	2.09	37.90	1.76	25.42	2.73	39.40	54.60
"Humin"*.....	1.02	24.20	1.07	19.40	2.85	41.20	2.29	33.05	17.35

* This fraction was determined by multiplying the carbon content in the alkali insoluble fraction of the humus by the factor 1.72.

1; the corresponding figures for the limed soils were 1.414 per cent carbon, 0.115 per cent nitrogen, and a C:N ratio of 12.34 to 1.

The influence of manuring upon the chemical composition of humus in field and orchard soils has been studied only to a limited extent. A series of results obtained in a recent investigation are presented in table 45. For comparative purposes, the table includes also the chemical composition of a soil produced from peat.

Influence of climate upon the accumulation and nature of humus in soil. Temperature, precipitation, and evaporation influence the nature and abundance of the surface vegetation of the soil, as well as the mechanism and rapidity of the decomposition of the plant remains, thus determining the rate of accumulation of humus, its abundance, and its chemical composition.

Mohr (719) demonstrated that no organic matter accumulates in well-drained and porous, i.e., well-aerated, soils, when the average temperature is 25°C. or higher, as is the case of most tropical lowlands. He suggested that this is due to the fact that the high temperatures are nearer to the optimum for the activities of the humus-destroying microorganisms than they are for the growth of higher plants, which furnish the raw material for the accumulation of humus in soil. Under these conditions, most of the organic matter is destroyed by the lower organisms as fast as it is produced by the higher plants. Humus can accumulate in well-aerated soils only when the average temperature is below 25°C.; the lower the temperature, within certain limits, the

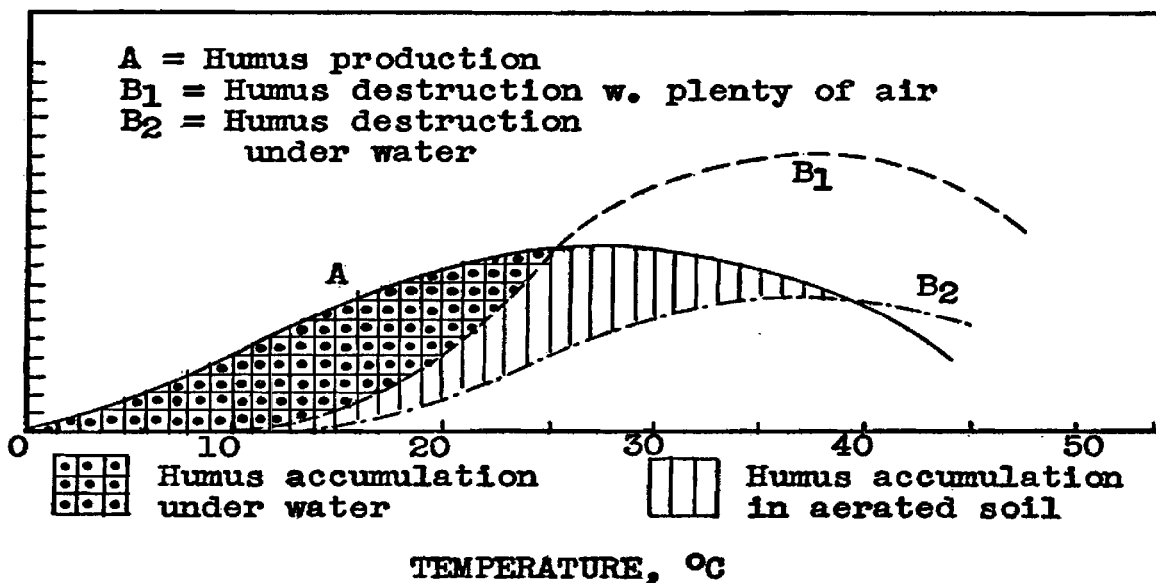


FIG. 26. Humus accumulation and humus decomposition in the soil (after Mohr).

greater is the advantage to the growth of higher plants and the greater, therefore, is the accumulation of humus (fig. 26).

In poorly drained and boggy soils, the lower organisms suffer more from the lack of oxygen than do certain higher plants. It is a well-known fact that the higher vegetation is usually fully as luxuriant in the marshes and bogs as on high ground, although the kinds of plants may be quite different. Thus organic residues are produced in abundance, but they are not destroyed by bacteria and fungi as fast as produced. As a result, peat or other forms of humus accumulate, even in spite of the high temperatures, in the tropical lowlands, provided the soils are waterlogged, thus leading to a deficient supply of oxygen for the best development of the lower organisms (996a).

As to the effect of rainfall, it was shown (930) that when the temperature is constant, the nitrogen and humus content of the soil increase logarithmically with increasing precipitation. In high altitudes where the annual temperature is below 0°C., the activities of microorganisms are considerably delayed, and even with a sparse vegetation, the content of humus in the soil may reach 20–30 per cent, as in the case of alpine soils (p. 239). The fact that the content of organic matter of forest soils in northern and cooler regions is higher than in the more southern and warmer regions has also been explained by the differences in the influences of climate on the growth of the higher vegetation, on the one hand, and on the decomposition of the residues by microorganisms, on the other (604, 432).

A detailed study of the rôle of humus in the formation of the soil profile, as well as further information on the humus content of podsoles, chernozems, serozems, and other soils predominantly inorganic in nature is given elsewhere (p. 376).

CHAPTER XI

HUMUS IN PEAT AND IN COAL

"Peat is a lignous complex, the decomposition of which is retarded by the presence of water."—LESQUEREUX.

Knowledge of the chemical nature of peat and coal is particularly important in connection with the study of the general chemistry and origin of humus, for three distinct reasons: 1. Peat and coal represent humus formations which have undergone extensive decomposition for periods of many years. The age of peats ranges from a few years to several thousands of years; coal deposits are much older, some being a million years old, others having been layed down more than a hundred million years ago. Peat and coal are said to be completely "decomposed" or "humified," i.e., the original plant residues have been fully changed into humus, although the original plant structures may still be recognized. 2. Historically speaking, the composition of peat has received more consideration from chemists, geologists, and botanists than any other form of humus; most of the isolations of the classical "humic acids" were made from various types of peat. 3. Because of the fact that both peat and coal contain relatively small amounts of inorganic constituents (except in the case of sedimentary peats) and that but little of the residue of the original plant materials is present in an undecomposed form (except in the case of highmoor peats), they can be considered as typical forms of humus. However, while the study of the chemistry of peat is interwoven with the study of other forms of humus, the chemistry of coal presents special problems which have already received exhaustive treatment (1104, 328, 229); this phase of humus will, therefore, be given only casual consideration here.

Remains

Most treatises on peat are concerned chiefly with the chemistry of its mineral constituents, which make up an insignificant part of the peat; others deal largely with its industrial or agricultural utilization; still others are so much influenced by the "humic acid" conception of peat as to overlook the fact that peat is a natural body, produced as a result of specific processes of transformation and having characteristic chemical composition. An appreciation of the chemical nature

of peat in general and of the specific types in particular can come only when their origin is taken into consideration; this requires knowledge of the plant vegetation which has contributed to the peat formation, of the terrestrial and climatic conditions, and of the processes of decomposition. The study of peat as a form of humus involves consideration of certain factors which are distinct from those encountered in the study of humus in forest and mineral soils.

Definition and nature of peat. The term "peat" is commonly used to designate a layer of the earth's crust which is largely organic in nature and which has been formed, under certain specific conditions, from plant residues and plant products submerged in water or from plants growing in very wet environments. Peat bogs are universally distributed, being most numerous in the temperate zones in locations having cool and humid climates. Peat soils are formed from drained peat bogs; they are known under a number of different names, which are usually of only local value.

The nature of the processes involved in the formation of peat from plant residues is still a matter of dispute. Certain evidence points to the fact that some of the transformations whereby the plant materials are gradually changed into peat are microbiological in nature. Some investigators, however, still adhere to the idea that the processes of peat formation are largely, if not entirely, chemical in nature, and are brought about by atmospheric agencies; peat formation is thereby distinguished from decomposition of plant residues under aerobic conditions: the former process is believed to lead to an accumulation of plant residues which are only partially transformed chemically, while the latter results in complete disintegration of the residues into simple inorganic and organic compounds. It will be shown later that this assumption is unjustified, the differences between the two processes being those of degree rather than of kind.

The geologist has been interested in peat because of its relation to the earth's crust, because of its ready availability as a source of fuel in many places, and because of the rôle that it is supposed to have played in the origin of coal. The botanist has been interested in peat from the ecological point of view and as a storehouse of residues of plants which grew at different historic periods. The geographer has been interested in peat as a source of information which enables him to trace climatic changes over the earth during different periods. The chemist either limited himself to a study of the inorganic constituents of the peat or was interested in demonstrating the presence in peat of

definite chemical substances, such as pentosans, cellulose, and waxes. The physical chemist looked upon peat as a colloidal system and studied its water relations and its absorption of bases. The microbiologist, as well, made only a limited contribution to the knowledge of peat; by looking for organisms which he was accustomed to find in field soils, he failed to recognize those bacteria which are most important in peat-forming processes. The agriculturist has been interested primarily in the practical utilization of peat for the growth of cultivated crops or in its exploitation for fertilizer purposes.

These are the main reasons why the nature and origin of peat have become highly confusing. The extent of this confusion is best illustrated by the citation of several of the commonly accepted definitions of peat. Weber, an outstanding investigator of peat, summarized the current knowledge of the nature of peat during the early part of this century as follows: "Peat is an organic mineral formed out of dead, cellulose rich plants, by a special process of ulmification or peat formation; it becomes colored brown to black when exposed to air; it is soft in its natural moist condition and is very rich in water; its specific color depends on its content of ulmin. Peat consists largely of the elements carbon, hydrogen, oxygen, and contains, in addition, varying amounts of nitrogen, sulfur and ash. Various animal residues are admixed in varying amounts in peat, in the form of excreta and chitin. On drying, peat shrinks quite considerably, giving fragments hanging loosely together or hard clumps, breaking apart with the formation of sharp edges, or often into fibrous or felt-like masses. According to the degree of ulmification and the manner in which peat has been formed, the plant residues can either still be recognized by the naked eye, or by use of magnifications, or they break easily apart. From the geological point of view, peat formation is limited to the quarternary system."

In this definition, no attention was paid to the chemical and microbiological processes involved in the formation of peat or to the rôle of the various constituents of the plant residues in the process. The nature of the plants which gave origin to the peat also received but scant consideration or none at all. The insufficient understanding of the chemical processes of peat formation and transformation is covered by such vague generalizations as "ulmification" or "humin formation." As has been discussed previously, "ulmin" and "humin" were mere labels for preparations obtained by certain arbitrary procedures and not for definite chemical substances; these labels were useful only

idea
relat

Too
more
or
less

when exact knowledge of the processes was unavailable. The fact that the elementary composition alone was considered, points further to an almost complete lack of appreciation of the chemical nature of the organic complexes that comprise the peat. The physical properties of the peat were over-emphasized and were used for purposes of characterization. The ultimate chemical analysis of peat and peat-forming plants frequently led to a hasty conclusion that there is no chemical difference between the two.

On comparing this conception of peat with that prevalent in the middle of the last century, or fifty years previously, one finds that very little progress has been made. This is brought out by the definition of Lesquereux (632), given at the head of the chapter, and by that of Johnson (506); the latter wrote in 1863 that "the production of peat from fallen and decaying plants depends upon the presence of so much water as to cover or saturate the vegetable matters, and thereby hinder the full access of air. Saturation with water also has the effect of maintaining the decaying matters at a low temperature, and, by these two causes in combination, the process of decay is made to proceed with great slowness, and the solid products of such slow decay are compounds that themselves resist decay and hence accumulate." One must confess, however, that most of the students of peat did not have such a clear conception of its nature and formation as did Johnson. More commonly, peat was defined as "a mass of dead organic matter," "a formation originating from plants or living beings," or "material originating in swamps."

It is sufficient to cite the definition of Dana (203a): "Peat is too well known to render it necessary to say that it is the result of that spontaneous change in vegetable matter which ends in geine. Peat is, among manures consisting chiefly of geine, what bone-dust is among manures consisting of animal matter. Peat is highly concentrated vegetable food. When the state in which this food exists is examined, it is found not only partly cooked but seasoned." Half a century later, Früh (321) emphasized that "the important transformation products of plant constituents which are characteristic of peat are the ulmic acids and ulmin, humic acids and humin, as well as the salts of these." It is this conception which served as the leading guide for investigators of the chemistry of peat during the first quarter of this century.

In very few instances was the rôle of microorganisms in peat formation considered at all. Fremy (317) stated in 1879 that the tissues of peat-forming plants disappear "by a peaty fermentation, as proven

by our colleague, M. van Tieghem, whereby the cellulose dissolves, having been fermented with the production of gas"; however, since Van Tieghem emphasized that this process does not apply to algae, mosses, lycopodia, and other plants which are important constituents of certain peats, Fremy's ideas cannot be generalized to apply to all types of peat, especially to highmoors. Früh recognized the function of "fermentation" and "putrefaction" processes, but could not demonstrate any bacteria active in the "humification" process. Wollny (1301) emphasized the fact that microorganisms play an important part in the process of peat formation, especially during the early stages of decomposition. According to Klason (784), when plants decompose under water, microorganisms destroy the carbohydrates while the lignin-like substances give rise to peat. These well-defined conceptions, which seemed to indicate both the nature of the processes taking place in the decomposition of plant residues leading to peat formation and the rôle of microorganisms in these processes, did not prevent De Lapparent (608a) from stating in 1900 that "in moist spots, under the protection of water, the slow decomposition of certain plants takes place, with their transformation into a fuel called peat, which stands midway between the organic and mineral kingdoms."

Considerable progress has been made, however, toward a better understanding of the rôle of plants in peat formation. The existence of a certain type of peat was definitely correlated with an association of plants which gave rise to it. It has also become recognized that the chemical composition of peat is dependent upon the composition of the original plants and upon the processes of transformation. This can be recognized from a recent definition (853) of peat as "a mass of dead plant residues, the decomposition of which took place very slowly due to a lack of sufficient oxygen and which has not been completed yet; the physics and chemistry of peat are partly the physics and chemistry of the plants from which peat originated and which may still be present in it in a slightly changed form."

This and other recent conceptions of the nature of peat (1103) can be considerably modified, when the decomposition processes brought about by microbiological activities are recognized. On the basis of this accumulated knowledge, peat has been defined (1240) as "a layer of the earth's crust consisting largely of organic matter, which has originated as a result of incomplete and partial decomposition of the various constituents of the natural plant materials, due to the anaerobic processes under which plant decomposition has taken place; the nature

of the peat depends upon the plant association which has given rise to it and the latter is controlled by the amount of mineral nutrients and reaction of the waters in which the plants are growing; chemically the composition of peat is influenced by the nature of the plant associations from which it has originated and the moisture relations, during and following the periods of its formation and accumulation."

The fundamental factors which influence the origin and nature of peat are predominantly functions of climate and of soil and water relations. These factors determine the nature of the vegetation, as well as the processes of decomposition of the plant residues (117). Peat is formed on land which is poorly drained and where water may collect and stand permanently. Peat-forming plants find these conditions favorable for their development, especially when the high humidity of the air prevents evaporation and the temperature is low; the decomposition processes are very slow under these conditions, and, as a result, the partly decomposed plant residues give rise to peat.

The highmoor peats are highly acid in reaction (pH 3.5–4.5), whereas the lowmoor and sedimentary peat are less acid (pH 5.5–6.5) and the latter may even be neutral (339, 388, 573, 582, 700, 940).

Classification and formation of peat. Various systems of peat classification have been proposed. They are based upon the following factors: 1. the nature of the plant associations at present growing on the surface of the bog; 2. the nature of the plants which gave origin to the specific type of peat; 3. the relation of peat formation to water level, namely, below or above the surface of the water; 4. the autochthonous (formed in place) or allochthonous nature of the plant residues which gave rise to the peat; 5. the relative concentration of nutrient elements available to the growing plants; 6. the physical and mechanical properties of the peat; 7. a combination of characteristics, such as the mechanical and physical properties and the botanical composition of the peat. Peat bogs and peat soils are usually classified on the basis of the degree of humus decomposition, color of humus, and industrial and agricultural utilization. Some of these systems do not emphasize sufficiently the fundamental characteristic properties of the peat and are, therefore, open to considerable criticism. Schreiber (964) stated that the chemical composition of peat, as determined by the common methods of analysis, does not yield sufficient information for its characterization.

The number of peat types that have been described creates considerable confusion primarily because of the various systems of classification used. By the adoption of one particular system, all peat forma-

tions can be included in a few major types; minor subdivisions of each type can be used for more exact differentiation. The nature of the plant residues which gave rise to a specific type of peat is at present recognized as the most logical basis of peat classification. The major types of peat can be summarized as follows:

1. Lowmoor peat. Various sedges and reeds, as well as certain trees and shrubs are the dominant and characteristic species of plants; sphagnum plants are either absent or are rare. This type is frequently subdivided upon the basis of the predominant plant, e.g., carex peat, phragmites peat, and cladium peat. It is usually produced in places where the waters, containing calcium and rich in nutrients, are slowly draining into lower regions on inclined planes; it is characterized chemically by high ash and nitrogen contents, by a low cellulose content, and by a low acidity.

Waters
low moor
high

2. Highmoor peat. The predominant vegetation consists of various species of Sphagnum, Calluna, Ledum, Andromeda, and Eriophorum. This type of peat is formed in waters originating either from atmospheric precipitation or from mineral-poor soils, and carrying very low concentrations of calcium. Highmoor peat may be formed upon one of the other peat types, or directly upon sand, clay, or rock. It is usually found in regions of cold or moderate temperatures with high rainfall. Chemically, this peat is characterized by low ash and nitrogen contents, by high contents of cellulose and hemicellulose, and by a high acidity (547a).

3. Forest peat. A vegetation consisting of various trees (*Betula*, *Quercus*, *Alnus*, *Pinus*, *Picea*) and of certain lower plants (*Calluna*, *Oxycoccus*, *Salix*, *Andromeda*, *Carex*) gives rise to forest peat. Certain species of Sphagnum (*S. recurvum* and *S. subicolor*) may form a continuous carpet in the forest. The bog is fed partly by ground waters, less rich in salts than those draining into lowmoor peat, and partly by precipitation; chemically this peat stands midway between the former two types.

4. Sedimentary or lake peat. This type of peat is formed under water, largely by algae and other aquatic plants and animals (insect shells), with an admixture of spores, pollen, and particles of clay and sand. It is usually found in the lowest layers of the peat profile, but it forms frequently independent peats of considerable depth. It varies considerably, depending upon the nature of the plant residues; upon the abundance of calcium carbonate, sand, and clay; upon its colloidal condition, etc. It has been described in the literature under the

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names "sapropel," "gyttja," "dy," and "liver peat," with numerous subdivisions.

The heath-peatland (*Calluna*, *Eriophorum*, *Scirpus*, *Vaccinium* associations) has been classified (315a) as "climatic moor" and as "basin moor", the latter being formed in hollows or depressions, due to bad surface drainage; those peat formations, which are produced by the slow percolations of water low in bases have been designated as "flush types". These humus formations have a certain similarity to alpine humus (p. 237).

According to Von Post (838), every exhaustive genetic characterization of peat types must consider several factors: 1. Deposition of the peat; the plant residues may either be deposited in the same place where they were formed (autochthonous) or they may be brought in by water or other agencies (allochthonous or sedimentary formations). 2. Degree of humidity during the stage of formation of the peat deposits; the bog may have been constantly or periodically covered with water or the moisture necessary for the accumulation of the organic matter may have been obtained through the high position of the water table. 3. Nutrient content of the peat deposits. 4. Chemical nature of the decomposition processes.

In the development of a peat bog, algae and other aquatic plants, residues of higher plants, such as spores, pollen, and leaves, as well as inorganic particles of dust, first accumulate under water, forming the bottom layer of the peat deposit. This process is followed, as soon as the waters become shallow, by a zone of aquatic vegetation, including sedges and reeds, which grow *in situ*. Because of the anaerobic conditions prevailing in the bog, the decomposition of the plant residues does not keep pace with new growth of plants, hence undecomposed and partly decomposed plant residues accumulate. When the level of peat accumulation has been raised by the deposit to that of the surrounding country, growth of various herbs, shrubs, and species of sphagnum takes place, and, finally, various coniferous trees appear; following these plants, deciduous trees develop and may even replace the conifers. At this stage, the surface of the peat is above the water level, and consequently decomposition processes begin to keep pace with plant accumulation. In case the water level is suddenly elevated, the trees are destroyed and various lower plants which are better adapted to these changed conditions will reappear. A new period of peat accumulation then begins; the whole plant association may be changed as a result of the establishment of the new conditions. Black-

falling under water remained preserved from any action of microorganisms and only undergo weak chemical hydrolyses, or that all the constituents of the plant remains undergo decomposition and are gradually transformed into a dark brown mass or "humus" (99, 100). The mechanism of transformation of the plant constituents into peat attracted only little attention. There has been a certain common idea (1065) that peat originates from cellulose by a process of carbonization; the cellulose was believed to lose hydrogen and oxygen as water, carbon and oxygen as carbon dioxide, and carbon and hydrogen as methane, these changes giving rise to humus:

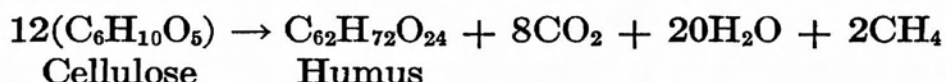


TABLE 46
Chemical composition of a woody peat (1153)
Per cent of dry material

DEPTH OF PEAT	HOT WATER SOLUBLE FRACTION	ETHER-SOLUBLE FRACTION	FRACTION SOLUBLE IN 3 PER CENT ClO_2	FRACTION SOLUBLE IN NH_4OH	FRACTION SOLUBLE IN SCHWEIZER'S REAGENT
<i>meters</i>					
0.08	1.80	36.50	9.90	24.97
0.15	3.77	21.30	15.15	38.85
0.23	2.48	3.83	18.12	14.60	38.81
0.53	4.25	3.45	41.30	15.53	14.46
0.91	3.55	8.57	21.30	33.20	9.21
1.22	3.08	4.66	27.70	38.54	6.85
1.83	2.30	4.28	28.81	37.37	7.24
2.44	0.90	5.67	20.15	42.86	0.88
3.04	4.45	10.00	51.05

The purely hypothetical character of these and other assumptions of a similar nature has already been discussed.

There is no doubt at the present time that microorganisms are active in peat formation, as they are in the aerobic processes of decomposition, with certain qualitative and quantitative differences. By placing bricks of peat forming plants upon cultures of different microorganisms grown upon artificial media and sand, Bielikova (85a) has shown that fungi are most active in the first stages of peat formation. The presence of large numbers of bacteria in those layers of the peat profile where active decomposition is still taking place further points to the function of microorganisms in the process.

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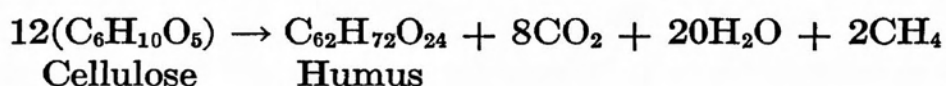


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In the decomposition of peat forming plants, the different plant constituents are not acted upon alike. The proteins and their derivatives, the sugars, and the starches are attacked readily. The hemicelluloses, the cellulose, the pectins, the oils, and the fats decompose less rapidly, especially in the case of highmoor peats. In the case of some peats (sedimentary, lowmoor), the decomposition of these complexes is so much more rapid that no cellulose is left, although some of the hemicelluloses may still persist. The hemicelluloses in the plant tissues comprise two groups, some of which are readily decomposed, while others resist decomposition even more than does cellulose (871); the microorganisms bringing about the decomposition of the plant constituents also synthesize certain hemicelluloses which are very resistant to de-

TABLE 47

Proximate chemical composition of a lowmoor peat profile in New Jersey (1940)
Per cent of dry material

DEPTH OF LAYER	pH	ETHER-SOLUBLE FRACTION	WATER-SOLUBLE FRACTION	HEMI-CELLULOSES	CELLULOSE	LIGNIN AND LIGNIN-LIKE COMPLEXES	PROTEINS	ASH
<i>cm.</i>								
12	5.9	0.66	3.08	10.31	0	38.35	22.48	13.22
18	6.3	1.10	1.24	8.95	0	50.33	18.72	10.13
160-180	6.3	0.49	2.31	7.02	0	57.83	14.81	10.15
160	6.7	0.78	1.14	7.51	0	42.10	19.81	15.00
Lake peat	6.8	0.67	0.81	12.14	0	33.25	19.38	24.87
Gyttja layer	8.0	0.36	1.24	5.92	0	15.62	9.81	59.55

composition (889, 1219). The persistence of cellulose and hemicelluloses in highmoor peats, especially in the younger sphagnum peats, is due to several factors: (a) the chemical nature of the constituent substances, (b) specific physical condition of the sphagnum plants, (c) conditions unfavorable for decomposition. The lignins, cutins, resins, waxes, terpenes, and alkaloids are the plant constituents most resistant to decomposition. The cuticles of many plants, the spore-exines, and the pollen-exines also undergo but little chemical change during peat formation (1152).

Formation of peat consists primarily of the following four processes: 1. Rapid decomposition of the water-soluble substances. 2. Slow decomposition of the cellulose and hemicelluloses which make up the bulk of the plant constituents; the nature of the peat which results from the

decomposition processes depends to a large extent on the completeness with which these complexes are disintegrated. 3. Gradual accumulation of resistant constituents; namely, lignins, resins, and waxes; some lignites may contain as much as 50 per cent of resinous matter, although the original woody material from which they originated contained only a few per cent of resins (1152). 4. Synthesis of microbial cell substance, which accounts for the increase in the protein content of certain peats (lowmoor, forest).

A detailed discussion of the processes involved in peat formation and of methods for measuring the degree of peat decomposition was presented previously (also 127, 205, 529, 858, 1251, 1259). A study of the chemistry of peat as a type of humus was also discussed in detail in the foregoing; attention is called here only to some of the specific problems involved in the study of the chemistry of peat.

Occurrence of peat. Numerous treatises have been published, in which detailed descriptions of peat formations are given (60, 67, 71, 73, 93, 190, 287, 305, 322, 370, 389, 394, 964, 1093, 1107, 1108, 1125, 1128, 1157, 1163, 1171). Of particular interest is the occurrence of peats in the tropics (68, 533, 718). The physical properties (p. 305), and the industrial (p. 365) and agricultural (p. 361) utilization of peats are discussed in detail later.

Chemical composition of peat. Peat represents a specific natural humus formation. Each of the several distinct types is characteristic in chemical composition, primarily because of differences in the chemical composition of the plants that gave it origin and of differences in the processes of decomposition. Just as the chemical composition of sphagnum plants varies from that of reeds and sedges, from that of the wood and pollen of trees, and from that of various algae, so does highmoor peat vary chemically from lowmoor, forest, and sedimentary peats which have largely originated from the above plant materials. The chemical differences among these peat types are not only quantitative but also qualitative in nature. One speaks of the hemicelluloses, cellulose, lignins, proteins, and waxes in peat, but these complexes are not exactly the same compounds in both highmoor peat and lowmoor peat, largely because the corresponding complexes in the sphagnum plants differ chemically from the corresponding complexes in sedges and reeds, in trees, and in algae.

Mulder (731) determined in 1839 the carbon content of peat in Holland and found it to range from 59.27 to 61.05 per cent. Somewhat lower results were obtained in later analyses, usually around 55-56

per cent. The concentration of carbon may vary in peat, according to its age and botanical composition, from less than 50 per cent to almost 64 per cent, increasing from the surface to the bottom of the profile.

Numerous systems of peat analysis have been used, usually adapted from the various systems of plant analysis. The results of the chemical analysis of peat in a woody peat profile, on the one hand, and of low-moor and highmoor peats, on the other, as determined by two methods are shown in tables 46, 47, 48. (For special analytical procedures, see 49, 284, 1131).

TABLE 48

Proximate chemical composition of a highmoor peat profile in Maine (1240)
Per cent of dry material

DEPTH OF LAYER	pH	ETHER-SOLUBLE FRACTION	ALCOHOL-SOLUBLE FRACTION	HEMI-CELLULOSES	CELLULOSE	LIGNIN AND LIGNIN-LIKE CONSTITUENTS	PROTEINS	ASH
<i>cm.</i>								
1-8	4.05	2.35	1.45	26.45	16.86	27.18	4.08	2.00
8-20	3.95	2.62	1.92	25.24	14.74	29.21	4.28	1.14
20-30	3.85	2.82	1.83	24.55	15.97	28.85	5.11	1.02
30-46	3.86	2.57	2.08	22.25	13.69	32.23	5.24	0.90
46-61	3.73	2.96	3.20	18.48	14.66	33.24	4.81	1.06
183-214	4.47	3.97	3.15	15.94	15.55	37.43	4.41	0.99
460-480	4.71	4.89	4.29	12.69	11.85	44.83	4.73	1.10
550-580	5.18	5.97	5.06	5.96	5.06	54.11	11.53	2.83

Lowmoor peats are practically free from cellulose. The lignins (or lignin-like complexes) and the proteins form the two major groups of chemical complexes found in this type of peat; they account for 60 to 72 per cent of the total peat, the ratio of lignin to protein being about 2:1 to 2.5:1. If one assumes that the inorganic constituents (ash) of the plants have accumulated in the peat, without any loss, one can calculate from the above results that it would take about three parts of plant residues to produce one part of peat. By a comparison of the lignin and protein concentrations in the peat with those of the original plants, it can thus be shown that these two complexes have undergone a certain amount of decomposition in the process of peat formation. The fact that some of the mineral constituents of the dead plant residues have no doubt been used by the growing plants, would tend to

make the above ratios wider. Miller (709) concluded that 7 parts of saw-grass plants (*Cladium effusum*) are required to form 1 part of peat. With this as a basis, he calculated that 33 per cent of the original nitrogen, 70 per cent of the phosphoric acid, and 96 per cent of the potash of the plants were lost in the formation of peat.

Highmoor peats contain a high concentration of cellulose and hemicelluloses, either because of the greater acidity of the sphagnum plants or of a difference in the physical and chemical nature of their carbohydrates (1003). The fact that there are greater amounts of fats and waxes, of lignins, and of lignin-like complexes in these peats than in the peat-forming plants, leads one to conclude that a certain amount of decomposition has taken place in these peats as well, especially in the

TABLE 49

Chemical composition of peat-forming plants and of highmoor peat in different stages of decomposition (671)

Per cent of dry material

MATERIAL	BENZOL EX- TRACT	ALCO- HOL EX- TRACT	CRUDE CELLU- LOSE	PEN- TOSAN	LIGNIN AND HUMIC BODIES	ASH
<i>Sphagnum parvifolia</i>	1.53	5.08	60.31	10.81	9.79	2.40
<i>Sphagnum fuscum</i>	1.49	3.99	2.37
<i>Sphagnum medium</i>	1.96	5.03	2.70
<i>Eriophorum vaginatum</i>	1.57	5.59	33.12	20.82	24.86	2.80
Sphagnum peat, weakly decomposed...	2.90	3.38	46.82	9.04	23.36	4.71
Sphagnum peat, medium decomposed...	7.28	7.04	34.56	6.52	39.12	1.19
Sphagnum peat, well decomposed.....	10.46	8.10	13.38	2.22	59.61	2.02

older formations. This becomes evident when one considers the nitrogenous complexes of these peats. In lowmoors, the proteins accumulate with the advance in age of peat; in highmoors, these complexes may actually diminish in concentration, as a result of their preferential decomposition by the bacteria. The continuous liberation of nitrogen in an available form, without its being reconsumed by bacteria and fungi, enables the sphagnum plants to continue growth in such a poor medium as is provided by the highmoor peat.

Further data on the chemical changes in the formation of highmoor peats, as determined by different methods of analysis, are given in table 49. The chemistry of peat is also complicated by the fact that the various layers taken from different depths are unlike in chemical composition. The explanation is to be found in the fact that the materials

have been exposed to decomposition for different periods and that these layers have originated from different plants and plant residues at different periods of time (fig. 27). Various methods have been proposed for determining the degree of decomposition of peat. These are all based either on the amount of residual carbohydrate (560) or accumulation of lignins and other carbon-rich compounds (537) or on the change in color, as shown (47) in the following summary:

NATURE OF PEAT	TOTAL CARBON	CELLULOSE CONTENT (560)	UNHYDROLYZABLE FRACTION (537)	COLORIMETRIC METHOD (781)
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
Sphagnum moss.....	49.57	54.72	23.7	1.0
Young sphagnum peat.....	54.21	14.98	44.6	45.9
Limiting horizon.....	11.37	56.0	68.2
Old sphagnum peat.....	58.57	8.50	66.6	88.3

The inundation of peat bogs with salt water produces a definite effect upon the transformation of the organic constituents (830).

Mineral complexes in peat. The chemical composition of peats and peat waters varies considerably, not only in the case of different types of peat, but also for the same type formed in different regions, depending on the nature of vegetation, chemical composition of the ground waters, nature of the subsoil, etc. The lime (CaO) content of dry sphagnum peat was found (773) to vary from 0.15 to 0.65 per cent; the P_2O_5 , from 0.04 to 0.12; the K_2O , from 0.06 to 0.15; and the total nitrogen, from 0.77 to 1.56, with an average of 1.15 per cent. In the case of lowmoor peats, the CaO content varies from 1.80 to 4.50 per cent; the P_2O_5 , from 0.06 to 0.35; the K_2O , from 0.06 to 0.20; and the total nitrogen from 1.21 to 3.73, with an average of 2.50 per cent. One cubic meter of wet sphagnum peat was reported to contain 45–90 kg. dry matter, while the same amount of wet lowmoor peat contained 85–250 kg. dry matter. The following concentrations of the essential nutrient elements were found in peat waters from highmoors and lowmoors respectively, in milligrams per liter: P_2O_5 —0.23 and 1.33, K_2O —3.0 and 3.43, Fe_2O_3 —0.32 and 0.50, SiO_2 —6.6 and 7.9, SO_3 —5.7 and 14.2, NH_3 —0.18 and 0.16, N_2O_5 —1.73 and 2.10, and total solids—183.0 and 225.0 (547b).

Sphagnum plants, which contribute largely to the formation of highmoor peats, are very low in minerals. They vary considerably in

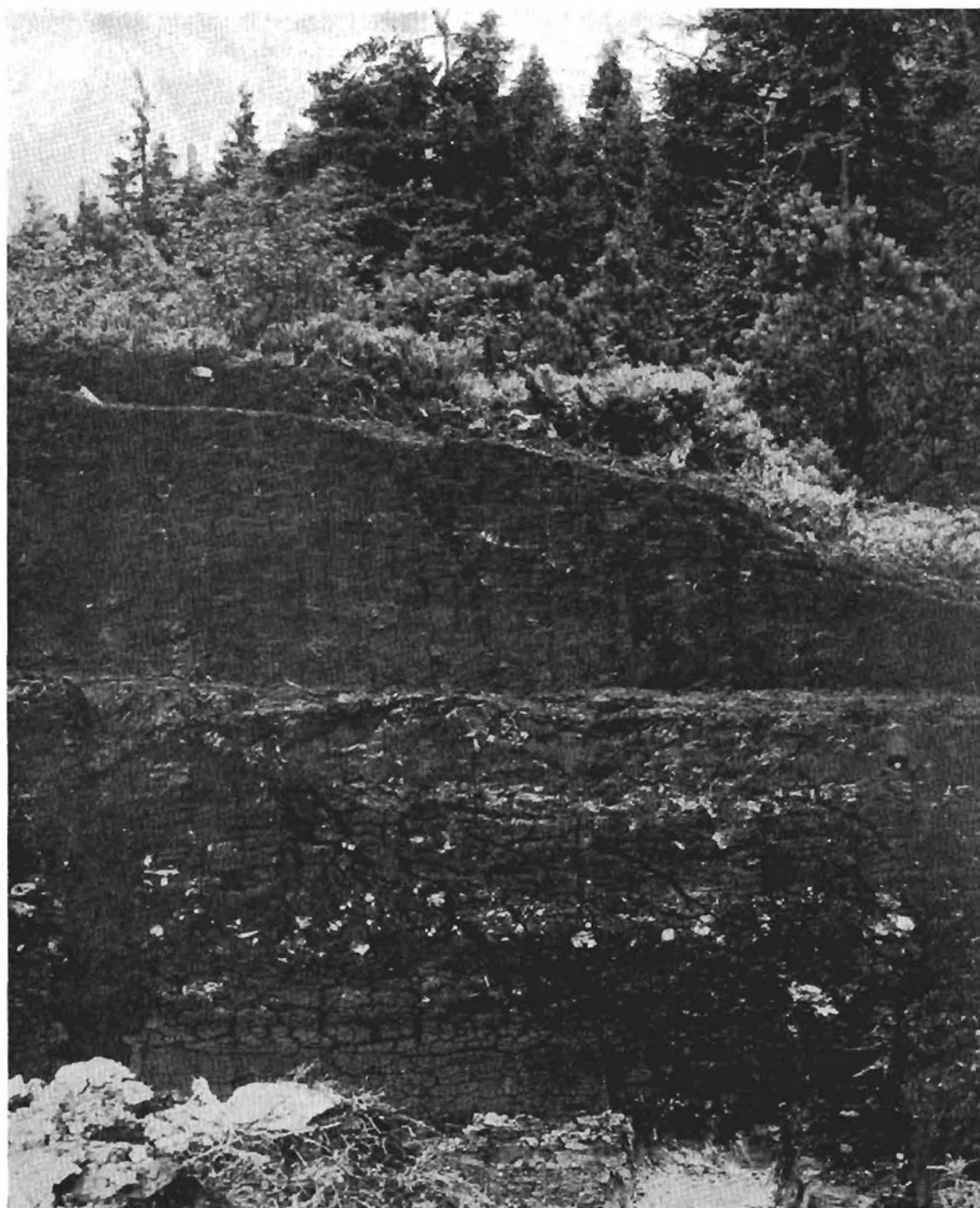


FIG. 27. Profile section of a highmoor peat showing a well marked sequence of younger sphagnum peat, followed by the woody Grenzhorizont, then by a layer of older sphagnum peat, a layer of forest peat and a compact layer of sedge peat (after Zailer).

chemical composition, depending upon the species and conditions of growth. *S. acutifolium* obtained from a highmoor was reported (377-8) to contain the following concentrations of minerals, in per cent of dry materials: CaO—0.25, MgO—0.12, K₂O—0.09, P₂O₅—0.05, and nitrogen—0.53; the same species of sphagnum collected from a forest peat contained 0.55, 0.09, 0.16, 0.14, and 1.20 per cent of the respective mineral constituents. Even the same plant grown in the same locality changes in composition with age, as one can recognize by a comparison of the living and dead portions (table 50). When the plants die and undergo decomposition by microorganisms, some of the minerals, especially the potash and phosphate, go into solution and are made available for new growth of plants; others, however, especially the

TABLE 50

Mineral composition of sphagnum plants found in different types of peat (378)
Per cent of dry material

	NATURE OF PEAT					
	Highmoor		Forest		Lowmoor	
	State of plant					
	Living	Dead	Living	Dead	Living	Dead
Nitrogen.....	0.759	0.620	1.524	1.080	1.444	1.195
P ₂ O ₅	0.072	0.054	0.223	0.148	0.198	0.172
K ₂ O.....	0.458	0.179	0.846	0.311	0.934	0.309
CaO.....	0.258	0.259	0.350	0.532	1.038	2.037
MgO.....	0.128	0.112	0.140	0.135	0.269	0.387

salts of calcium and magnesium, tend to remain in the dead plant. This is one of the reasons why peat formed from sphagnum plants is very poor in potassium and phosphorus. The fact that the waters of the highmoor bogs are largely of atmospheric origin and are very poor in mineral salts, further accounts for the low ash content of the resulting peat.

Lowmoor and forest peats, and especially lake or sedimentary peats, are considerably richer in ash. The plants growing in these bogs assimilate large quantities of minerals, which remain to a large extent in the decomposing plant residues and contribute to the ash content of the peat; the terrestrial waters which supply these bogs are also rich in minerals. Phragmites peat was reported (1305-6) to contain 10.46 to 14.65 per cent ash, as compared with 1.93 to 3.92 per cent

ash in sphagnum peat and only 0.59 per cent in Eriophorum peat. Typical highmoor peats, with a calcium content of less than 0.5 per cent, were shown (377) to contain, for every 100 parts of calcium, 635 parts nitrogen, 62 parts P_2O_5 , and 14.7 parts potassium; peats containing 0.5–1.0 per cent calcium had, for every 100 parts of calcium, 260 parts nitrogen, 18.7 parts P_2O_5 , and 5 parts potassium (1289).

Peat-forming plants are richer in phosphoric acid and potassium than the peats to which they give rise (table 51); this is also true of the other important mineral constituents (301–2). When the plant dies, the easily soluble salts, especially the alkalis (Na, K), are immediately reabsorbed by the growing plants and are used for the building of new plant substance. The plants are thus able to utilize from the dying

TABLE 51
Nitrogen and mineral content of peats and peat-forming plants (712)
Per cent of dry material

NATURE OF PEAT OR PLANT	NITROGEN	PHOSPHORIC ACID	POTASSIUM
Young sphagnum peat.....	0.64–0.74	0.03–0.04	0.02–0.03
Phragmites peat.....	2.29–3.23	0.09–0.28	0.04–0.19
Carex peat.....	2.94–2.47	0.20–0.14	0.06–0.05
Pollen peat.....	0.69–1.09	0.03–0.06	0.01–0.16
Liver mud.....	2.01–3.68	0.09–0.28	0.13–0.33
<i>Hylocomium squarosum</i>	1.27	0.44	0.87
<i>Calluna vulgaris</i>	1.04	0.23	0.51
<i>Sphagnum medium</i>	0.73	0.09	0.23

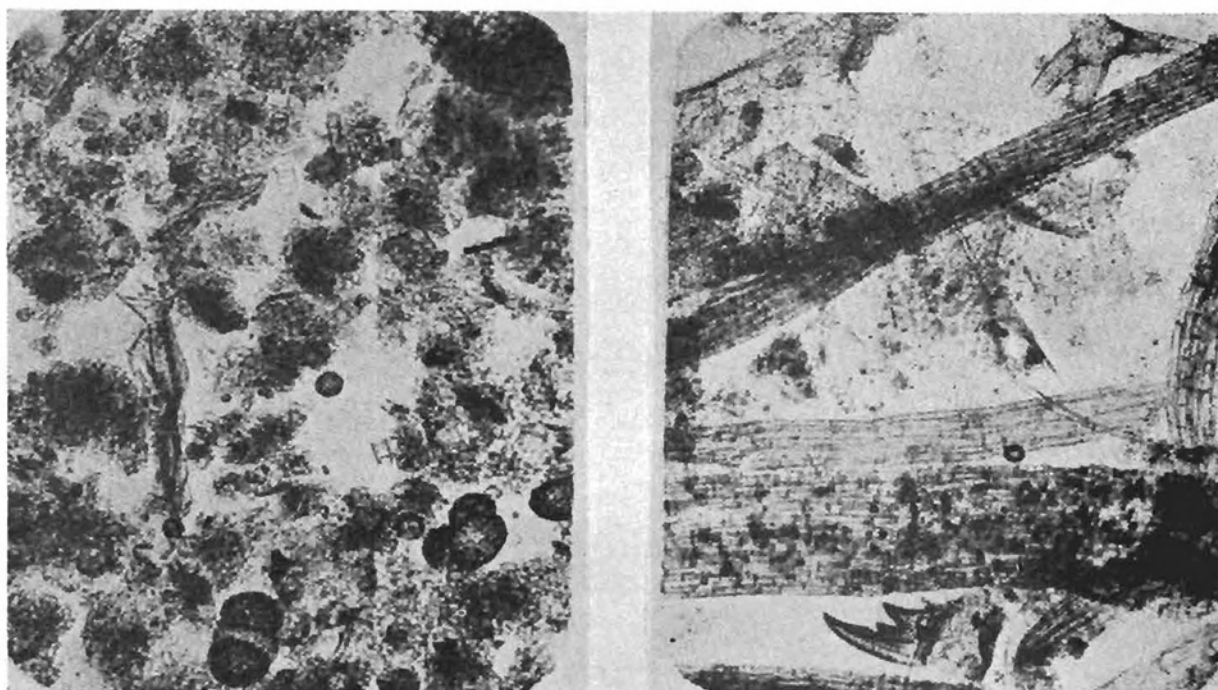
and decomposing plants a large part of the nutrients required for their growth.

Lowmoor peat is characterized by a high content of nitrogen and calcium, whereas highmoor peat is poor in both. Both types of peat contain little phosphorus and potassium. The so-called transition peats, or forest peats, contain about 2 per cent nitrogen and 1 per cent calcium; they are also low in potassium and in phosphorus. The ash content of peat does not increase with depth of the deposit, but is largely controlled by the nature of the profile and by the amount of contamination with sand, silt, and calcium carbonate. Accumulations of marl, calcium carbonate, and silicates, especially in the lower layers of lowmoor peats, are of common occurrence. Phragmites peat and peat mud are frequently found to be rich in sulfur; highmoor peats, however, are almost free from sulfur or contain only small amounts of

it. Both sulfur and phosphorus are present in peat largely in organic combinations.

Organic constituents in peat. A detailed study of the organic constituents of the humus in peat has been given previously. Attention will be called here only to the specific nature of some of the complexes.

The total nitrogen content of *Phragmites* plants is reported as 1.5 per cent; of *Hypnum*, 1.4 per cent; of *Sphagnum*, 1.1 per cent; and of *Eriophorum*, 1.3 per cent (540). When the carbohydrates of the



A

B

FIG. 28. Magnified view of sedimentary (A) and lowmoor (B) peat, from Florida: A. pollen grains, diatom shells, epidermal strips and amorphous material; B. root and stem structures, and the insect remains pointing also to some allochthonous material (Forsait).

plants undergo decomposition by microorganisms, in the process of peat formation, the nitrogen content increases in lowmoor and forest peats to two or more times the original concentration in the plants. In highmoor peats, however, no increase in nitrogen takes place; frequently a decrease is actually found. This is due to more rapid decomposition of the nitrogenous compounds than of the carbohydrates in the formation of highmoor peat, with the result that nitrogen is liberated as ammonia and left in the peat; it is not reassimilated by microorganisms because of the slower decomposition of the carbohydrates

in sphagnum and eriophorum plants. As a result of this, about one-fifth of the nitrogen of the dead sphagnum plants is immediately made available to the young growing plants. Highmoor peats have to depend almost entirely upon rainfall to bring down sufficient nitrogen to support growth of the bog. One may assume that about 11.7 kg. of nitrogen in the form of N_2O_5 and NH_3 are brought down yearly by rainfall, per hectare of land; if the nitrogen content of highmoor plants is taken as 0.76 per cent, the above amount will be sufficient to produce 1,540 kg. dry substance or 30,800 kg. moist peat, giving a volume of 6.160 cubic meters; it was calculated, from these results, that it would take about 648 years to produce a layer of peat 1 meter in thickness.

When peat bogs are drained and cultivated, active decomposition of the various organic, including the nitrogenous, complexes, takes place. In order to grow agricultural crops, it is essential to lime highmoor peats. The addition of excessive quantities of lime may lead to rapid destruction of the nitrogenous substances, involving even considerable losses of nitrogen (45). Further studies on the changes produced in the nitrogenous complexes of peats as a result of cultivation are reported by Fittbogen (300) and others (894, 1039, 1122, 267).

Among the non-nitrogenous organic constituents of peat, the fats and waxes have received special consideration, because of the ease with which they are extracted with neutral solvents, such as ether, alcohol, and benzol. The relative concentration and chemical nature of this group of peat constituents, frequently referred to as bitumen, vary considerably, as shown in tables 47 and 48.

Ether extracts from plants ethereal and fatty oils, oleoresins and resins, certain wax-like substances and nitrogenous fats; alcohol extracts certain waxes, tannins, resins, bitter substances, alkaloids, chlorophyll and other pigments, and certain carbohydrates. Lowmoor peats of the *Carex* and *Phragmites* types contain the lowest amounts of ether- and alcohol-soluble substances; sphagnum peat has a considerably greater proportion of these complexes; pollen peat contains much more than the other peats, this group of complexes frequently being almost one-third of the total organic matter. With an increase in age of sphagnum peat, there is an increase in the amount of ether- and alcohol-soluble substances. When peat is first treated with hydrochloric acid, the content of extractives is increased (992). Certain Russian peats were shown (1083) to contain over 20 per cent bituminous substances. One sphagnum peat yielded 18.8 per cent bitumen, but,

after treatment with 10 per cent HCl, the total yield was increased to 26.8 per cent (308).

The wax constituents of peat bitumen were reported (1164) to contain a large amount (15–20 per cent) of highly molecular hydrocarbons, such as tri-triacontane and penta-triacontane. The saponifiable part of the wax was found to consist of certain acids ($C_{25}H_{50}O_2$), namely, carboceric and an unknown oxy-acid; of esters of these acids; and of the alcohol $C_{27}H_{56}O$. This peat bitumen seemed to be distinctly different in nature from the bitumen of German brown coal. The resinous materials present in peat were at first believed (731) to be formed in the process of peat formation; it was later shown (1049), however, that these compounds, being resistant to decomposition, originate from the plant residues.

In certain peats there are organic formations which result from the infiltration of various complexes from one layer to another, and which are characterized by a high content of wax which is soluble in ether-alcohol and in toluol; this condition appears in the "pech" soils. It was explained (6) that these layers are formed as a result of the penetration of certain extracts of humus into the underlying mineral layers and their precipitation as aluminum compounds. The formation of dopplerite is probably due to a similar process (p. 281).

Cellulose and hemicelluloses are particularly abundant in highmoors but occupy only a secondary place in the other types of peat. Von Feilitzen and Tollens (285) reported the presence of 15.36 per cent pentosan in *Calluna vulgaris*, 14.70 per cent in *Sphagnum cuspidatum*, and 11.41 per cent in peat moss or "peat straw"; the pentosan content of sphagnum peat was 6.25 to 12.75 per cent in the surface layer but diminished with depth, so that below 200 cm. from the surface there was only 2.65 to 5.87 per cent pentosan. The cellulose content of *S. cuspidatum* was found to be 21.3 per cent and that of sphagnum peat, at a depth of 20–100 cm., 15.2 per cent, and, at 100–200 cm., 6.87 per cent. Zailer and Wilk (1305) also recorded a decrease in the pentosans with depth of peat; they found 10.26 per cent at the surface and 5.05 per cent at a depth of 7.5 meters.

The disappearance of the cellulose and pentosan with depth of peat explains the increase in total carbon content; these substances are low in carbon, whereas the waxy substances and the lignins, which have a much higher carbon content and which are more resistant to decomposition, increase with depth (fig. 29). The amount of cellulose found in peat depends largely upon the method used for its determination.

tivated, the cellulose will be gradually decomposed by the microorganisms inhabiting the peat (762).

Because of its great resistance to decomposition under anaerobic conditions, the lignin content was found to increase with age of peat (1086). It does not remain as such, however, but undergoes various chemical changes, such as loss of methoxyl, reduction, and condensation; as a result of these changes, substances, usually referred to as "pure humus" or "humic acids," are formed which are more readily soluble in alkali solutions and precipitated by acids and which are insoluble in acetyl bromide.

The chemistry of peat is thus found to be involved with numerous specific problems bearing upon humus investigations. Since the content of inorganic materials in peat bogs and even in peat soils is comparatively small, peat represents a type of humus which can be studied more easily than humus in mineral soils. This need not indicate, however, that the humus in peat and that in soil are identical chemically. Even peats differ markedly in chemical composition. This can be further emphasized by a consideration of a limited specific deposit known as "dopplerite."

Dopplerite. Dopplerite was found by Döppler (233) in a peat bog in Austria at a depth of 6–8 feet below the surface. It occurred in a natural state as a black gelatinous substance, which, on exposure to air, became elastic and later brittle, with the lustre of coal. It contained 48.06 per cent carbon, 4.98 per cent hydrogen, 40.07 per cent oxygen, 1.03 per cent nitrogen, and 5.86 per cent ash. More recently (1162), dopplerite was reported to contain 57.9 per cent carbon, 2.1 per cent nitrogen, 0.7 per cent sulfur, and 3.5–5 per cent ash, 57 per cent of which was CaO and 17.3 per cent Fe₂O₃.

A similar humus formation was described by Gumbel (381), who referred to it as "peat-pitch-coal"; dopplerite was believed to have the same composition as peat; it was also regarded as being the cementing material of brown coal or "carbohumins," which had passed into an insoluble state. Kaufmann (528) suggested that dopplerite consists of one or more "humus acids," and that peat contains both dopplerite and partly decomposed plant residues; he concluded that, in the formation of coal from peat, the latter first gives rise to dopplerite, which is then transformed into a substance less readily soluble in alkalies and richer in carbon, namely, coal (178, 213, 475).

Dopplerite has also been discovered in America, usually associated with certain types of peat (637); this form, however, was reported to

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contain 30 per cent carbon, which suggests either mistaken analysis or a high ash content. Dopplerite may contain spores and pollen of higher plants. It is insoluble in ether, alcohol, or water, but it is completely soluble even in cold dilute alkali solution, from which it can be precipitated by an acid. The generic name "phytocollite" was suggested for the black jelly-like substance formed in the decomposition of plant materials; dopplerite would be one variety of phytocollite. The relation of humus gel to the formation of brown coal has been further emphasized by Kirchheimer (544). The term "humogelit" was proposed for all forms of humus produced by dissolution and precipitation under natural conditions. In a more recent contribution (1094), dopplerite is still spoken of as "a mixture of various humic and ulmic compounds, which, after losing an indefinite proportion of water, is so changed that it cannot regain plasticity, even after prolonged submergence in water."

Humus in coal. Coal represents a number of humus types in an advanced state of decomposition, produced from various plant residues at different periods during prehistoric times, and later stratified and compressed by superimposed layers of mineral matter. This definition, however, is not commonly accepted. According to Stopes and Wheeler (1101, 1263), coal is "a conglomerate of morphologically organized plant tissues, natural plant substances devoid of morphological organization, together with the degradation products of a portion of the plant tissue and cell contents comminuted, morphologically disorganized, or present in the form of varying members of the ulmin group"; later they defined coal as "a compact, stratified mass of 'mummified' plants (which have in the past suffered arrested decay to varying degrees of completeness), free from all save a very low percentage of other matter," thus pointing to the varying nature of the heterogeneous mass of compounds.

Several types of coal are recognized (842):

1. Humus coal, originated from wood,
2. Sapropel, originated from material rich in fats and albumin.

Both forms may occur in alternate layers. Striated coal may consist of hard, bright or humus coal, dull or sapropel coal, and mineral charcoal or mother of coal. These three layers have been designated (1101) as clarain (vitrain), durain (atritus), and fusain.

Since the origin, chemical nature, and utilization of coal have been treated in a number of excellent monographs published in various languages (1216, 842, 1269, 1277, 1101, 275, 229, 1104, 328, 1084, 1085),

attention is called here only to the significance of coal as a humus formation. Two opposing views prevail in the literature concerning the origin of coal: 1. the autochthonous hypothesis, whereby coal is considered as an advanced stage of peat; 2. the allochthonous hypothesis, in which coal formation is visualized as organic matter, accumulated from floating plant residues which settled to the bottoms of open lakes or lagoons (1094, 486). Since most of the peat bogs are autochthonous formations, only the allochthonous or sedimentary peats have a bearing upon the origin of coal, according to the second hypothesis.

The mechanism of coal formation, through the peat state, is commonly explained as follows: peat changes first to lignite, the latter to bituminous coal and finally to anthracite, through the action of heat, as a result of which, fractional distillation takes place. The brown coals or lignites differ considerably in mode of occurrence and in their physical and chemical properties, some being more closely allied to peat and others to Paleozoic coals. It is recognized now, however, that different coals have originated at different periods from different types of plant residues, accumulating and decomposing under different conditions. Studies of the chemical processes involved in the formation of coal return us once more to the various hypotheses concerning the "humic acids," "ulmic acids," "humins," and "ulmins." Alkali extraction has been used for the separation of these complexes from coal and for distinguishing various coal types. Coal was called "lignite" when a brown solution was obtained on treatment with potassium hydroxide; it was considered as bituminous coal when the solution was colorless or only straw-colored. The rôle of alkali-soluble substances or the "ulmin compounds" in coal formation was frequently unduly stressed. In 1861 Hertz (517) gave the formula $C_{20}H_9O_8$ to "ulmin" of coal without even mentioning nitrogen or indicating the rôle of this element in the origin and composition of coal. These "analyses" were followed by numerous others, usually of equal value. It was commonly agreed that "ulmins" occur abundantly in peat and in lignites, but rarely in bituminous coals, and are entirely absent from anthracites. The formation of "ulmin compounds" was considered by Berthelot (102) as an essential preliminary step in coal formation.

According to Tideswell and Wheeler (1161), the organic substances of coal can be divided into three groups: 1. those that are resistant to decomposition, including the spore exines, cuticular tissues, and resins; 2. those that are subject to decomposition, including organized tissues (cellulose and lignins) and amorphous plant materials; 3. products of decomposition, namely, the amorphous "ulmins."

Jeffrey (486) recognized three groups of coal constituents: 1. spores or canneloid; 2. modified wood or lignitoid; 3. unmodified carbonized wood or mineral charcoal (mother of coal). Coals rich in spores (cannels, bogheads, oil shales) are petroliferous or highly bituminous and are considered to be the mother substances of oil and gas.

The occurrence of spores and spore exines in coal (1277, 1309) can be readily understood, since these substances are resistant to microbial decomposition and are chemically inert. The organized plant constituents occur as remnants of the plants and plant residues which gave origin to the coal. However, the origin of the amorphous material in the coal, variously described as "humic acids" or "ulmins," is still disputed.

TABLE 52
Chemical analysis of peat and coal (328)
Per cent of dry material

	PEAT	LIGNITE	BITUMINOUS COAL	SAPROPEL COAL	ANTHRA- CITE COAL
Carbon.....	50-60	60-65	75-90	76-82	92-96
Hydrogen.....	5-7	5-6	4-6	8-11	2-3
Oxygen.....	30-40	20-30	4-15	8-12	2-3
Nitrogen.....	1-4	0.4-2.5	0.4-2.0	0.6-1.2	0.5-0.7
Sulfur.....	0.2-2	0.1-3	0.3-2	0.6-3	0.4-0.8
Methoxyl.....	1.3-3.5	9.5-5	0-0.8		0
OH-groups.....	2-5	2-8	Trace to 0.1		0
CO-content.....	1-3	2-3			1
COOH groups.....	4-6	1-10	0-0.2		0

The major part of the coal constituents, usually referred to as "ulmin," is made soluble in alkalis by oxidation in air at 150°C. (407, 828). These soluble complexes are homogeneous, although they can be separated into several groups by different solvents. An equivalent weight of 170 has been obtained from the Ca-salt, while a "molecular unit" of 680 was calculated from the nitrogen content. Because of its inertness, the nitrogen was believed to occur in a closed ring combination. The nuclear structure of coal is considered to be a compact system of annular six-membered groupings connected by heterocyclic structures, such as pyrrole and furan or their derivatives. The "ulmins" of coal are colloids of great complexity, in which internal condensation has eliminated most reactive groupings. These complexes, obtained from different coals, are remarkably uniform in chemical characteristics.

The elementary composition of coal has been stated as follows: carbon—76.9 per cent, hydrogen—5.2 per cent, nitrogen—1.78 per cent, sulphur—0.81 per cent, and ash—3.03 per cent. There is considerable variation, however, not only among different coal types but also among different samples of the same coal, as shown in table 53. An examination of specific chemical groups also reveals considerable difference between peat and coal, as well as between different forms of coal. True carboxylic groups have been found in peat, but not in bituminous coals. Hydroxyl groups, as well as carbonyl groups, however, have been found in coal (table 52). Methoxyl groups have been demonstrated in brown coals and in lignites but not in bituminous coal. Pearson (811) separated bituminous coal into several fractions on the basis of solubility in pyridine.

Numerous botanical and chemical theories have been proposed to explain the origins of the different coals. It was at first believed that plant substance as a whole gives rise to coal (275, 1082, 870, 759). However, Fremy (379) emphasized in 1879, that in the fermentation of plant residues, the organic substances do not decompose as a whole; some of the plant constituents are left and these may preserve the structure of the original plant. Since cellulose is the most abundant single plant constituent, it was considered to be the mother substance of coal. More recently, however, the lignins have received much consideration in this connection, as brought out in Chart II.

These results were substantiated in a general way by many investigators (963, 1104, 327, 460, 824, 1218). Bone (126a) demonstrated that coal substance has an essentially benzenoid structure and that lignins have been its chief progenitors, the essential continuity of lignin-peat-coal-anthracite being emphasized. On the other hand, numerous other investigators (94, 675, 676, 95, 96, 97) believe that both cellulose and lignin gave origin to coal; they have been able to demonstrate that coal formation from cellulose takes place under conditions of high temperatures and pressures. Berl and his associates (97) concluded that the lignin theory of the origin of coal is not fully justified; coking coals could not be formed from brown coals. Bituminous coals originated largely from plants containing resins and waxes but low in lignins; cellulose, therefore, played an important part in the formation of these coals. However, brown coals were formed from more organized, lignin-rich plants. In the formation of bituminous coals, there was a longer coalification period, pressure and high temperature playing an important part. The ideas of Bergius (94) on the formation of coal from

cellulose are given elsewhere. Hawley (405) heated cellulose and obtained lignin-like substances. According to recent work of Terres (1138) and Fuchs (328, 329), proteins have also played a part in the formation of bituminous coal. This is in conformity with the investigations reported previously (1232) on the rôle of proteins in the formation of humus in the process of decomposition of plant residues. Whatever hypothesis of coal formation is finally accepted, it is important to recognize that microorganisms have played a prominent part in this process (1201, 110, 1135).

Source beds of petroleum. The various theories explaining the origin of petroleum have been divided into the following three groups (95, 100): 1. inorganic, through the formation of carbides, which give rise first to simple hydrocarbons; 2. Engler's theory, in which fish are supposed to play the most important rôle, giving rise to hydrocarbons in the process of decomposition; 3. the theory that the flora of the sea and lagoons is the source from which the petroleum is formed.

According to Engler (273), petroleum originated from animal fats, through processes of decomposition; plant waxes and resins also took part, but were of only secondary importance. Petroleum always contains optically active substances and usually a large amount of organic nitrogenous bodies. These observations point to the origin of petroleum through life processes (663). Other theories assume that diatoms are the mother substances of petroleum. The presence of chlorophyll and humin derivatives in bitumens also tends to prove that plants and animals took part in their formation (1175). Hackford (383) suggested that the carbohydrates of algae were gradually changed into bitumen and petroleum (347a).

From the point of view that petroleum is a product of decomposition of marine animals and plants, it may be considered as a form of humus which has been derived from living organisms by specific processes. The process of formation of petroleum from algal material has been represented (1084) by five stages: 1. synthesis of fatty substances by algae, 2. decomposition of the algal cells and liberation of fats, 3. hydrolysis of the fats and liberation of fatty acids, 4. decarboxylation, 5. polymerization.

The action of bacteria was shown to be of importance not only during the first stages of decomposition of the algal material but also during the subsequent steps of hydrocarbon formation (916, 1142). Stadnikoff (1084) concluded that petroleum was formed under high pressure. During the first stages of the formation of petroleum from organic

residues (either of plant or animal origin), bacterial processes of fermentation and decomposition have been important; the carbohydrates and proteins were at first decomposed by bacterial action, either completely or to fatty acids; the fats and fatty acids were then gradually transformed into hydrocarbons.

Various other theories were proposed to explain the origin of petroleum, through the process of gradual combustion of peat and brown coals. According to Berl (95), young coals are transformed into petroleum-like hydrocarbons, by reactions similar to those produced by artificial hydrogenation. Marine muds containing about 5 per cent organic matter were found to give, on distillation, about 2 gallons of oil per ton of dry mud. Although certain paraffins (caproic acid, $C_6H_{12}O_2$, melissic acid- $C_{30}H_{60}O_2$, sterols, and paraffins) were shown to be normal constituents of fresh sediments, the conclusion was reached that the petroleum present in these cannot be a major factor in the formation of oil pools (1173).

CHAPTER XII

ORGANIC MATTER FORMATIONS IN WATER SYSTEMS

“This material must be considered to have gone out of organic circulation and represents slowly accumulating waste products.”—KROGH.

Organic matter formations resistant to rapid decomposition by microorganisms may be found, not only in soils and in composts, but also in water basins, both in the water itself, in solution or in suspension, and in the sedimentary formations on the bottom. Here belong the organic matter formations in fresh and in salt waters and in sewage purification systems. Peat accumulations, especially sedimentary peats, are close to these in the manner of their formation; however, in the case of the peats, decomposition is much slower, with the result that extensive depositions of organic matter are made possible. The difference between the accumulation of organic matter in the case of allochthonous peats and lake bottoms, especially muds, is more quantitative than qualitative in nature.

The organic matter found in water basins not only resembles typical humus formations in origin and chemical nature, but some of it has probably originated in land soils and subsequently has been carried by streams and rivers into lakes and seas, where it has been deposited or remained for some time in solution or in suspension (398). Aschan designated the last form of organic matter found in the rivers and streams as “water humus”; the term “marine humus” was applied (1226) to the organic matter found in the sea bottom. Just as the chemical nature of humus formed in peat bogs varies from that of the humus in the forest floor or in mineral soils, so does humus found in river and lake waters and in river, lake, and sea bottoms vary from other types of humus found in nature.

Two outstanding characteristics distinguish the humus found in water or below the water from other humus formations: 1. The humus in field and in garden soils and in forests, as well as in highmoor and lowmoor peats, is produced chiefly from autochthonous plants, namely, plants growing in the same region where the humus was formed; in river, lake, and sea bottoms, humus is formed chiefly from allochthonous

plant residues, brought in by wind and water currents; water humus is probably composed partly of soil humus which has been carried by flowing waters and partly of the organic substances produced during the decomposition of the aquatic plant and animal residues. 2. The second difference is based upon the chemical nature of the organic residues: humus in mineral soils, in forests, and in lowmoor peats originates largely from higher plants (grasses, trees), the major chemical constituents of which are cellulose and lignin; however, humus in lake bottoms, and especially in deep sea bottoms, has been contributed largely by diatoms and various algae, the organic complexes of which consist largely of hemicelluloses and proteins, and by residues of small and large animals rich in proteins and in chitinous substances.

Although our knowledge of the chemical nature of this type of humus is still fragmentary, sufficient evidence has already accumulated, especially regarding the humus in lake and in sea bottoms, to permit certain generalizations.

Sources of humus in rivers, lakes, and seas. The organic substances found in rivers, lakes, and seas arise from four different sources: 1. organic matter washed in by streams from land; 2. organic matter formed by the growing plants *in situ* or floating, as well as by animal populations; 3. organic residues which are deposited from the air; 4. contamination by human refuse, particularly sewage. The organic matter in lakes and seas may be found in three states: 1. in solution, 2. in suspension, 3. incorporated in the bottom deposits.

The amount of organic matter dissolved in lake and sea water depends upon the nature of the water, the plankton organisms, and the higher forms of plant and animal life inhabiting lake or sea. This type of humus may play an important part in the removal of certain elements from land and in supplying these elements for the development of fish and other forms of water life at distances not far from shore. The organic matter found in suspension in water consists of the dead members of the phytoplankton and zooplankton as well as their decomposition products and also those of higher forms of life. The jelly-like material found on the bottoms of lakes and seas is similar in nature to the suspended substances. The content of organic matter in bottom sediments varies considerably with distance from shore, nature of bottom material, and configuration of bottom. This organic matter, especially in mud bottoms, is partly of terrestrial and partly of marine origin. The decomposition products of plankton and of higher marine plants and animals contribute directly to this form of organic matter, namely, the lake and marine humus.

According to Birge and Juday (115), the net plankton per cubic meter of water of Lake Mendota averages 332.5 mg. of dry organic matter (42 to 1,135 mg.). This amount of plankton was found to contain 28.6 mg. nitrogen or 8.37 per cent, equivalent to 52.31 per cent protein. The materials extracted by ether represented 11.78 per cent; the pentosans, 2.88 per cent; and the crude fiber, 6.54 per cent; the remaining part of the organic constituents of the plankton was believed to consist of other carbohydrates. In another lake, 850 mg. of organic matter were found per cubic meter of water; the nitrogen content was 9.36 per cent; the ether extract, 6.02 per cent; the pentosans, 5.73 per cent; and the crude fiber, 3.62 per cent. The total organic matter content of both the net- and the nannoplankton varied from 1.884 to 4.938 mg. per cubic meter of water; the nitrogen, from 7.11 to 9.21 per cent of the dry plankton; the ether extract, from 4.61 to 7.53 per cent; the pentosans, from 4.57 to 5.76 per cent; and the crude fiber, from 4.35 to 5.32 per cent. By assuming a regeneration of the plankton once a week, the annual production was calculated to be equivalent to 12,000 kg. of dry organic matter per hectare of surface area of water.

According to analyses reported by Brandt (149), the marine plankton contains 14 to 48 per cent carbon, 1.5 to 10.6 per cent nitrogen, and 13 to 65 per cent ash; zooplankton is rich in protein and low in ash, whereas diatoms are low in nitrogen and high in ash. The various marine forms of life, with the exception of the Peridineae, are free of cellulose but are high in various hemicelluloses (594).

Considerable quantities of organic matter reach the sea from land. Aschan (52) calculated that the streams and rivers of Finland carry 1,400,000,000 kg. of soluble organic matter yearly into the North Sea. This organic matter consists of the water-soluble, yellow to brown colored substances; it was found to originate generally in nature, especially in peats and swamps and on the bottom of lakes, where plant residues undergo decomposition in the presence of large amounts of water. One hundred liters of river water were shown to contain two grams of organic matter. This form of humus is carried in the water through regions of granitic soil formations, acid in reaction, without much diminution in quantity; when it comes into contact with the calcium and magnesium salts of the sea water, it undergoes oxidation. Salts of aluminum (1044) or iron precipitate this organic matter, giving rise to insoluble humates; 30 to 60 mg. of FeCl_3 were found necessary to precipitate the humus from 1 liter of water. The ferrous iron

compounds do not bring about any precipitation of the humus, but when these humates are oxidized to the ferri-compounds, precipitates are formed. The chemical composition of water humus was reported as follows:

	<i>per cent</i>
Carbon.....	45 to 54
Nitrogen.....	1.46 to 4.23
Hydrogen.....	3.86 to 5.05
Oxygen.....	38.8 to 47.9
Phosphorus (P ₂ O ₅).....	0.15 to 0.41
Sulfur.....	Small amounts

Humus compounds are known to have a strong solvent effect upon soil minerals. Aschan proposed the theory that iron is washed out from the soil in the form of soluble ferro-humates. In the sea these compounds are oxidized by the action of oxygen and bacteria to the ferri-compounds, which are then precipitated; the gradual decomposition of both ferro- and ferri-compounds through the agency of bacteria leads to the liberation of the iron as Fe₂O₃, which gives rise to iron ore. This ore still contains small amounts of organic matter, varying in concentration from 2.18 to 7.48 per cent. Humus was thus considered to play a rôle of great importance in the weathering processes in nature (1268).

The nutrients which pass into the sea from land, however, are only of minor significance in the nutrition of marine life, as compared with the nutrients produced in much larger quantity from the dead organic residues in the ocean itself (399). The algae and animal members of the plankton will, after death, sink to the bottom and undergo decomposition by bacterial action. A part of the organic matter suspended or dissolved in the water of rivers, lakes, and seas is also sooner or later deposited on the bottom, and becomes gradually incorporated with the inorganic constituents into a homogeneous bottom mass. The highest concentration of organic matter is found in the rivers of tropical countries.

It has been suggested recently (116) that, following the decomposition of the plankton in the water, stable organic compounds are produced. Krogh (593) found that sea water contains a uniform amount of dissolved organic matter, from the surface downward; there were 0.244 gm. nitrogen and 2.36 gm. carbon present in each cubic meter of water, equivalent to 5 gm. of organic matter. This represents 300 times the total amount of organic substance present in the living

organisms in the sea. The total quantity of the organic material dissolved in the water was believed to be altered only very slowly, not only by plant and animal life, but even by the action of bacteria. Krogh suggested, therefore, that this material should be considered as having gone out of organic circulation. The organic matter in true solution in a Danish lake was found to be about 9 mg. per liter with a combustion value of 42 gm.-calories. Krogh (591-2) emphasized the fact that a certain portion of the nitrogen in the water is combined in the waste products which cannot be utilized further by animals, while

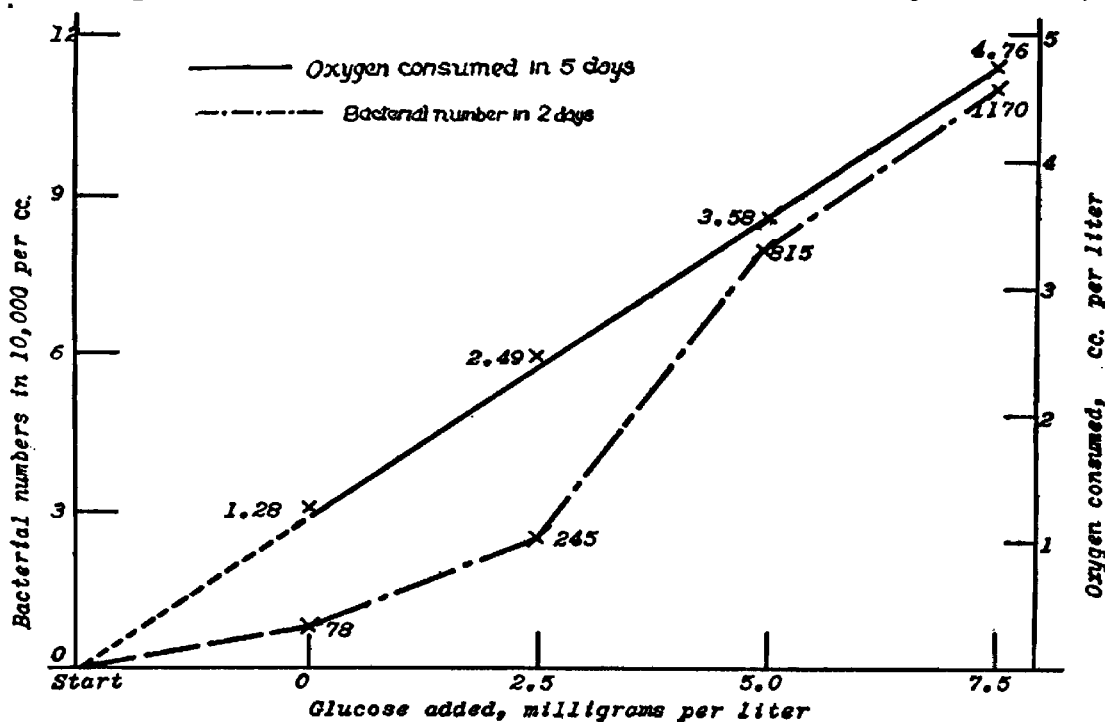


FIG. 30. Transformation of organic matter in sea water (Waksman and Carey)

another fraction of the organic matter consists of humus which seems to be very resistant to the attack of all organisms including bacteria.

More recently it has been found (1227a) that although the organic matter content of sea water is uniform in concentration, under certain conditions it can undergo active decomposition. When a quantity of water is placed in a glass vessel and incubated in the laboratory or in the sea, rapid decomposition of the organic matter in the water takes place, as measured by the rate of bacterial multiplication, oxygen consumption, and ammonia liberation. The last has been measured directly as well as indirectly, namely, by the amount of glucose decomposed in the water, whereby the bacteria have as the only available source of nitrogen that liberated from the decomposition of the organic

matter in the water. By these procedures, it was calculated that at least about a half of the organic matter in the water is readily subject to bacterial decomposition (fig. 30).

The exact chemical nature of this organic matter and the specific mechanism of its formation still remain to be determined. The fact that it has a characteristic carbon-nitrogen ratio (about 10:1) and the fact that it is produced as a result of bacterial action, point definitely to its being a typical form of humus. Ohle (787) has shown by methoxyl determinations that it is probable that true "humic acids" or their salts are present in solution in lake waters.

The following explanation has been submitted (1227a) for the formation of the organic matter complex in water and its comparative resistance to decomposition by bacteria under natural conditions. In the decomposition of algal and other plant (*Zostera*) substance by bacteria, certain constituents, lignin-like in nature, are formed, which are highly resistant to bacterial attack. These combine physically or chemically with the proteins and polyuronides, also present in the plant and animal bodies, and with their decomposition products. Complexes are thus formed which are similar in nature to the humus of lake and marine bottoms and land soils. These complexes are not readily available, therefore, as nutrients for animal life. The slight alkalinity of the sea water and its salt concentration are sufficient to keep a certain amount of these complexes in solution; any excess will precipitate out and gradually settle upon the bottom of the sea or lake. One would expect that near land, where the algal and higher plant growth is particularly abundant, a greater amount of the humus complex should be formed during the decomposition processes and more of it should settle down. Since sea water is well buffered, one would expect that a certain equilibrium should be established between the organic matter dissolved in the water itself and the organic matter in the bottom material, as well as between the organic matter in solution at different depths of water and in different regions.

Nature of humus in river and lake bottoms. The bottoms of rivers and lakes become covered with a colloidal mass of finely divided material in which the residues of dead plants and animals are thoroughly incorporated. These residues are in a partly decomposed condition and are usually covered with a gelatinous substance of bacterial origin. In the course of time, there is formed on the bottom of every river and lake a type of mud, usually designated as "sapropel" or "dammgyttja," the organic matter of which is rich in nitrogen and phosphorus

and is able to adsorb potassium and calcium. The nature of the organic matter in lake bottoms has been studied more extensively than that in river bottoms; the two materials undoubtedly have much in common.

River and lake muds originate largely by processes of sedimentation, either of forms living in the water, including diatoms, algae, protozoa, and other invertebrates of the floating plankton, or of residues of higher vegetation brought into the water by wind or dust, such as spores, pollen, particles of leaves and needles, and cuticular material. These muds, which may be many meters deep, contain a considerable amount of organic matter. Most of the available information concerning lake muds, of recent and of older origin, has been limited to ecological characteristics. The chemical nature of the organic substances in these muds, as well as the processes of transformation to which they have been subjected, is still little understood. Since in due time these muds give rise to sedimentary peats, knowledge of the chemical composition of the latter (p. 265) contributes to a better understanding of the nature of the various humus constituents of these muds.

The various lake bottom formations have been classified as follows (746-7, 658), on the basis of the ideas originally proposed by von Post (837):

1. Limno-autochthonous muds. These comprise the gyttja of von Post and of subsequent Swedish investigators and are frequently known as "sapropel" (839). The animal excreta, plant particles, and diatom shells from which these muds have been formed originated in the lake itself. These muds are subdivided on the basis of the plant and animal residues of which they are composed, namely, sediments of the zooplankton-type (Cladocera), rich in chitinous substances, and sediments of the phytoplankton type. These groups may be further separated on the basis of predominance of specific organisms in the plankton.

2. Limno-allochthonous muds, embracing Dy, as conceived by Swedish investigators, and Dopplerite (p. 281). The mother substances of the humus in these muds have not been formed in the lake itself, but in the immediate vicinity; the humus is washed from local peat and raw humus deposits and is brought into the lake in a colloidal state; it is precipitated in the lake, giving rise to the specific type of humus. This humus is mixed with various residues of water life, both plankton and benthos. Planktogenic sedimentation, which plays such an important rôle in gyttja formations, is only of secondary importance in

Dy formations. The chemical composition of a typical lake deposit is given in table 53. A discussion of the chemical nature of curative muds is presented elsewhere (p. 359).

Abundance and nature of humus in sea bottoms. Marine muds are frequently classified in two groups: 1. those that are formed in deep water distant from land (pelagic), and 2. those which are formed in deep or shallow waters close to land (terrigenous). The first group of muds is subdivided on the basis of the predominating microscopic plants and animals (especially their shells), such as Radiolarian ooze, Diatom ooze, Globigerina ooze, and Pteropod ooze, as well as red clay. The second group of muds is subdivided on the basis of the predomi-

TABLE 53
Chemical composition of lake deposits (23)

CHEMICAL CONSTITUENTS*	PER CENT OF DRY MATERIAL
Ash.....	72.3
Total carbon.....	10.5
Inorganic carbon.....	3.4
Organic matter (C × 1.92)†.....	13.6
Nitrogen.....	0.69
Crude protein (N × 6.25).....	4.3
Ether-soluble.....	0.33
Alcohol-soluble.....	1.14
Lignin.....	5.23

* pH = 7.4-7.6, moisture of fresh material 90.4 per cent.

† Assumption is made that the carbon content of the organic matter is 52 per cent.

nating inorganic particles, which are responsible for the characteristic color or structure of the muds; namely, blue mud, red mud, green mud, volcanic mud, coral mud (741), and black mud. Mud of the latter group contain considerable organic matter and colloidal hydrous ferrous sulfide; they occur abundantly in enclosed seas, in gulfs, and in bays connected with the open ocean (235), such as the Black, Azov, and Caspian Seas, the Mediterranean, and sections of the Baltic Sea. The blue muds, as well as other varieties of mud, contain, besides humus or amorphous organic matter, also various recognizable remains of Foraminifera, Radiolaria, diatoms, sponge spicules, fragments of mollusk and echinoderm shells, nematodes, and protozoan cysts.

The content of organic matter in the bottom sediments is frequently

determined by loss on ignition; this is usually found to be 1 to 12 per cent of the total dry material. Since a part of the loss on ignition is due to the inorganic constituents of the mud, especially in the case of muds rich in clay, the actual amount of organic matter is lower. In these cases, as in soils, it was found that the calculation of the organic matter content from the amount of total organic carbon is more reliable. The factor to be used in calculating the results, however, is still a matter of dispute. Boysen-Jensen (144) suggested that the factor 2.0 is quite adequate; Trask (1172) multiplied the carbon content by 1.7; from the chemical composition of the humus in the mud, Waksman (1226) calculated that the factor 1.887 is most reliable.

Almost pure sand obtained from the North Sea was found (144) to contain 0.34 per cent carbon and 0.027 per cent nitrogen. The carbon content of the bottom material from various parts of the Limfjord varied from 0.58 to 4.3 per cent, while the mud of the inner part of the Roskilde Fjord contained as much as 10.2 per cent carbon. At great ocean depths, such as 800 to 2,000 meters, only 0.3 to 1.6 per cent organic carbon was found in the bottom material. According to Moore (724a), the organic matter content of marine mud, as measured by total nitrogen, changes with the depth of the deposit; in the case of muds and sandy muds of the Clyde Sea area, the nitrogen content varied from 0.089 to 0.379 per cent at a depth of 0 to 5 cm., from 0.083 to 0.330 per cent at 5–10 cm., from 0.074 to 0.295 per cent at 10–15 cm., and from 0.074 to 0.302 per cent at 15–20 cm. The decrease with depth is gradual and comparatively small. In a few instances Moore noted an increase in the nitrogen content with depth of mud. No correlation was observed, however, between the depth of water and the nitrogen content of the mud.

Trask (1174) found that the organic carbon in marine bottom material varied from 0.2 per cent for a sand bottom to 4.2 per cent for a clay bottom, with an average of 1.8 per cent for 25 near-shore formations. The organic matter content of the sea bottom is influenced by bottom configuration; it increases in concentration as the texture becomes finer, favoring its transportation. Deposits in depressions and in closed basins contain more organic matter than do those adjoining ridges and slopes. A rapid drop in the organic matter content of marine sediments was correlated with depth, the rate of change becoming smaller with increase in depth of sediment; the rate of decomposition is of considerable importance in this connection, being responsible for the condition in which the organic matter content is sometimes higher deep in the deposit than in the superficial material.

The surface layer of mud or of other marine bottom material is rich in detritus, consisting of plant and animal residues which are in the process of decomposition, as evidenced by their abundant bacterial population. This detritus is different in nature from true marine humus or from organic matter which has already undergone extensive decomposition and has become an integral part of the bottom material. Murray and Hjort (741) suggested that the organic substance of the marine deposits serves as a fertilizer for the surface layers of the marine

TABLE 54

Abundance of marine humus in muds of the Gulf of Maine (1226)

STATION NUMBER	DEPTH OF MUD IN PROFILE	MOISTURE CONTENT	CARBON* CONTENT	NITROGEN* CONTENT	C/N
	<i>cm.</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	
1329	0-30	65.0	2.52	0.290	8.7
1329	30-60	60.8	2.45	0.250	9.8
1329	60-90	58.8	2.32	0.238	9.8
1330	0-30	59.9	2.74	0.296	9.3
1330	30-60	58.2	2.75	0.254	10.8
1330	60-90	57.4	2.60	0.236	11.0
1331	0-35	50.0	1.59	0.148	10.7
1331	0-35	49.5	1.56	0.132	11.8
1331	35-65	46.9	1.64	0.130	12.6
1331	65-90	48.8	1.61	0.128	12.6
1331	90-115	46.9	1.57	0.126	12.4
1331	90-115 (reddish mud)	46.8	1.04	0.080	13.0
1332	0-25	31.2	0.67	0.050	13.4
1332	25-50	36.7	1.12	0.092	12.2
1332	50-75	37.7	1.43	0.096	14.9
1351	†	0.43	0.043	10.0

* On dry basis.

† True oceanic deposit taken at a depth of 5000 meters.

bottom. It still remains to be determined, however, to what extent true marine humus can be of use as nutrient material for animal life.

There may be considerable variation in the humus content of muds that occur relatively close together (1226). In most cases, there is a gradual decrease in humus content with depth of mud; in some cases, however, there may be an increase, as shown in table 54. The humus content of true oceanic sediments is usually less than 1 per cent.

In view of the fact that humus of sea bottoms is derived principally from marine plants, results of interest may be derived from comparisons

between the chemical composition of the humus and that of these plants. Boysen-Jensen (144) found that a relationship existed between the carbon content of bottom samples from Danish waters and the relative abundance of *Zostera*; no such correlation existed between the carbon content and the density of the floating plankton. These observations led him to the conclusion that *Zostera* is the chief source of organic matter in the sea bottom of that particular region. The cell wall of *Zostera* is rich in pentosans, that of diatoms consists chiefly of silica, and that of the peridineans is nearly pure cellulose; the existence of a rather uniform relationship between the contents of total

TABLE 55

Chemical composition of marine plankton, Zostera and marine humus (144)
Per cent of dry material

MATERIAL	TOTAL CARBON	ORGANIC MATTER	PENTOSAN	C	ORGANIC MATTER
				PENTOSAN	PENTOSAN
Green <i>Zostera</i>	33.9	73.8	8.4	4.04	8.8
Brown <i>Zostera</i>	30.7	74.0	8.4	3.68	8.8
Dead <i>Zostera</i>	33.0	76.5	7.6	4.35	10.1
Chaetoceras plankton.....	11.7	27.2	1.24	9.4	21.9
Peridinean plankton.....	22.0	47.0	1.22	18.0	38.5
Copepod and Peridinean plankton..	14.1	1.52	9.3
Sea bottom, N. F.* upper layer.....	2.3	0.42	5.5
N. F. upper layer, washed.....	5.4	0.83	6.5
Detritus.....	2.8	0.49	5.7
L. B.,* upper layer.....	3.7	0.53	7.0
L. B., upper layer.....	2.1	0.28	7.5
Kattegat.....	5.5	1.06	5.1
Kattegat.....	2.5	0.29	8.6

* N. F. = Nyborg Fjord, L. B. = Livø Bredning.

organic matter and of pentosan in *Zostera* and in marine mud further suggested that this plant may be the chief source of the humus in the mud (table 55).

The ratio between the total carbon and the amount of pentosan in marine humus was shown to lie between the ratio found in *Zostera* and in plankton. The fact that the nitrogen content of the organic matter in the sea bottom is comparatively high suggested that the non-nitrogenous compounds had undergone considerable decomposition. Boysen-Jensen therefore concluded that in the more sheltered waters of the fjords, the organic matter of the sea bottom is formed by *Zostera*, to

a large extent; in the more open waters, at least half of the organic matter is formed by these plants; and in the deeper waters, such as Kattegat, the plankton organisms are the principal contributors to the humus of the sea bottom.

The nitrogen content of *Zostera* varies (144) between 2.97 per cent in the living green plants and 0.88 per cent in the dark brown leaves. The decrease in nitrogen content which accompanies aging of the plant is due to the extraction of some of the nitrogenous constituents by the sea water. When the plants undergo bacterial decomposition, the

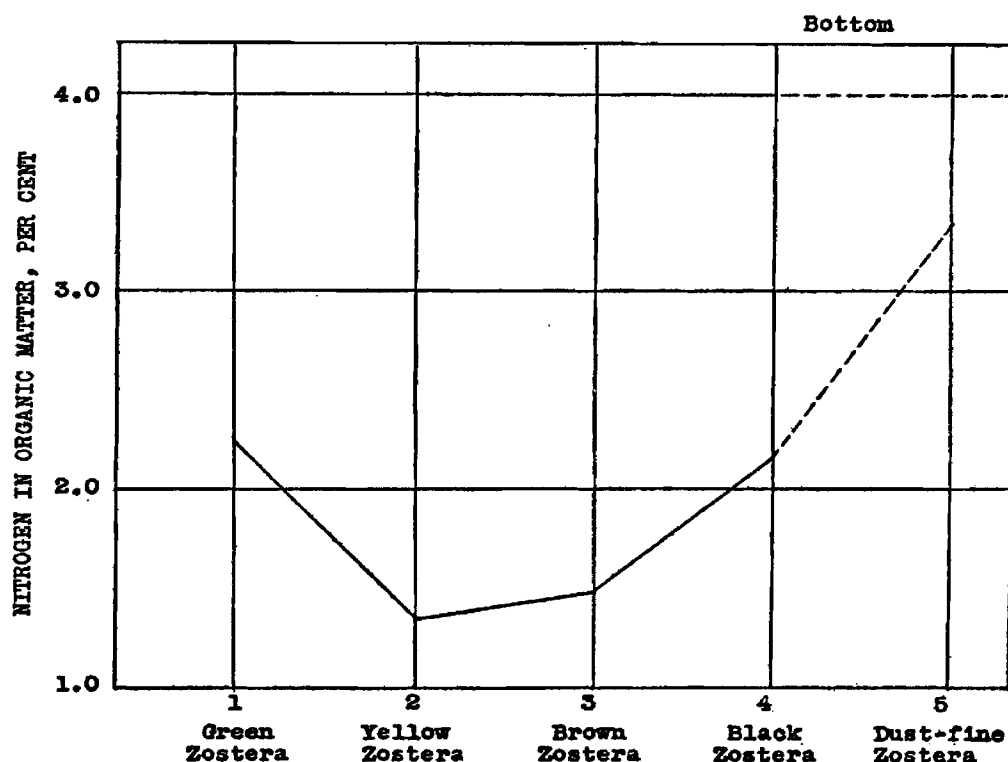


FIG. 31. Nitrogen transformation during the growth and subsequent decomposition of *Zostera* in the sea (Boysen-Jensen).

nitrogen content increases to 1.39 per cent. *Zostera* plants which had been completely broken down contained 29.6 per cent C, 65.2 per cent organic matter (loss on ignition), and 2.2 per cent N; the C:N ratio was 13.4. The increase in nitrogen of the residues as a result of bacterial decomposition is shown in figure 31. The older the plant material the less was the amount of nitrogen made soluble through the action of proteolytic enzymes; in the case of young plants, 23 per cent of the nitrogen was made soluble by enzyme action; in the brown plants, 7.7 per cent; while only 6.6 per cent of the nitrogen in the organic matter of the sea bottom was thus made soluble.

The average C:N ratio of the humus in the sea bottom was found to be 11.1:1. This led Boysen-Jensen to conclude that the nitrogen content of this humus is 4 per cent, if a carbon content of 50 per cent is assumed, as indicated by the dotted line in figure 30. The increase in total nitrogen of *Zostera* residues, which accompanies decomposition, was explained as follows: 1. The non-nitrogenous substances in the sea bottom are destroyed by bacteria to a greater extent than are the nitrogenous constituents; the latter may be transformed into humic compounds, which are less resistant to decomposition. 2. Inorganic nitrogenous compounds may be transformed into organic forms, or free atmospheric nitrogen may be fixed; the first process involves the assimilation of ammonia and nitrates from the sea water by bacteria, while the second depends upon the activities of nitrogen-fixing bacteria. The excreta of the sea fauna may also contribute to making the humus in the marine bottom richer in nitrogen; the excreta of oysters, for example, contained 5.8 per cent C and 0.71 per cent N, with a C:N of 8.2:1, whereas the bottom material at the same location contained 2.07 per cent C and 0.187 per cent N, with a C:N of 11.1:1. The fauna itself gives rise, after death, to a certain amount of detritus, which contributes more nitrogen to the humus of the sea bottom.

The gradual increase in carbon-nitrogen ratio of the humus (1226) with an increase in depth of mud is possibly due to the fact that under the anaerobic conditions prevailing in the mud below the layer at the immediate surface, a greater decomposition of the nitrogenous than of the non-nitrogenous constituents occurs. Trask (1172) also reported that, while marine deposits of recent origin may have a C:N of 8.4:1, older formations are poorer in nitrogen in respect to carbon, resulting in wider ratios of C:N.

Schokalsky (959a) measured the stratification of the muds at the bottom of the Black Sea; he suggested that the alternating layers found there are probably formed by winter terrigenous deposits (gray) and spring and summer planktonic deposits (black); this relationship enabled him to calculate that it takes 50 years to deposit a layer of mud 1 cm. in thickness. Similar stratifications were observed by Moore (724a) in the marine mud formation of the Clyde Sea area.

The organic matter of the mud can be divided (1262) into several fractions following alkali extraction. Four per cent sodium hydroxide solution at 120°C. removed 84 per cent of the organic matter, when calculated on the basis of the nitrogenous complexes, and only 70 per cent, on the carbon basis. This extract was separated into two frac-

tions, one of which (α -fraction) was found to be a ligno-protein complex, and the other (γ -fraction), a carbohydrate-protein complex. These results were interpreted to indicate that the marine humus in bottom deposits, especially those not far from land, is partly of terrestrial and partly of marine origin. The presence of lignin-like complexes points to the fact that at least part of the humus came from land or from plants growing near land such as *Zostera* (50, 52). The presence of carbohydrates and of organic matter of high protein content suggests the conclusion that marine plants and animals have contributed to the humus, after having undergone extensive decomposition by bacteria.

The chemical nature and abundance of humus in the sea bottom depends upon: 1. the nature of the bottom material, 2. distance from land, 3. configuration of the basin, 4. nature of marine plants and their residues, 5. nature of the fauna feeding upon these microscopic and macroscopic plants, 6. faunal residues, and 7. microorganisms bringing about the decomposition of both the plant and animal residues.

Hensen (420) found that the annual production of organic matter in the sea amounts to 15–18 gm. of dry matter per square meter, exclusive of the amount of phytoplankton consumed by the plankton fauna. Brandt (150) calculated that 100,000 copepods contain 0.322 gm. dry organic matter, 100,000 peridineans contain 1.605 gm., and 100,000,000 diatoms contain 0.13 gm. dry organic matter. The amount of phytoplankton produced in the sea varies throughout the year, being highest in the spring and in the autumn.

The marine plants are quite different from land plants in chemical composition and in susceptibility to decomposition. The autumn plankton of the Western Baltic was shown (150) to contain 20.2–21.6 per cent protein, 2.1–3.2 per cent fat, 60.0–68.5 per cent carbohydrate, and 8.5–15.7 per cent ash. The higher marine algae are rich in uronic acid complexes, described as algin, alginic acid, fucin, fucoidin, laminarin, etc., as well as in pentosans, in methyl pentosans, and in galactans. The differences between these carbohydrates and those of land plants are primarily responsible for the differences in the decomposition processes in the sea and in land soils.

Rôle of humus in ore accumulation in lake bottoms and in sea bottoms. According to Senft (996), limonite formation takes place as a result of several distinct processes:

1. Carbon dioxide in solution dissolves the iron oxide or the iron carbonate from the rocks, forming iron bicarbonate; during evapora-

tion of the water, the iron is precipitated as iron carbonate and is deposited around the inorganic particles in the form of aggregates; the carbonate is oxidized to ferric hydroxide.

2. Certain excretions of living plants, such as tannins, interact with iron compounds; when the organic substances are decomposed, the iron is precipitated.

3. The products of decomposition of plant residues ("humic acids") also exert decided solvent effects, giving water-soluble compounds of iron. When these come in contact with the oxygen of the air, the "humic acids" are oxidized to CO_2 and the iron is oxidized to ferric hydroxide. Similar ideas concerning the rôle of humus compounds in the precipitation of ore were expressed by Stapff (1090), Emeis (268), and others (376, 813).

Humus compounds were found to be of importance in the weathering of rocks, as well as in the sedimentation of manganese and iron compounds. The humus content of lake ores varies, according to Aschan (52), from 1.98 to 8.22 per cent and the iron oxide varies, according to Senft (996), from 21 to 82 per cent. Aarnio (5) concluded that humus substances and various electrolytes are associated with the removal of iron oxide from the soil and its precipitation in the sea as iron ore. The iron sulfide which occurs in sedimentary rocks has been formed in part during the decomposition of organic matter; the latter causes a reduction of the dissolved iron sulfate to iron sulfide; hydrogen sulfide produced during decomposition also interacts with other dissolved iron salts. In the case of various ochraceous scums, most of the organic matter may consist of cells of iron-precipitating bacteria or their residues (390).

Various theories have thus been proposed to explain the accumulation of iron ore in lakes, in swamps, and in ortstein formations. In some cases, the process was considered to be purely chemical or physical; it has been thought to be associated with colloidal changes; it has also been suggested that the process is biological. The rôle of iron and aluminum in coagulating humus compounds was emphasized particularly by Ramann (855). The process of precipitation of iron ore is similar to that of ortstein formation in podsol soils (p. 391). However, since aluminum is precipitated much more readily than iron, only the latter is washed into the lakes (5). The rôle of humus in the sedimentation and accumulation of lime formations and iron-ore formations is discussed further by Naumann (746) and by Aschan (52).

Humus in sewage sludge. Humus formation is synonymous with

stabilization of plant and animal residues, from a readily decomposable or putrescible state into an innocuous form. The chief objection against organic wastes in waters, from a sanitary point of view, is that they are readily subject to decomposition and that they may carry human or animal pathogens. When the organic residues have passed through the first active stages of the decomposition process, whether under aerobic or anaerobic conditions, by mesophilic or thermophilic microorganisms, they are changed into a state, largely colloidal in nature, in which they are no longer considered dangerous. At that state, the pathogenic microorganisms have largely disappeared or have been otherwise made ineffective.

The disposal of sewage and garbage ("habitation") wastes has been left usually to sanitary authorities, who were primarily interested in disposing of them as quickly as possible, without regard to the loss of plant nutrients and possible humus sources. Howard (465) calculated that the average annual quantity of such waste for each person is about 200 lbs. organic matter containing 15 lbs. nitrogen, 4 lbs. potash, and over 5 lbs. phosphoric acid. A number of methods have been introduced for the purpose of preserving the nutrient elements. Fowler (306a) combined, in his activated-sludge process, conservation of the plant nutrients with proper sanitation. A process described by Jackson and Wad (465) results in a dry powdery residue, formed within a month, and resulting in the preservation of about 50 per cent of the original material.

Considerable information has accumulated recently concerning the chemical composition of the organic residues in fresh sewage, as well as the processes of decomposition of the organic matter under both aerobic and anaerobic conditions. However, the chemical nature of ripe sludge has still been incompletely studied. Most of the available information is limited to the total nitrogen content and the mineral constituents of sewage and sludge. The concentration of fats in fresh sewage is known to be high (25–35 per cent); these decompose readily under aerobic and anaerobic conditions (748). The content of cellulose and hemicellulose is low, and these, as well, decompose rapidly and, especially in the case of the cellulose, even more completely than do the fats.

Adeney (11a) concluded that the decomposition of organic substances in polluted waters takes place in two stages: (a) The organic matter is first attacked with the formation of mineralized products (CO_2 , NH_3 , H_2O), on the one hand, and on the other, of organic complexes which possess the physical and chemical properties of the humus in

cultivated soils and of the organic matter usually found in unpolluted waters. (b) The humus substances and ammonium compounds are further attacked with the formation of CO_2 , NO_3^- and H_2O ; the second stage does not take place under anaerobic conditions.

The results presented in table 56 clearly illustrate the changes which take place in the process of decomposition of the organic constituents of sewage, as well as the chemical nature of the organic complexes found in the sludge. The sludge humus consists predominantly of protein, lignin, and fat, with some admixture of hemicelluloses and water-soluble substances. In the process of decomposition of the organic constituents in sewage and in sludge, the greatest relative reduction takes place in the cellulose, fats, and hemicellulose complexes, in the

TABLE 56

Chemical composition of solids in fresh sewage and of ripe sludge (434)

Per cent of dry material

	SOLIDS IN FRESH SEWAGE	DECOMPOSED SLUDGE
Ether-soluble fraction.....	34.4	8.2
Cold and hot water soluble*.....	8.5	5.5
Alcohol-soluble.....	2.5	1.6
Hemicelluloses.....	3.2	1.6
Cellulose.....	3.8	0.6
Lignin.....	5.8	8.4
Protein.....	27.1	19.7
Ash.....	24.1	56.0

* Water-soluble ash not accounted for, hence results are too high.

order named; the greatest relative increase was found to occur in the lignin fraction (434, 861).

Summary. Various forms of humus are produced under water, as in rivers, lakes, seas, and sewage disposal plants; these types of humus show chemical similarities to typical soil humus.

Humus produced under water is not uniform in composition, but varies considerably depending on the nature of the plant and animal residues which gave it origin, the microorganisms bringing about the decomposition processes, and the conditions under which the decomposition takes place. Humus formed under water can be separated into several types: water humus, lake humus, marine humus, sewage humus. These can be considered as forms of the general class of organic materials described as humus.

CHAPTER XIII

PHYSICAL AND PHYSICOCHEMICAL PROPERTIES OF HUMUS

"The general effect of humus colloid on a mineral soil may perhaps best be summed up as that of a 'buffer' substance, using the word in its widest sense."—H. J. PAGE.

The presence of humus in soil gives to the latter certain physical and physicochemical properties which make it a more favorable and more balanced medium for plant growth. Humus does not exist in the soil as a mere mechanical admixture with the mineral substances, but forms various adsorption and chemical compounds with a number of inorganic soil constituents. As a result of this, the study of physical and physicochemical properties of humus isolated from soil or from peat by chemical reagents cannot be interpreted in terms of soil processes, without proper modification. In view of the fact that different types of humus vary considerably in chemical composition, it is only logical to expect that their effect upon the inorganic portion of the soil also varies. The interaction between the organic and inorganic colloids depends further upon the reaction of the soil, upon the nature and abundance of bases, upon climatic conditions, and upon a number of other factors.

Many of the investigators of the function of humus in the physical or physicochemical soil complex made no distinction between humus and "humic acid," and did not emphasize sufficiently the mode of extraction of humus from soil. In some cases, even the source of the humus was not taken into consideration, so that whether it came from an inorganic soil, forest soil, highmoor peat, lowmoor peat or compost, or whether it was obtained by boiling sugar with acid is obscure. Very few physicochemical investigations of the function of humus in soil processes were made with humus as a whole; in the majority of cases, the materials used were only "humic acid" preparations, obtained by extraction of soil or peat with alkali solutions and precipitation with acids.

Frequently, the function of humus in a certain soil process was interpolated, by comparing the behavior of a normal soil with that of the

same soil from which humus had been removed by special treatment. The organic matter was usually eliminated by igniting the soil, a process which was found to modify the physicochemical behavior of some of the inorganic soil constituents. More recently, the tendency has been to destroy humus in soil by treatment with concentrated hydrogen peroxide solution. However, a soil from which the organic matter has thus been removed does not give a true picture of the contribution of the latter to the soil system.

Physical properties of humus and its effect upon the physical condition of the soil. Humus possesses certain physical characteristics which make it a highly important soil constituent. Of these, it is sufficient to mention the following: 1. color, 2. characteristic structure, 3. volume weight, 4. properties of cohesion and adhesion, 5. specific weight, 6. high water-holding capacity, 7. high permeability, 8. heat capacity and heat absorption, 9. shrinkage on drying, 10. coagulation by electrolytes, 11. absorption of salts and gases (high base exchange capacity), 12. high buffering power, and 13. specific odor.

The nature and depth of color of humus are not always the same; they depend upon the extent of the decomposition of the plant and animal residues as well as their original nature, upon the degree of oxidation as controlled by the oxidation-reduction potential of the soil, upon the presence of certain salts and their concentration, upon the reaction of the soil, and upon a number of other factors. In the case of mineral soils, of loess origin, it was found (156) that with an increase in humus content, the color was changed from ash-gray to a deeper brown and black color. The color effect created by humus in mineral soils is frequently utilized for purposes of soil classification. However, as pointed out previously (p. 72), the color of the soil cannot be taken as the true criterion of its humus content; the colorimetric method may give much lower results than the gravimetric, especially when applied to subsoils (26).

The structure of humus depends upon the nature of the materials from which it originated, upon the degree of their decomposition, upon the reaction of the soil, and upon environmental conditions under which decomposition is taking place. This can well be illustrated by comparing differences in structure of mull and raw-humus types of forest soil, as well as of highmoor and lowmoor peat soils; these differences are due largely to the characteristic nature and structure of the humus in these soils.

The volume weight of humus undergoes considerable change in the

on the other hand, carex peat, containing the same amount of moisture, absorbed only an average of 12.4 gm. ammonia. The greater the acidity of the peat, the greater is its capacity for NH_3 absorption; at a pH greater than 6.5, the absorbed ammonia is readily lost. Largely because of this property, sphagnum peats have found extensive application as absorbents in stables (765). Humus also absorbs, in varying concentration, different ions containing elements which are of great importance in plant nutrition; namely, P, K, Ca, Mg, and Fe; the presence of humus in soil will, therefore, tend to prevent the salts containing these elements from being washed out rapidly. While they are thus retained in the soil, they are still available for plant growth. Humus, especially in a state of unsaturation with bases, as in the case of high-moor peat, is capable of interacting with insoluble phosphates, absorbing the base and liberating phosphoric acid (650, 908, 1096, 1129).

The effect of humus upon soil texture is not the same for different soils. Schloesing was the first to observe that clay does not flocculate so readily in the presence of humus as in its absence (291). According to Ehrenberg (257), the humus sol first peptizes or disperses the aggregated clay particles; this is followed by the formation of a layer of absorbed humus sol around the clay fractions; as a result of this, the latter require much higher concentration of electrolytes for flocculation, since they behave as if they were made up entirely of humus (89). A similar protective effect of humus is observed upon ferric hydroxide, a phenomenon of considerable importance in pan formation. In the presence of CaCO_3 , the humus-clay gel is flocculated, giving the "crumb" structure to the soil. According to Page (800), the "puffing up" effect of humus in the soil can best be explained by the successive influence of moisture, frost, and drying upon the humus gel and the calcium carbonate, rather than by the liberation of CO_2 by soil organisms.

The calcium, magnesium, and iron play an important part in the precipitation of the organic-inorganic complexes (1141). The influence of humus on moisture content of the soil is chiefly a result of its influence upon tilth. In a soil with favorable texture, one finds good drainage and aeration, while too much leaching and evaporation are prevented; this is due to the fact that the clay particles are coagulated and the sand grains are cemented together, through the action of the humus. An increase in the humus content of the soil is accompanied by an increase of the moisture holding capacity (30), probably due largely to the inhibition of water by the humus gel. Dry peat is a

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highly hydrophile powder which possesses extensive surface. It is highly resistant, however, to wetting by water, once it has become desiccated (655a). This has been said to be due to the presence of air in the fine capillaries of the soil or on the humus particles (800), as well as to the presence of waxy or resinous constituents in the humus (856); the first explanation was found to be (1186) the correct one, since by removing the layer of adsorbed air, wetting was greatly accelerated.

The specific heat of humus is usually considered to be about twice that of clay, on a weight basis, namely, 0.44 to 0.47 cal./gm. (214a, 532a); on a volume basis, the former is lower. The heat conductivity of humus is poor; peat soils, for example, are cooler in the summer and warmer in the winter than mineral soils. The effect of humus upon

TABLE 57
Effect of color of soil on temperature (729)

TIME OF DAY	COLOR OF SOIL			
	Light-colored		Dark-colored	
	Depth of soil			
	2.5 cm.	5.0 cm.	2.5 cm.	5.0 cm.
	°C.	°C.	°C.	°C.
11 A.M.	25.5	23.3	27.8	23.9
12 M.	27.2	25.5	30.3	27.2
1 P.M.	28.3	26.7	32.8	30.0
2 P.M.	29.4	27.4	33.3	31.1
3 P.M.	30.0	27.8	32.8	31.1
4 P.M.	29.4	27.8	31.7	31.1
5 P.M.	27.5	27.2	29.4	30.0

soil temperature is a direct result of improvement in tilth, prevention of excessive evaporation, and better drainage, resulting in a soil which warms up more quickly. These factors also favor a reduction in the conduction of heat. The dark color which humus imparts to the soil enables the latter to absorb more of the radiant heat, thus leading to a rise in temperature (699), as shown in table 57. The humus content of the soil changes its heat of wetting, especially the ratio between the wetting with water and the wetting with organic fluids; this ratio increases with an increase in humus content (485).

The effect of humus upon the chemical composition of the soil solution is exerted through its buffering properties; the reaction does not undergo rapid change in either acidity or alkalinity (522-3); the chemi-

cal composition of the soil solution is also modified. Organic substances influence the physical condition of the soil not only directly, but also indirectly, by modifying the concentration of the electrolytes in the soil solution (186). The formation of ammonia or nitrate changes the pH value of the soil, as a result of which the colloid dispersion of the soil and the specific conductance are both changed. On the other hand, the decomposition of carbohydrates and the resulting products bring about another series of changes, as most easily expressed by an increase in pH value and in colloid dispersion; later, a reversal in these processes may take place.

The physical condition of the soil is thus found to be greatly affected by the supply and nature of the humus. When, as a result of continuous cropping, the humus content of the soil is reduced, the latter is said to be in a "run down" condition. A poor physical and chemical condition of the soil is considered to be largely associated with the destruction of the humus; this is probably largely due not so much to the destruction of the humus as a whole, but to the breakdown of the plant residues and roots, which tended to increase the porosity of the soil.

Colloidal nature of humus. The colloidal constituents of the soil are frequently divided into two groups: 1. the inorganic or clay fraction, and 2. the organic or humus fraction; these do not exist in the soil independent of each other, but give mixed or compound colloids. A considerable amount of clay tends to make a soil heavy, sticky, and impenetrable to water and to air; the clay can be coagulated by lime or by humus, thus reducing its unfavorable physical effect. On the other hand, the clay colloid forms compounds with the humus colloid, thus preventing its rapid decomposition; it is, therefore, easier to build up the humus content in a clay-rich soil than in a clay-poor one.

Humus exerts an additional effect on soil in forming insoluble humates which coat the soil particles, preventing them from agglomerating into a compact mass, thus maintaining the soil in a loose porous condition; these particles also probably give rise to electrochemical phenomena through which the nutritive elements present in insoluble forms in soil are solubilized and rendered available to plants (595).

The first reference to literature dealing with the colloid-chemical behavior of the soil organic compounds, namely, the so-called "humic acids," is found in the work of Berzelius (113). It was not until 1888, however, that van Bemmelen (86) recognized the importance of Graham's investigations of the colloidal state of matter and applied them

to soil problems. He definitely emphasized the fact that the various "humic acids" are not true chemical compounds, but are colloidal substances which have originated from chemical residues and their decomposition products, by various processes of hydrolysis, reduction, and oxidation. Although certain constituents of humus were found to be soluble in water, since they pass through colloidal membranes on dialysis, most of the complexes give colloidal solutions, which are opalescent. By means of electro dialysis, it is possible to separate humus into several fractions (647). The solubility of humus in the soil water usually depends upon the presence of small quantities of alkalis. This dissolved or colloiddally suspended humus usually becomes precipitated by the addition of acids or salts, as well as by drying.

Carefully purified "humic acid" migrates in the electric field with a negative charge (796, 798); the charged humus particles can be purified and concentrated by electrophoresis (795-7, 679). Alkalies, alkali reacting salts, and pyridine bring about the peptization of humus complexes (1207), whereas acids affect their flocculation according to the degree of their dissociation. Large quantities of monovalent salts are needed to bring about flocculation; divalent salts are much more active; and polyvalent cations are most active; the H-ion exerts a greater effect than the other monovalent cations. Aluminum sulfate flocculates more rapidly than the acetate, although less of it is absorbed. Oden (782-3) determined the amounts of different electrolytes (as normal solutions) which will coagulate, within two hours, a solution of "humic acid" containing 20 mg. per liter:

Nature of electrolyte..	NaCl	NH ₄ NO ₃	Ca(HCO ₃) ₂	Fe(HCO ₃) ₂	HCl
Coagulation value....	0.25	0.05	0.007	0.004	0.008

"Humic acid" preparations obtained from peat were found to consist of particles about 0.02 μ in diameter, which could be readily flocculated by calcium salts and other electrolytes. The process of coagulation can be expressed in terms of an increase in viscosity or rapidity of filtration. Freezing causes the flocculation of the humus sol, which may be irreversible.

Humus colloids demonstrate low electric conductivity. They form absorption compounds with bases or salts; the quantity of base that a given colloid can absorb varies with conditions. Humus was found to give absorption curves, typical of colloids, whereby the cations are absorbed and the anions liberated. According to van Bemmelen, the absorption phenomena shown by humus are similar to those of inor-

ganic gels, especially the hydroxides of manganese, tin, and silicon. Baumann and Gully (75) have emphasized particularly the colloidal nature of the organic complexes in peat and in soil; they denied the common assumption that "humic acids" are formed as a result of decomposition of plant materials. They demonstrated that sphagnum plants possess the same "acid" properties as sphagnum peat; hence the "acid phenomena" of peat are associated with substances existing in the peat-forming plants. The low electrical conductivity and the course of reaction with soluble and insoluble salts were believed to be sufficient proof that one is dealing here, not with acidity reactions, but with surface or absorption phenomena; a relatively greater amount of base was absorbed by humus from dilute solutions than from concentrated ones. However, Ehrenberg (260), Oden (780), and others believed that the acid nature of humus is due to the existence of true organic acids (p. 45).

Humus solutions can act as protective colloids (782, 164), which are limited by their sensitiveness to electrolytes. In this connection, attention should be called to the function of humus in transporting iron in a sol condition, as $\text{Fe}(\text{OH})_3$ (1193). The presence of $(\text{HCO}_3)_2^-$, in sufficient concentration, will bring about the flocculation of both the $\text{Fe}(\text{OH})_3$ sol and the humus sol.

Humus can be divided into dialyzable and non-dialyzable fractions. When alkalis act on humus partial peptization or swelling takes place, accompanied by apparent solution of the neutral colloids and a partial solution of the acid colloids, namely, the "humic acids" (296, 782). Alkali humates are not in a colloidal state, because ultra-microscopic study of their solutions gives no trace of visible particles. They diffuse readily through parchment paper and can be filtered through Chamberlain filters; on being shaken with charcoal or BaSO_4 , no change in concentration results. The alkali humates give in the polarization microscope a true interference cross, thus showing that they possess a spherocrystalline structure.

The humus gel swells considerably in water. The swelling is enhanced by hydroxyl-ions, especially in the absence of polyvalent cations. The water from the gel is removed only with great difficulty, except in the presence of a flocculating agent; on drying, there is considerable shrinkage of the humus.

Complexes of humus with inorganic soil constituents. Soil humus, or a certain fraction of it, forms compounds with some of the inorganic soil elements or compounds, especially bases and the clay fraction.

Schloesing (947) first suggested that clay combines with soil humus to give colloidal compounds. The extent of combination between the two complexes depends on the reaction, increasing with an increase in pH value, and on concentration of exchangeable bases, such as calcium.

Sokolovski (1060-1) recognized the existence in soil of two humus fractions: 1. that absorbing calcium, and 2. that combined with inorganic colloids. Calcium is present in humus only in an absorbed condition, but does not form any salts. Humus is fixed in the soil in the presence of calcium; when this base is removed, the humus is readily lost. This fraction, which forms the active part of the humus colloid of the soil, is equivalent to the *matière noire* of Grandeau. It can be removed by leaching with distilled water, after the calcium has been replaced.

Wolf and Schlatter (1295) shook a coarse sandy soil for eight days with distilled water and obtained a humus preparation which contained 64 to 70 per cent inorganic matter, as determined by loss on ignition. The inorganic part of the complex was made up of 18.65 per cent Fe_2O_3 , 20 per cent Al_2O_3 , 53.4 per cent SiO_2 , and small amounts of CaO and MgO . Demolon and Barbier (215) demonstrated that humus and clay form definite compounds, the concentrations of the two interacting complexes depending on the degree of acidity or alkalinity. The influence of reaction upon the fixation of humus by clay is shown in the following summary:

<i>pH</i>	<i>Parts of humus fixed by 100 parts of clay</i>
3.85	9.60
5.0	8.08
5.9	7.26
6.95	6.28
7.25	5.37
7.55	4.65
8.5	2.05

The relative concentration of humus was found to be of importance, the smaller concentrations being fixed more energetically. Demolon (215) concluded that the soil contains a clay-humus complex; the cations absorbed by the clay, especially the calcium ion, influence the formation of this complex.

Waksman (1222) demonstrated that an organic-inorganic complex (β -fraction), varying considerably in chemical composition, can be isolated from the soil by treatment with alkalies. This complex is

soluble in alkalis and in acids, and is precipitated at a pH of about 4.8. Antoniani (44) treated a soil with 5 per cent HCl, then extracted it with 10 per cent NaOH solution, and purified the humus with 5 per cent KCl; a complex was obtained containing 82.75 per cent organic matter, 5.05 per cent Fe_2O_3 , 4.35 per cent Al_2O_3 , 4.65 per cent SiO_2 , and 2.90 per cent P_2O_5 . The alkaline dispersion of the humic colloid was exerted only over a definite range of hydroxyl-ion concentrations. The isoelectric point of the complex was pH 7.4, where it was flocculated. When dispersed again by NaOH and placed in an electric field, anodic

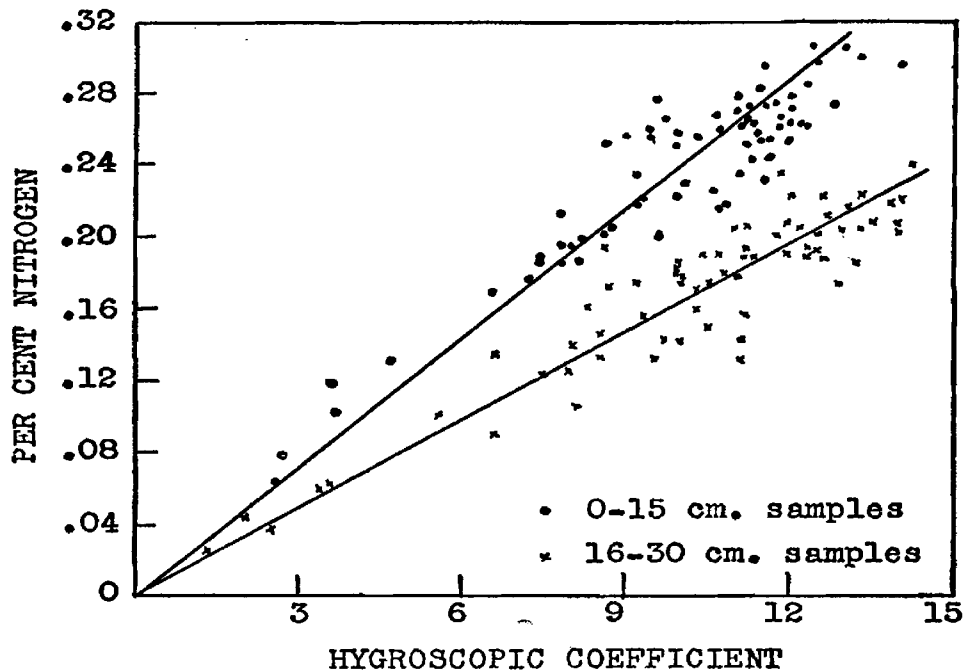


FIG. 32. Relation between humus (nitrogen) content of soil and hygroscopic coefficient (texture) (Russell and McRuer).

migration occurred. Gradual increase of hydroxyl-ion resulted in an increase in migration to a maximum, followed by a decrease to zero, then by a change to cathodic migration.

Turner (1190) also established a close relation between the humus and the clay fractions in tropical soils; when the ratio between the clay and humus exceeded 20, the latter occurred in the form of surface films on the inorganic particles. According to Gedroiz (341), mutual relation between the organic and mineral parts of the soil is of great importance in influencing the dispersing action of monovalent cations introduced into the soil-absorbing complex. The organic colloids in the soil exert an aggregating effect upon the inorganic colloidal particles of the soil, favoring the formation in the soil of micro-structural units,

which possess a marked resistance against the disaggregating action of adsorbed monovalent cations; the removal of the colloidal humus part of the soil increases the dispersing action of these cations.

These considerations permit the conclusion that there exists in the soil a humus-zeolite complex, which is responsible for many of the physicochemical reactions of the soil.

Adsorption and base exchange capacity of humus. When humus complexes are treated with neutral salts, such as KCl, the extract shows a much greater acidity than an ordinary water extract. This phenomenon has attracted considerable attention on the part of soil chemists and has been designated as "neutral salt decomposition." Eichhorn (261) and König (563), who were the first to study this phenomenon, explained it by the fact that the insoluble "humic acid" forms humates with the cation of the salt, thus liberating free HCl. Baumann and Gully (75) denied the acid nature of the humic acids and explained the aforementioned phenomenon by the adsorption of the cation by neutral colloids. Daikuhara (202) suggested that the aluminum and iron salts adsorbed by the humus are replaced by the KCl and are brought again into solution. Oden explained the phenomenon by the action of the "humic acids" present in the humus complex. Kappen (522) and Heiman (413) considered the reaction to be more complicated, namely, that, on the one hand, the humic acids interact with the neutral salt ("humic acid" + KCl = K humate + HCl), and, on the other, that the Al^{+++} and Fe^{+++} present in the humus are replaced by the K^+ [Al (humate) $_3$ + 3KCl = 3 K humate + $AlCl_3$]. Tacke and Arnd (1127) and Behrens (83) have contributed further to an understanding of this process. Ganguli (335) suggested that KCl is first adsorbed by humus, then hydrolyzed. Trenel and Harada (1176) confirmed Kappen's observations, namely, that the acidity of "neutral salt decomposition" by humus compounds is due to the presence of aluminum in the organic complex, to the greater solubility of the difficultly soluble organic acids in neutral salts, to the adsorption of bases from the neutral salt, and to the liberation of corresponding amounts of mineral acid.

The nature of the humus and its specific constituents and the nature of the cation and anion of the salt, as well as the concentration of the latter, were found to be of great importance in the reactions involved. In many instances, observations made on the adsorption by coal or by artificial humus prepared from sugar were applied indiscriminately to explain the function of soil humus. The adsorption of ammonia from

ammonium hydroxide and from ammonium salts by peat, by decomposed wood, and by forest humus was first definitely established by Brustlein (158), soon followed by others (553, 866, 219). The adsorption of phosphoric acid and silicic acids by organic soils was first demonstrated by Eichhorn and Liebig; the higher the organic matter content of the soil, the greater was the degree of adsorption. König (563) concluded that humus is capable of mechanically binding the alkali from alkali solutions. The fact that the higher the ash content of peat, the less was the amount of alkali adsorbed, the adsorption being highest in sphagnum peat and lowest in lowmoor peat, was explained by the greater decomposition of the latter; the generalization was thereby made that the greater the decomposition of a peat, the lower its absorbing capacity for bases. A comparison of the two types of peat was unjustified, since the lower adsorption by the lowmoor peat was due largely to its higher base content and to the distinctly different botanical origins of the two types of peat.

Figure 33 shows how decomposition of plants and their transformation into peat increase their capacity for adsorption of bases. In the case of forest soils, the highest base exchange capacity is found in the F- and H-layers where the humus is high and where active decomposition has taken place (288). Anderson and Byers (35) came to the conclusion that both the colloidal material extracted from decomposed organic residues and microbial cell substance possess colloidal properties similar in character to preparations extracted from soil. They had a pronounced acid character.

Gedroiz (341) noted that the soil-absorbing complex consists of both inorganic and organic soil constituents; the greater importance of one or the other in this process varies with different soils and with different horizons of the same soil. He suggested that the combination between the two constituents of the absorbing complex is not merely mechanical but is more intimate (482). Tiulin (1165-6) found that the absorptive capacity of the soil, measured as calcium, is parallel to the humus content, measured as carbon. The carbon (per cent) in the absorbing complex was found to be in constant relation to the absorptive capacity (m.e. or mg. equivalents in 100 gm.), the ratio being 2.7 for chernozem soils. This could hold true only if a mutual precipitation of the humus by the sesquioxide and silicate were assumed. The ratio was much less for podsols, namely, about 1.2, since, in addition to the humic-alumino-silicic complex, these soils also contain a considerable amount of alumino-silicates, which also exert an absorptive action. McGeorge

(687) also found a close correlation between the total base exchange capacity and the carbon content of the soil, there being an increase of 35 m.e. for each 10 gm. of carbon in the soil.

Hissink (447) emphasized the fact that the humus fraction possesses a far greater power of base adsorption than does the clay fraction. He assigned to humus an adsorptive value for CaO five times greater than that of clay. Alben (16) found that humus has an absorptive capacity

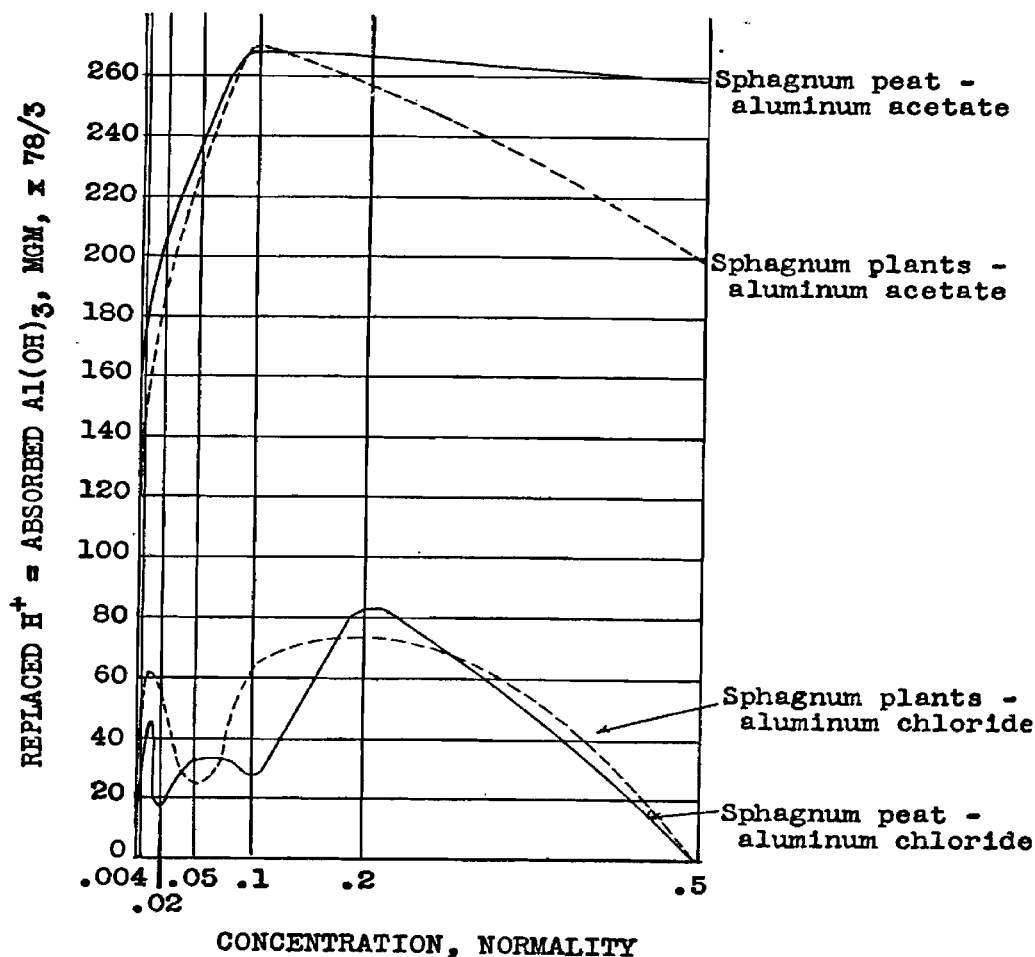


FIG. 33. Absorption of $Al(OH)_3$ from aluminum acetate and aluminum chloride by sphagnum plants and sphagnum peat (Baumann and Gully).

seven times as great as that of bentonite. Sokolovski (1061) demonstrated that the removal of humus from a podsol soil by oxidation with hydrogen peroxide free from acid brought about a reduction of 65 per cent of the absorption capacity; in the case of chernozem soils, however, the reduction was very small. This is no doubt, partly at least, due to the fact that, as shown by Gedroiz (343), the removal with hydrogen peroxide of humus from soils saturated with sodium or hy-

drogen is much more rapid than from soils saturated with calcium or magnesium. Some investigators found that igniting soil to 350°C to remove the organic matter does not affect the base exchange capacity of the soil zeolites (713). According to Bradfield,¹ the oxidation of organic matter, even in podsollic soils, by H₂O₂ may not reduce the base absorbing power, although the organic matter is removed. His conclusion was that humus and clay are not always additive in their ability to absorb bases. Demolon's (215) work points to the fact that there is some weak chemical combination between clay and humus; it is, therefore, likely that some of the bonds used to absorb bases when they are separate entities are satisfied by the other component when

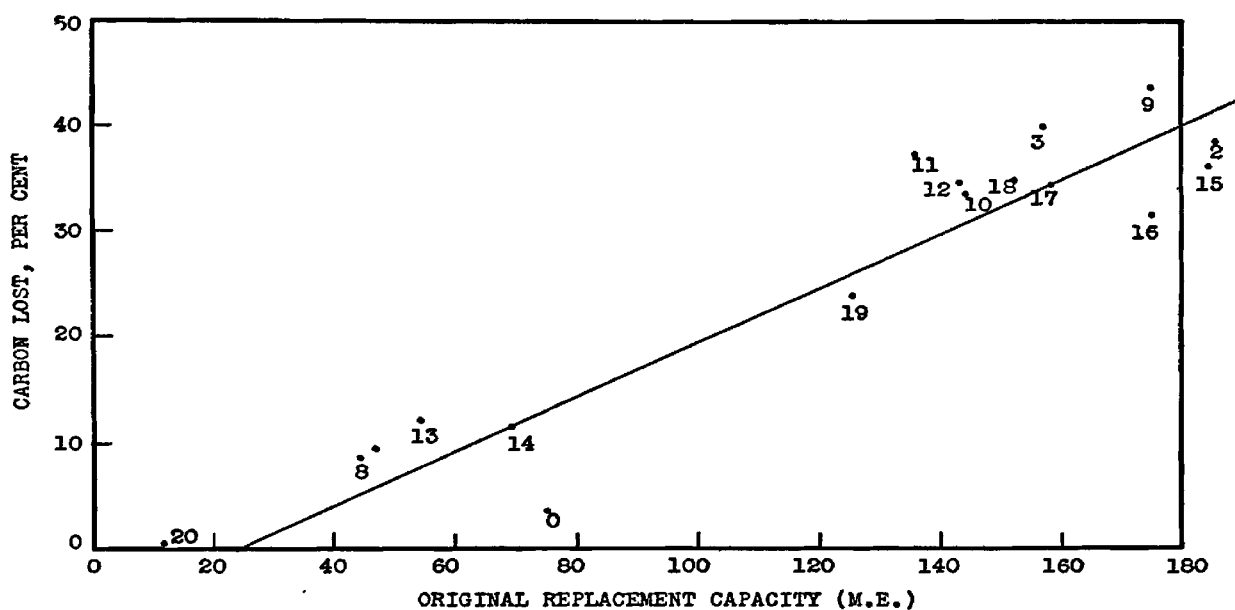


FIG. 34. The relation between the original replacement capacity and percent age carbon lost by treatment with H₂O₂ (McGeorge).

they are present together. The combination between clay and humus seems to take place largely in a slightly acid medium where the weakly basic groups would be expected to function (680).

Gedroiz (343) concluded that one-half or more of the base exchange capacity of the soil is due to the humus part of the absorbing complex, one part of humus, by weight, absorbing 8 or more times as many exchangeable cations as one part of the mineral fraction of the complex. According to Mitchell (713), the base exchange capacity of the organic constituents of mineral soils ranges from 41 to 61 per cent of the total base exchange capacity of these soils (1283). Turner (1190) found that the humus of the soil has a base exchange of 151 m.e. per 100 gm.,

¹ Personal communication.

while the clay fraction has only an equivalent of 24 for 100 gm., or about one-seventh of that of the humus (788, 541).

Base exchange in highly organic soils was shown by McGeorge (688) to take place in chemically equivalent proportions. By oxidizing the humus of the soil with hydrogen peroxide, he showed that the loss in exchange capacity approximates a linear function of the organic matter destroyed (fig. 34). The exchange capacity of different humus preparations, such as those soluble in aqueous NaOH and in alcoholic NaOH, was found to differ; that of the former was much higher (382 m.e. for 100 gm.) than that of the latter (116 m.e.). However, there was considerable variation in the exchange capacity of both complexes obtained

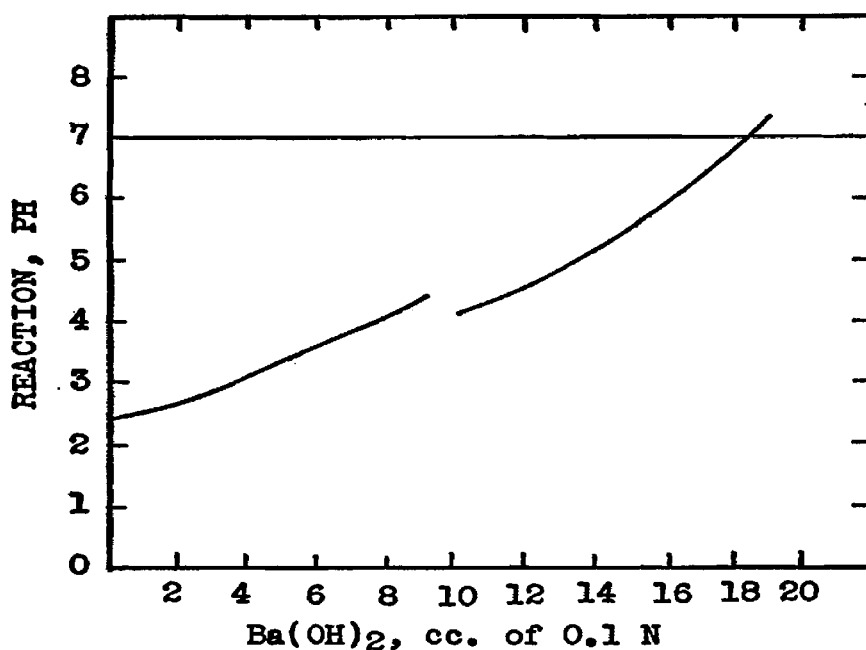


FIG. 35. Titration curve of "humic acid" with 0.1 normal Ba(OH)₂ solution (McGeorge).

from different soils. The sodium and potassium salts of the organic complexes show a high degree of ionization, whereas those of Ca, Ba, and H are low (43a). The curve of the humus fraction of the soil dissolved in aqueous NaOH titrated with Ba(OH)₂ is shown in figure 35; the influence of dilution upon the ionization of the same complex is given in figure 36.

In view of the fact that lignin is important in the formation of humus, it is of interest to determine the absorption capacity of this complex. Wedekind and Garre (1260) found that lignin carries a negative charge and is capable of adsorbing alkalis, NH₃, and basic dyes. The absorption is irreversible and indicates the formation of compounds, probably of a molecular type. The quantity of material taken up depended

on a number of factors, such as water content of the lignin preparation and duration of the process.

An equivalent relation between bases and lignin has been reported (520), 100 gm. of lignin absorbing 170 m.e. of barium; this corresponds to an equivalent weight of spruce lignin of about 590. The term "alkali number" was used to designate the maximum absorption by lignin of NaOH from 0.5 N solution. The concentration of the alkali and its nature were shown to be of importance in this connection. One hundred grams of acid lignin prepared from spruce wood gave an increase from 96 to 127 m.e., with an increase in normality of NaOH from

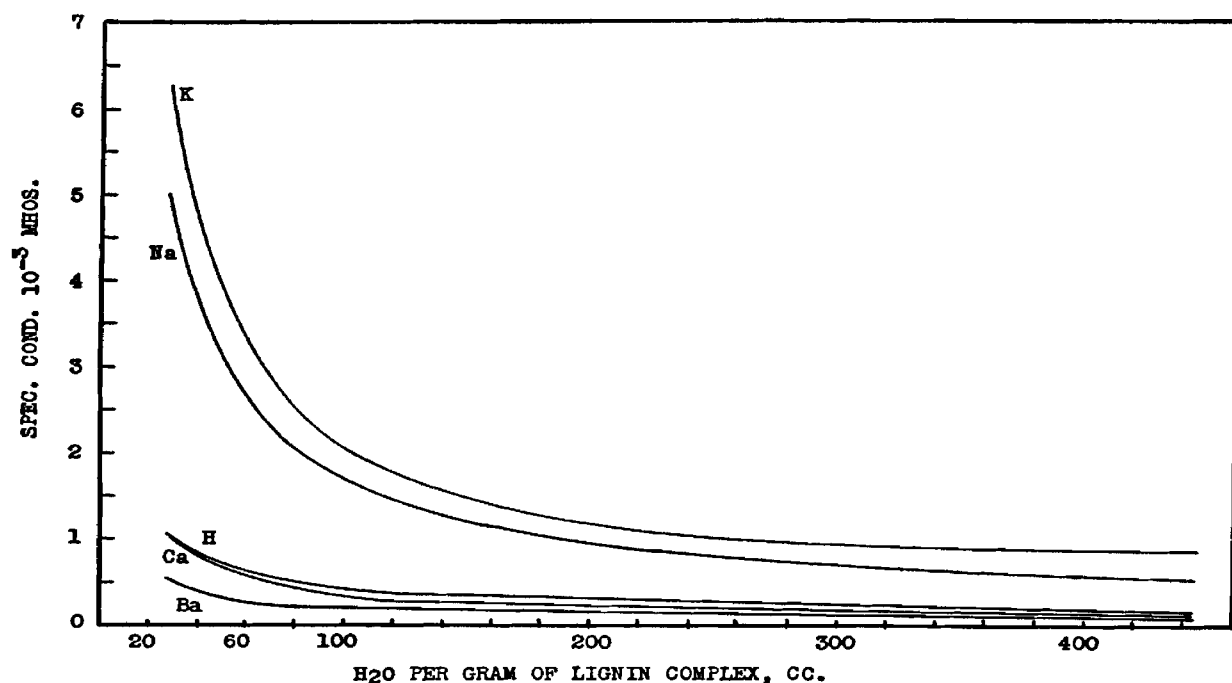


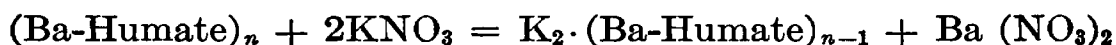
FIG. 36. Effect of dilution upon the ionization of humates (McGeorge)

0.1 to 3.91. For $\text{Ba}(\text{OH})_2$, the increase in m.e. was from 150 to 168, for an increase in normality of the solution from 0.15 to 0.42.

A balanced reaction can be obtained between a neutral salt and free "humic acid," thus giving a "humus salt" and a free acid (413). On treating 5-gm. portions of dry "humic acid" preparation with 100 cc. of a cold saturated K_2SO_4 solution (shaking for 1 hour), and titrating the acid liberated, a close correlation could be established between the latter and the absorption of potassium. It was suggested that this phenomenon is due to ion exchange, the H-ions of the humus complexes being replaced by the cations of the salt. On diluting the salt solution to 0.5 N, larger amounts of acid became liberated; when the dilution was increased 12 times, the amount of acid liberated was more than

doubled. In the case of the humus compounds, dibasic ions (Mg, Ca, Ba) were found to be more active in replacing the H-ions, whereas in the exchange reactions for mineral complexes, the K-ion was most active; potassium- and other sulfates were also more readily decomposed than chlorides. This was explained by Kappen (523) as due to dilution phenomena, to the solubility relations of the salts formed, and to differences in the degree of dissociation of the acids produced. A replacement reaction was also demonstrated between iron- and aluminum-humates and neutral salts.

Humus can be saturated with bases to different degrees, depending on the method employed; the conclusion was therefore reached (583) that bases will combine with humus both chemically and physically. An equivalent of 308.7 was obtained for ammonia absorbed by humus, with a similar equivalent for calcium. The exchange of bases during the interaction of "humic acids" or "humates" with neutral alkali salts consists in the gradual replacement of the hydrogen-ion of the "humic acid" and the alkali-earth ion of the "humate" by an alkali ion, according to the following reaction (1087):



Acids, with the exception of phosphoric, were at first believed not to be absorbed by humus; the exception was ascribed to the mineral content of the peat, which forms insoluble phosphates (918). It was later shown (679, 43), however, that both cation and anions are adsorbed by the soil complex (335).

Kawamura (530, 531) determined the adsorption of bases and acids by "humic acid," either prepared by treatment of sugar with a mineral acid or isolated from peat. A "humate" was produced as a result of combination of the "humic acid" with bases; this material continued, however to adsorb the free base. The adsorption of NaOH was lower than that of Ba(OH)₂, due to the greater solubility of the sodium "humate" (fig. 37). "Humic acid" was also found able to adsorb anions, to a very low extent however, the amount adsorbed being a logarithmic function in all cases; hence no evidence was obtained concerning the formation of a definite chemical compound. One gram of dry "humic acid" took up the total amount of base from 100 cc. of solution whose content was below 3.0 equivalent millimols; this was analagous to the case of stearic acid treated with a base whose content was below 3.5 equivalent millimols. In the case of the humate, the adsorption of the base continued further, while the stearate did not

react appreciably in this manner. On treating "humic acid" with AlCl_3 solution, the formation of an aluminum tri-humate took place, the amount of aluminum taken up being 0.7–0.8 millimols per 1 gm. "humic acid." Five grams of air-dry "humic acid" from peat were treated with 50 cc. of 1.0 *N* KCl solution, filtered, and 10 cc. of filtrate titrated with 0.05 *N* NaOH, phenolphthalein being used as an indicator. The amount of base replaced corresponded to 2.3 equivalent millimols of AlCl_3 per gram of "humic acid." The reaction was written as follows, *R* being the humus complex:

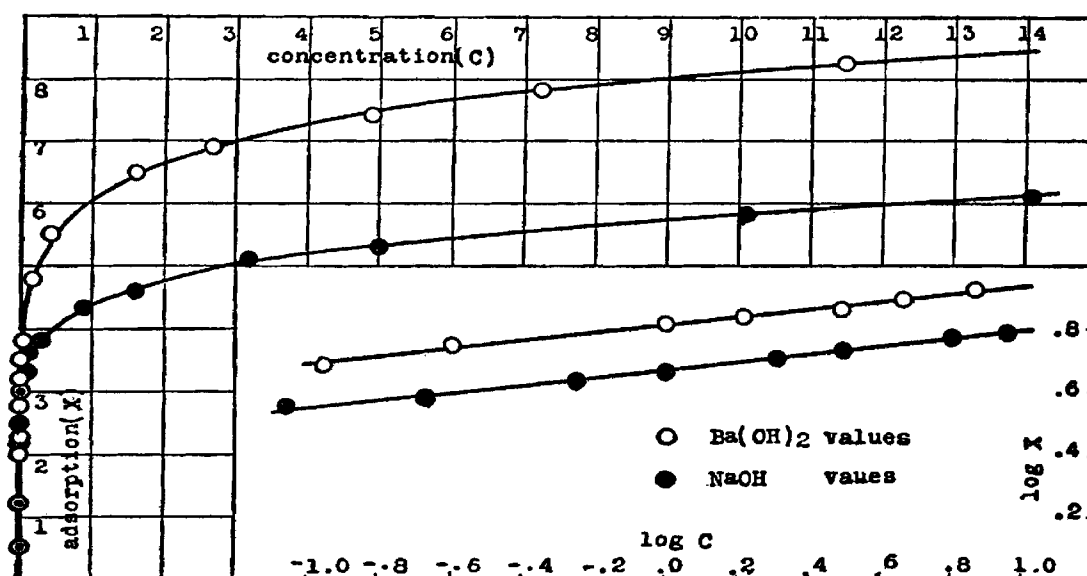
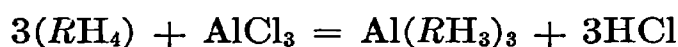


FIG. 37. Adsorption—concentration diagram of bases by humic acid from peat (Kawamura).

The isoelectric precipitation of humic acids from peat in the presence of proteins, on the one hand, and of iron and aluminum, on the other, has been investigated by Mattson (680). He found that the colloidal humic complex lowers the isoelectric point of the proteins. The "humates" of iron and aluminum show an electropositive maximum on the acid side of the isoelectric point, and when the proportion of humus is high, a second isoelectric point. The exchange capacity of humus at pH 7.0, increased with the proportion of humus to the sesquioxide. The humate-ion was found to displace the PO_4 -ion and to a still greater extent the SiO_3 -ion.

The chemical nature of the humus constituents which are responsible

for the reaction of base exchange and adsorption is not definitely established. Gedroiz emphasized that "it is at present impossible to state anything definite concerning the composition of the organic part of the adsorbing complex; concerning the humus of the soil in general, it is certain that it contains various compounds." Although it has been shown that the lignin part of the complex probably is important in this process, there is no doubt that lignin alone cannot be responsible for it. The base exchange capacity of free lignin is rather low, not more than a fraction of that of the entire humus complex. However, on treating lignin with alkalis, its base exchange capacity increases.

TABLE 58

The absorption of Ca-ions by humus and by albumin "humate" at various pH values (680)

NATURE OF SOLUTION	HCl	pH	Ca IN	Ca
	<i>m. equiv.</i>		SOLUTION	ABSORBED
			<i>m. equiv.</i>	<i>m. equiv.</i>
Humus* + CaCl ₂ †.....	2.0	3.8	3.07	0.93
Humus + CaCl ₂	4.0	3.0	3.70	0.30
Humus + CaCl ₂	6.0	2.5	3.86	0.14
Humus + CaCl ₂	8.0	2.15	3.97	0.03
Humus + CaCl ₂	12.0	1.8	4.00	0.00
Humus* + CaCl ₂ † + albumin‡.....	3.0	4.2	3.27	0.73
Humus + CaCl ₂ + albumin.....	4.0	3.8	3.85	0.15
Humus + CaCl ₂ + albumin.....	6.0	3.0	4.14	-0.14
Humus + CaCl ₂ + albumin.....	10.0	2.5	4.19	-0.19

* 3 m. equiv. Na-humate = 1.05 gm. humus.

† 4 m. equiv. CaCl₂ in 500 cc.

‡ 2 gm. albumin.

Waksman and Iyer (1232) found that when lignin is combined with protein, a ligno-protein complex is formed, which possesses a considerably higher base exchange capacity than either lignin or protein alone. The exchange capacity of the synthesized complex was found to be similar to that of "humus" obtained from mineral soils or peat by extraction with an alkali solution and precipitation with acid. In view of the fact that the synthesized complex is similar in nature to humus and is probably the mother substance of the humus in mineral soils, in lowmoor peats, in forest soils, and in composts, it was concluded that it is largely responsible for the high base exchange capacity of soil humus. Certain differences were obtained between different humus preparations, both synthetic and natural, which were found to be partly

due to differences in the chemical nature of the humus and partly to accompanying inorganic substances. The nature of the inorganic ion combining with the organic substance was found to be of the greatest importance in determining the base exchange capacity.

Other constituents of humus, such as those which are hydrolyzed by treatment of humus with acid, namely, the hemicelluloses and especially the polyuronides, as well as certain free proteins, are also responsible for this reaction.

Reaction and buffering properties of humus. In combination with calcium or magnesium, humus is practically neutral or slightly alkaline, having a reaction of pH 7.0–7.5. In the absence of calcium and magnesium, humus combines with aluminum hydroxide, iron hydroxide, or clay fractions, these being acid in reaction (pH 3.8). The first form of humus is saturated with bases and has little protective action for colloids; the acid form is unsaturated, liberates hydrogen when allowed to interact with neutral salts, and exerts a protective action upon colloids. One need not think of two forms of humus, but of two states of the same general type of humus. By adding lime, the acid state is changed to the neutral state, whereby it exerts a highly favorable effect upon the soil.

It was observed by early students of soils that when plant residues undergo decomposition in the absence of bases or in the presence of relatively small amounts of calcium or magnesium, the resulting humus has an acid character; such humus was considered to be rather unfavorable for plant life, whereas humus produced in the presence of sufficient lime, namely, the "mild humus," was looked upon as very favorable for plant growth.

Some plant residues are originally very acid in reaction: the needles of spruce and pine have a pH of 3.8 to 4.2, the leaves of red oak—pH 4.8 to 4.9, the leaves of *Betula*—5.0 to 6.1, the leaves of *Fagus*—pH 5.8 to 6.6, while *Mercurialis perennis* has a pH of 7.4 (432). When plant residues acid in reaction undergo decomposition, the resulting humus may become even more acid. This is particularly evident in the case of peats; sphagnum peat usually has a pH of 3.9, while the pH of sedge peat is 6.0 to 7.5 (1054, 46, 47). There is considerable variation in the reaction of peat during the year.

Sprenkel (1074) was among the first to suggest that the acid nature of humus originating in the absence of an abundance of bases is due to the formation of free acids, namely, the "humic acids." With the development of colloidal chemistry, the idea was brought forth by Bau-

mann and Gully (75) that humus is not an acid, but that the acidity appears subsequent to the addition of a salt, from which an acid is liberated, as a result of the adsorption of the base by the humus. Ganguli (335) observed that when 1 gm. of "humic acid" is treated with 1 *N* solutions of various electrolytes, the following pH values were obtained:

Electrolyte.....	Water	NaCl	KCl	BaCl ₂	AlCl ₃	K ₂ SO ₄
pH value.....	4.56	3.35	2.8	2.64	2.28	4.0

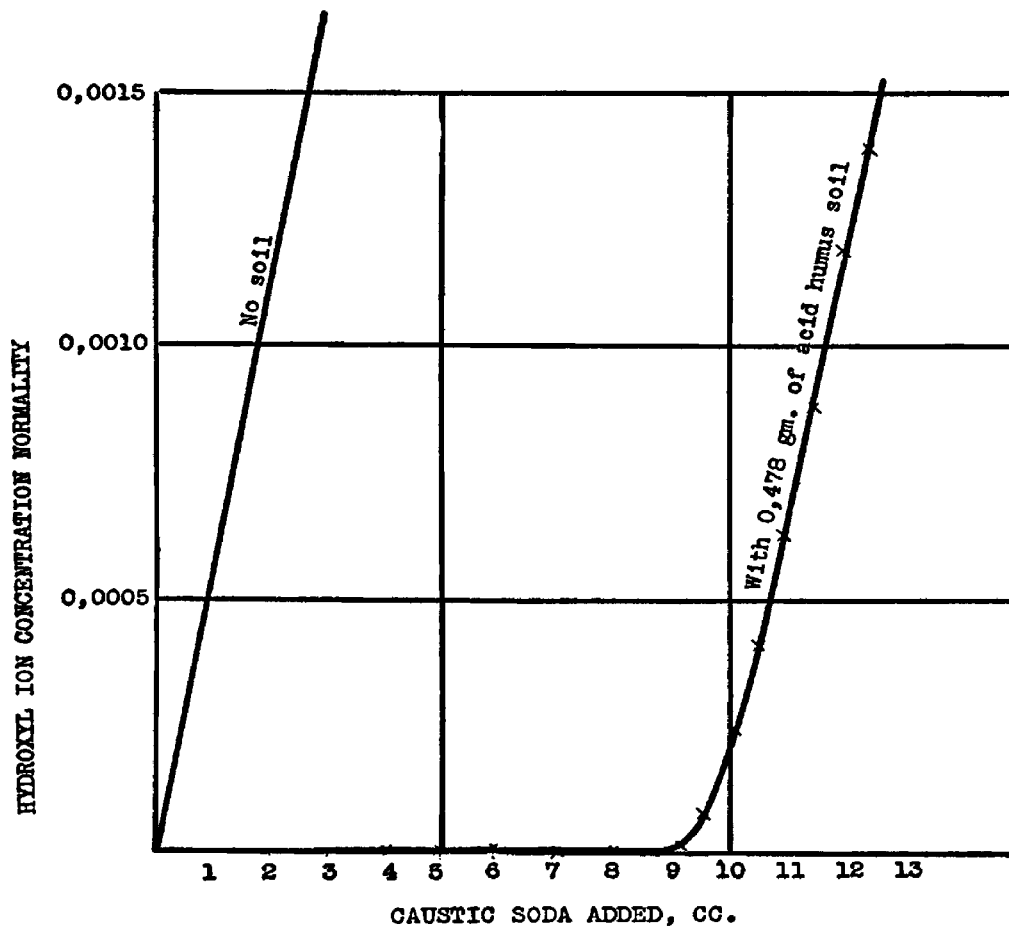


FIG. 38. The buffering properties of soil humus (Oden)

Oden (780) demonstrated by potentiometric measurements (fig. 38) that humus possesses free hydrogen ions: 0.478 gm. of sphagnum peat required 1.64 m.e. of NaOH, thus accounting for 3–4 mg. of hydrogen per 1 gm. of dry material. Natural peat had a greater acidity than the "humic acids" prepared from peat; it was stated that this was due to the presence in the peat of free inorganic and organic acids (acetic, propionic, etc.) produced as a result of the activities of microorganisms. Tacke (1130) and Süchting (1115) also claim to have demonstrated the

existence of free H-ions in "humic acids"; they were able to invert sucrose on treatment with humic preparations. As to the very low conductivity of these "acids," they argued that other acids, like stearic and oleic, have even a lower conductivity (524, 159).

Rindell (886-7) attempted to bridge the conflicting ideas of Baumann and Gully and of Tacke and Süchting, by the conception that "humic acids" comprise both colloids and true acids, as is the case with silicic acid. When "humic acid" is titrated with NaOH and Ba(OH)₂, various values are obtained; this was explained as due to the fact that alkali humates, as salts of weak acids, are hydrolyzed and give a weakly alkaline reaction, whereas the alkali earth humates which are soluble only with great difficulty do not free an appreciable amount of hydroxyl-ions.

Gillespie and Wise (347) have shown that "humic acid" prepared from soil, after complete removal of the mineral acid used for its precipitation, had a pH of 4.55 to 4.65. On treatment with normal KCl solution, the acidity increased to pH 3.3, showing that there is a considerable increase in hydrogen-ion concentration on treatment of humus with neutral salts; BaCl₂ exerted an even greater effect than KCl.

The question of the nature of soil acidity, and the rôle played by humus as a whole, as well as by some of its specific constituents, have attracted considerable attention. This is due to the fact that humus possesses certain definite acidic or acidoid properties, which favor its combination with bases, thus resembling weak organic acids. The two theories proposed to explain this phenomenon, can be summarized as follows: 1. in humus there exist definite organic acids, the so-called "humic acids"; 2. the absorption by humus from neutral salts, liberating the acid radical, accounts for the acidity of the humus. The investigations of Oden and others tend to indicate that humus has a replaceable hydrogen, which may be a replaceable carboxyl hydrogen as in organic acids, a hydroxyl hydrogen as in phenols, or a hydrogen of water activated through the fixation of the OH-groups (p. 49).

Humus is electronegative and is readily dispersed or dissolved when free from electrolytes, giving, in the presence of a monobasic alkali, soluble compounds frequently referred to as "humates." The "humates" of calcium and magnesium are less soluble or dispersible. The "humates" of the trivalent ions aluminum and iron are insoluble or non-dispersible at the isoelectric point but become soluble readily with increasing acidity or alkalinity. These compounds possess distinct amphoteric properties; the ferric humates are isoelectric at a much lower pH value than the aluminum humates of similar composition,

The buffering properties of various types of humus differ considerably, depending on the nature of the plant residues (432, 832), on the degree of their decomposition, and on the nature of the inorganic soil constituents. When the exchangeable cations are removed, the buffer capacity of the humus toward acids is diminished while it is increased toward alkalies (1210).

Humus as an oxidation-reduction system. Humus plays an important rôle in the oxidation-reduction system of the soil. According to Willis (1286), humus constitutes a system having a potential pH curve with a slope of 0.06 in the acid range and a zero slope in the alkaline range. "Humic acid" was not reduced at a dropping mercury electrode, but "hymatomelanic acid" was, at about 1.4 volts in alkali solution (1169). The reducible group in the latter complex is not aldehydic, but conjugated (ketonic); the unsaturated linkage is not in the furan ring. Mineral acids were found to hydrolyze slowly the first complex into the second.

Summary. Physically, humus exists in nature as a hydrophile colloid with water as the dispersing medium, which is itself adsorbed. The stability and properties of the colloid depend largely on the adsorbed medium and less on the electric charge; the colloidal solution is less sensitive to added electrolytes. The phenomena of base adsorption and base exchange can be explained by the fact that the humus particles are negatively charged and will, therefore, adsorb the positive ion of the added electrolyte.

Colloidal suspensions of clay will be stabilized by the colloidal soil humus. The presence of calcium or magnesium will bring about the precipitation of the colloid. The amount of water and of nutrient salts adsorbed by the colloidal humus system is of great agricultural significance, since it is in this system that the major microbiological activities take place; it is this system and not the free soil solution which is of greatest importance in the study of the availability of various nutrient elements for the growth of higher plants.

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PART C
DECOMPOSITION OF HUMUS,
ITS FUNCTIONS AND APPLICATIONS

CHAPTER XIV

DECOMPOSITION OF HUMUS IN NATURE

“L'expérience apprend que les matières végétales et animales ne peuvent servir d'engrais que lorsqu'elles commencent à fermenter.”—SENEBIER.

Humus results from the decomposition of plant, animal, and microbial residues by microorganisms. Its rate of formation and accumulation, as well as its chemical nature, depend upon the nature of the residues and upon the conditions under which decomposition is taking place; among the latter, the influences of temperature, moisture content, aeration, and reaction of medium (including supply of bases) are of primary importance. The formation of humus involves the transformation both of the more complex constituents of the plant and animal residues to simpler substances, as well as of simple elements or compounds to more complex compounds; the former includes processes of hydrolysis, oxidation, and reduction, whereas the latter consists of synthesis (microbial) and condensation (chemical). Both groups of processes run parallel, the former, in accordance with thermodynamic principles, predominating, since the energy which was stored away originally by the growing plants continues to be dissipated into space, as a result of the activities of microorganisms. Although various chemical reactions are involved in the transformation of the constituents of the original plant and animal substances, in the processes of humus formation, the evidence points definitely to the fact that microorganisms play the predominant rôle in the decomposition of the plant and animal residues and in their subsequent transformation into humus; microorganisms also decompose humus itself.

In view of the fact that most forms of humus, especially those in composts, soils, and peat bogs, are in a dynamic state, it is frequently difficult to differentiate between the formation and decomposition of humus. The distinction is purely arbitrary, since both processes take place simultaneously. They differ, however, both quantitatively and qualitatively; humus decomposes much more slowly than fresh plant and animal residues; while most microorganisms attack the latter materials, humus itself is attacked primarily by certain specific groups of

microorganisms as a result of which the rate of decomposition is greatly affected by the environmental conditions. Under natural conditions, a certain equilibrium becomes established between humus accumulation and humus decomposition (14). A change in conditions, such as removal of trees in forest and plowing under of pasture land, produces a change in this equilibrium.

Resistance of humus to decomposition. It was early recognized that humus represents a state of organic matter highly resistant to decomposition by microorganisms. As early as the first decade of the last century, Thaer (1140) stated definitely that "humus is not susceptible to putrefaction, properly so-called,—it seems rather to be the opposition of it." He emphasized, however, that it is not absolutely resistant, since "the vegetation of plants and the formation both of extractive matter and of carbonic acid, which takes place when humus is exposed to the air, at length entirely consume that substance, if it is not renewed and replaced by the addition of fresh manure."

Years later, Hoppe-Seyler (459) stated that humus "shows such extraordinary constancy that one can look upon it with right as indestructible, under conditions prevailing on the surface of and in the soil. It must be classified with the most resistant minerals. It harbors a large number of various animals, also many bacteria and other fungi and algae, but no plant or animal is capable of digesting it and using it as nutrient, and no bacterium brings about its decomposition." As contrasted to this idea of the indestructibility of humus, one finds the opposite opinion expressed by as early an investigator as de Saussure (942): "The destructibility of this vegetable earth is an undeniable fact; and those agriculturists who have endeavored to avoid the necessity of manuring their land, by bestowing repeated plowings upon it, have been convinced of this fact by painful experience. They have seen the soil become gradually more and more exhausted, and their fields rendered sterile and barren, by the absence of vegetable mould."

The claims of those who considered humus to be absolutely resistant to decomposition were frequently based upon two assumptions, which were not always applicable:

1. The rate of decomposition of humus was compared with that of fresh plant and animal substances; humus accumulates in peat bogs, in soils, and in lake and sea bottoms by reason of the resistance to decomposition of certain organic complexes which were either originally present in the plant residues or which were formed from these by decomposition or by microbial synthesis; one should not expect, there-

fore, that humus would decompose readily under the same conditions under which it had been formed and accumulated.

2. Many of the studies on the decomposition of humus have been based upon the use of "humic acid" preparations obtained from soils or from peats. Aside from the fact that these preparations consist largely of lignins, modified lignin complexes, and certain hemicelluloses, none of which is readily attacked by microorganisms, the treatment of humus by alkalies and acids frequently results in a change in the chemical nature of the complexes which tends to render them even more resistant. This effect is well illustrated by changes occurring in organic composts. During growth of the common edible mushrooms in the composts, the lignins are readily utilized; however, purified lignin complexes prepared from such composts are no longer available to the organism as sources of food.

Were the humus complexes as indestructible as suggested by Hoppe-Seyler (459), the soil would soon become covered with a layer of humus, and all the available carbon in the atmosphere and lithosphere which had not been stored away in the form of coal, oil, and forest vegetation would soon be changed into humus, either in peat bogs, in the forest floor, or in the surface layer of field soils. It is evident that this is not the case; furthermore, it is difficult even to maintain the supply of humus in cultivated soils. Humus undergoes gradual, even if slow, decomposition, as shown by the continuous stream of carbon dioxide and ammonia liberated from a given quantity of soil placed under optimum conditions of temperature and moisture. These changes are largely a result of decomposition of humus by microorganisms, as demonstrated by the fact that when the same soil is sterilized, decomposition under normal temperature conditions ceases almost completely. Some specific organisms, as *Psalliota campestris*, various higher fungi inhabiting the forest floor (280), and probably a number of actinomyces, are capable of active decomposition of humus, even that comprising the normally resistant humus constituents.

Humus represents a considerable amount of stored energy most of which sooner or later becomes available to microorganisms. Portions become changed by physical or chemical agencies into forms which are no longer subject to ready decomposition; this is the case with coal, which has been formed from peat. Since humus is not a homogeneous chemical complex, it is not decomposed *in toto* and the energy liberated at once. Just as the chemical nature of humus depends on the composition of the original materials from which it has been formed, on the

microorganisms concerned in its formation, and on the environmental conditions, the processes of decomposition of humus are also determined by a number of factors, primarily the nature of humus, climatic and soil conditions, and the nature of active microorganisms. The decomposition of humus can be hastened considerably by various treatments, as will be discussed later.

The processes involved in the decomposition of humus and the importance of these transformations in plant nutrition and plant distribution have been studied from many angles. Usually the products of decomposition have been determined as follows: 1. The carbon dioxide liberated from the organic matter has been measured either (a) as total CO_2 arising from a given volume of soil, during a certain period of time under favorable conditions (1199, 1100, 1239, 1091), or (b) as the amount of CO_2 in the atmosphere of the soil under field conditions (657, 910, 872, 232). 2. The mineralized nitrogen liberated from the soil has been measured either as ammonia or nitrate; in most soils the former does not accumulate as such but is rapidly oxidized to nitrate. 3. In addition to determinations for these products, measurements have also been made of the quantitative disappearance of humus as a whole or of some of its specific chemical constituents. 4. In some cases, the change in calorific value of the humus complex or the evolution of heat accompanying processes of humus decomposition have been measured.

Subsequent extensive decomposition of humus may reach a definite equilibrium in chemical nature, as shown by its more or less constant carbon-nitrogen ratio; this is particularly characteristic of humus in field soils. In this condition, further decomposition of humus results in a parallel liberation of carbon as carbon dioxide and of nitrogen as ammonia (rapidly changed to nitrate under field conditions), as shown in table 59. However, in the case of composts, forest soils, and peats, the ratio of CO_2 liberated to nitrate produced varies considerably, depending upon the nature of the material and the stage of its decomposition.

Various other methods can be utilized for measuring the rate of decomposition of humus; some of these are simply modifications of the aforementioned general procedures. It is sufficient to mention the following: 1. the determination of the decrease in total carbon and nitrogen; 2. the change in ratio of carbon to nitrogen in humus, this ratio either widening or narrowing, depending on the environmental conditions and on the transformation of the several constituent com-

plexes of the humus; 3. the increase in water-soluble substances; 4. the change in the ether-, alcohol-, and alkali-soluble substances; 5. the disappearance of the methoxyl groups; 6. the change in the pentosan content, in the uronic acid content, and in other specific humus constituents; 7. finally, the growth of plants as a measure of humus decomposition and of liberation of the constituent elements in available forms.

Carbon dioxide evolution as an index of decomposition of humus in soil. Ingenhousz (476) can be considered to be the first to undertake a study of the decomposition or combustion of organic matter in soil. At the end of the 18th century, he demonstrated that the factors controlling the CO₂ production in soil are the abundance of organic matter, oxygen supply, temperature, and humidity. Humboldt (467) recognized the fact that not all soils act alike in this respect. The absorp-

TABLE 59

Influence of carbon-nitrogen ratio in soil upon the decomposition of soil organic matter (1027)

CARBON	NITROGEN	C/N RATIO	CARBON LIBERATED AS CO ₂	NITROGEN LIBERATED AS NITRATE	C/N RATIO OF MINERALIZED ELEMENTS
<i>per cent</i>	<i>per cent</i>		<i>mgm.</i>	<i>p.p.m.</i>	
0.910	0.091	10.0	119.6	15.4	7.77
1.684	0.143	11.8	187.8	18.3	10.26
1.860	0.155	12.0	167.5	17.6	9.52
2.889	0.233	12.4	230.9	26.3	8.78

tion of oxygen by the carbon compounds of the soil and the formation of CO₂ were established by de Saussure (942), who stated definitely, "Le gas oxygène a enlevé du carbone au terreau." Davy emphasized the fact that this process is one of fermentation and produces an effect similar to combustion. Liebig (639), who pointed out emphatically that humus cannot serve as a direct nutrient for plants, stated that humus gives rise to a continuous stream of carbon dioxide in the soil.

Boussingault and Lewy (143) were the first to demonstrate, by exact measurements, that after a soil is moistened there is an increase in the liberation of CO₂; they also found that this increase corresponds exactly with the amount of oxygen absorbed. They measured the CO₂ content of the soil atmosphere. Corenwinder (193), on the other hand, placed a sample of soil in a receptacle, passed through it a current of air, and measured the CO₂ produced. These two methods were used

as the basis for many subsequent investigations, the latter method being more appropriate for a quantitative measurement of rates of decomposition of organic matter in soil. Pettenkofer (818) soon demonstrated that the atmosphere of the lower layers of soil is richer in CO_2 than that of the upper layers; a certain relation was also observed between the temperature and abundance of CO_2 ; he suggested that the microorganisms are largely responsible for the formation of this gas.

On comparing the decomposition of humus, as represented by peat, with that of plant and animal materials, Wollny (1301) had no difficulty in demonstrating from measurements of the evolution of CO_2 , that humus decomposes much more slowly than the others. In the soil itself, the carbon dioxide content rises and falls with the amount of organic matter present. The addition of sand to peat was shown (547) to stimulate the process of humus decomposition; temperature was found to be among the most important factors influencing decomposition.

Dehérain and Déroussy (212) placed the soil under examination in closed glass containers and kept them at different constant temperatures; at the end of a definite period of incubation, the gas was extracted and the carbon dioxide present determined. The formation of carbon dioxide was found to be due almost entirely to the action of microorganisms; it increased with temperature to about 65°C ., then decreased; at 90° , another increase took place, which was due to the chemical oxidation of the humus. A certain amount of moisture was also required for the maximum production of carbon dioxide; the state of division of the soil and its aeration were found to affect the rate of decomposition. Sterile soils produced only small amounts of carbon dioxide; when soil infusion was added, the process was increased twenty-five times. Sterilized and inoculated soil gave two to five times as much carbon dioxide as unsterilized and uninoculated soil, which points to the fact that the process of sterilization renders humus more susceptible to decomposition.

Stoklasa and Ernest (1100) placed 1-kg. portions of sieved soil in glass cylinders; a current of air was passed through the soil, at the rate of 10 liters in 24 hours. They were able to show that measurement of the evolution of carbon dioxide from a soil, under definite conditions of moisture and temperature, and within a certain length of time, can serve as a reliable and accurate index of the rate of humus decomposition and of bacterial activities in soil; the abundance and nature of the organic matter and the temperature were shown to be of the greatest

importance in controlling decomposition. Carbon dioxide is liberated most abundantly from neutral or slightly alkaline soils, well supplied with readily assimilable plant nutrients and properly aerated. The rate of evolution of the gas was not, however, proportional to the total organic matter in the soil, but rather to a certain fraction of it, which was designated as available organic matter. It was therefore suggested that this process be used as an index of the availability of humus in soil; this suggestion was ascribed (298a) quite incorrectly to Van Suchtelen (1199). The rapidity of decomposition of humus, as measured by the evolution of carbon dioxide, was found to be affected by the treatment of the soil and its depth, as shown in table 60.

TABLE 60

Influence of soil depth and soil treatment upon the decomposition of humus, as measured by the rate of CO₂ evolution (1097)

Milligrams of CO₂ produced in 24 hours from 1 kg. of soil

SOIL DEPTH	SOIL TREATMENT		
	Uncultivated, unfertilized	Cultivated, fertilized, under clover	Manured and fertilized, under beets
<i>cm.</i>			
10-20	16.5	38.6	47.5
20-30	19.4	38.8	49.7
30-50	9.8	20.2	28.5
50-80	3.3	6.3	6.6
80-100	2.1	2.7	2.3

Further studies of the process of decomposition of humus in soil (927, 928, 1199) brought out the fact that the curves for bacterial numbers, nitrate accumulation, and carbon dioxide evolution are sufficiently similar to justify the view that these are all closely related. A rise in bacterial numbers is accompanied by an increase in the carbon dioxide content of the soil air and somewhat later by a rise in the amount of nitrate in the soil. The rate of decomposition of humus in soil may, therefore, be looked upon as a function of microbiological activities. Cultivation, aeration, and presence of nutrient salts exert a stimulating effect upon these processes; however, moisture content and abundance and nature of humus are among the most important factors. A direct relation between temperature and humus decomposition was also reported in more recent studies (630); the process of decomposition goes on even at temperatures below 0°C.; it is greatly

hastened, however, by a rise in temperature. Variations in production of carbon dioxide with season of year commonly observed (478) are, therefore, due to temperature and available organic matter. In general, the amount of CO₂ evolved in 24 hours from 1 square meter of soil ranges from 2 to 20 gm., measured as carbon; the actual amount depends on the kind of soil, treatment, season of year, and other factors (468, 402).

The influence of treatment of soil upon the formation and decomposition of humus in soil is further emphasized by table 61. The soil receiving yearly additions of stable manure contained about twice as much humus as the soil receiving no manure, measured both by total carbon and nitrogen contents; however, about four times as much CO₂

TABLE 61

Influence of soil treatment upon the rate of humus decomposition, as measured by CO₂ evolution (1239)

TREATMENT OF SOIL FOR A PERIOD OF 20 YEARS	pH	ORGANIC CARBON	NITRO- GEN CONTENT	CO ₂ LIBERATION FROM 1 KG. OF SOIL		NITRATE FORMA- TION FROM 1 KG. OF SOIL
				mgm. in 2 days	mgm. in 14 days	mgm. in 14 days
Manure and minerals.....	5.5	1.73	0.146	197.2	999.0	8.86
Untreated.....	4.9	0.96	0.083	43.8	240.8	2.08
Minerals and NaNO ₃	5.8	1.17	0.099	105.2	479.2	6.62
Minerals and (NH ₄) ₂ SO ₄	4.4	1.23	0.106	77.8	418.3	2.16
Manure, minerals and lime.....	6.7	1.74	0.143	247.4	1100.1	12.07
Lime only.....	6.5	1.18	0.087	111.0	488.6	7.87
Minerals, (NH ₄) ₂ SO ₄ and lime.....	6.1	1.10	0.095	113.9	523.1	8.75

was given off from the manured as from the unmanured soil. The humus in the limed soils decomposed more rapidly than that in the corresponding unlimed soils, as shown by the evolution of carbon dioxide and by the accumulation of nitrate. The foregoing results prove conclusively: 1. that humus, as characterized by the humus type commonly found in mineral soils, can decompose readily under favorable conditions; 2. the rate of humus decomposition depends upon its chemical nature and is modified by the soil treatment; 3. this process is primarily a function of the growth of microorganisms.

Lemmermann and Wiessmann (626) calculated that the CO₂ evolution from soil under controlled experimental conditions can be expressed by the following formula:

$$x = aKt^m$$

where x is the amount of CO_2 formed in time t , a the initial CO_2 content of soil, K and m are constants. Corbet expressed the evolution of CO_2 from soil, at constant temperature, by the reaction,

$$y = Ft^m$$

where y is the total CO_2 liberated in time t , and F and m are constants; m expresses the retardation of gas evolution due to laboratory conditions and F the yield of CO_2 in a unit of time at the beginning of the experiment.

$$m = \frac{\log y_2 - \log y_1}{\log t_2 - \log t_1}$$

where y_1 and y_2 are the amounts of CO_2 given off in time t_1 and t_2 .

$$\log F = \log y - m \log t$$

Corbet (192) concluded that the amount of CO_2 liberated can be taken as a measure of the fertilizer requirement of soils. The base saturating the organic matter complex in the soil influences considerably the rate of decomposition of the organic matter (176). The evolution of CO_2 in 130 days from a control chernozem soil was 728 mg. CO_2 , from the Ca-saturated soil—524 mg., from the Fe^{++} -saturated soil—770 mg., from the H-saturated soil—1172 mg., and from a Na-saturated soil—1210 mg.

The rate of evolution of carbon dioxide from soil has a direct bearing upon plant nutrition, since it has been definitely established (657, 888, 1113) that plants are able to draw very extensively upon this CO_2 for their synthetic needs.

Ammonia and nitrate formation as an index of decomposition of humus. When plant materials of a wide carbon-nitrogen ratio are decomposed by microorganisms, very little nitrogen is commonly liberated in an available form. On the contrary, this process manifests itself by extensive CO_2 liberation with little ammonia formation. As a result of humus formation, the C:N ratio of the plant residues becomes gradually narrower, until a point is reached when ammonia is set free. This phenomenon explains many of the seemingly conflicting observations on the decomposition of plant residues and the liberation of these elements in an available form. The nature and chemical composition of the original material are of considerable importance in this connection, especially the abundance of water-soluble substances and lignins and the nature of the carbohydrates. In the decomposition of protein-rich substances, the nitrogen is rapidly liberated as ammonia and, since

the residual humus has a wider C:N ratio than protein, the rate of ammonia liberation is greater than that of CO₂ (1239, 628).

Bréal (153) observed in 1897 that ammonia is produced when soil humus is decomposed by microorganisms. Numerous subsequent observations lead to the definite conclusion that decomposition of humus in field and garden soils results in a gradual liberation of the nitrogen in an available form, first appearing as ammonia but soon being changed to nitrate in properly buffered soils. This is true of humus in which the carbon-nitrogen ratio has been narrowed to about 15:1 or less. In view of the stable relation of C to N in such soils, the amount of nitrogen liberated is also in definite proportion to that of carbon liberated as CO₂, as shown in table 59. When the humus has a wide C:N ratio, as is the case in soils shortly after receiving large applications of plant stubble or little-decomposed manure, or in the F-layer of raw-humus forest soil, there is still considerably greater liberation of the carbon as CO₂ than of the nitrogen as NH₃, with the result that the C:N ratio of the humus tends to become narrower. Humus preparations obtained from different forms of manure and from soil decompose at different rates, depending on their C:N ratios (494). When the initial ratio of the complex was 17.9:1, no nitrate was produced in a sand culture; however, when the C:N ratio of the humus preparation was 13.1:1, considerable nitrate was formed (10).

Boussingault recorded observations on a humus-rich soil in 1873, which indicated that one-half of the carbon became changed to CO₂ in a period of 11 years and one-third of the nitrogen appeared as nitrate. The Rothamsted experiments show a loss of only one-third of the nitrogen in 50 years, from soils free from crops but cultivated (926). In the case of prairie soils, a loss of one-third of the nitrogen was shown (1022) to take place in 22 years, as a result of cultivation. Only one-third of the nitrogen liberated during the decomposition was recovered in the crops. The nature of the soil is of considerable importance in determining the extent of these changes.

During the decomposition of lowmoor peats supporting an active surface vegetation, just enough nitrogen is liberated by the bacteria during the growing season to supply the plant needs. However, in the autumn more nitrogen is liberated than is consumed by the plants (873). Whether any actual loss of nitrogen takes place or whether the microorganisms attacking the plant residues and transforming them into humus use this nitrogen and change it into microbial cell substance still remains to be determined (901).

The study of the decomposition of humus in different layers of the forest soil profile effectively lends itself to a comparison of the influence of the chemical composition of humus upon the rate of its decomposition and comparative liberation of carbon and nitrogen in available forms. It has been shown (table 62) that in the case of mull soils,

TABLE 62
Decomposition of humus in some forest soil profiles (128)

NATURE OF SOIL AND SOIL LAYER	DEPTH	REACTION	TOTAL ORGANIC MATTER	TOTAL NITROGEN	NITROGEN LIBERATION FROM 1 KG. OF DRY SOIL, AFTER 6 WEEKS INCUBATION		
					NH ₂	NO ₂	Total
	cm.	pH	per cent of dry soil	per cent of organic matter	mgm. N	mgm. N	mgm. N
<i>Beech mull:</i>							
Newly fallen leaves.....	1.5	5.9	87.6	1.47	Tr.	2.2	2.2
Layer of old leaves.....	0.5	6.1	58.7	1.70	84.0	1200.0	1284.0
Worm casts.....	5.8	22.7	1.91	8.0	264.0	272.0
Upper mull soil.....	0-5	5.4	14.3	2.07	4.0	48.0	52.0
Lower mull soil.....	5-15	5.2	7.1	2.14	2.0	7.5	9.5
<i>Beech, raw humus:</i>							
Newly fallen leaves.....	2	5.9	92.1	1.45	0	3.0	3.0
Layer of old leaves.....	2	5.6	89.9	1.97	252.0	20.0	272.0
Upper raw humus.....	0-4	4.3	84.4	2.21	388.0	Tr.	388.0
Middle raw humus.....	4-7	3.7	64.1	2.08	95.0	Tr.	95.0
Lower raw humus.....	7-9	3.6	69.2	2.00	32.0	0	32.0
Leached sand.....	15	3.8	3.0	2.00	0	0	0
Soft pan.....	30	3.9	4.0	2.00	0	0	0
<i>Spruce, raw humus:</i>							
Moss and needle layer.....	4	4.3	87.5	1.91	462.0	7.5	469.5
Upper raw humus.....	0-5	3.6	86.3	1.87	115.0	0.8	115.8
Middle raw humus.....	5-8	3.5	77.8	1.69	32.0	0	32.0
Lower raw humus.....	8-10	3.5	52.7	2.16	21.0	0	21.0
Leached sand.....	20	3.6	2.0	2.00	0	0	0
Soft pan.....	30	3.7	6.1	1.83	2.0	0	2.0

the most active decomposition, as measured by nitrogen liberation, takes place in the layer of old leaves just below the freshly fallen leaves. The deeper layers decompose much more slowly. The rate of decomposition of the humus in the raw-humus profile is much slower. In the mull soil, the ammonia is rapidly changed to nitrate, whereas in the raw-humus soil, the nitrogen is left largely as ammonia.

An extensive literature has accumulated on the subject of ammonia and nitrate formation during humus decomposition in soil. This process is of considerable importance in economic plant production; it has frequently been used as an index for measuring the productivity capacity of the soil and the availability of nitrogen in organic fertilizers. The amount of humus, its chemical nature, the reaction of the soil, soil aeration, and temperature are among the most important factors that control the transformation. The amount of fixed inorganic nitrogen added to the soil in the form of artificial fertilizers is but a small portion of the total nitrogen which cultivated and uncultivated crops obtain from the soil. Much more nitrogen is usually liberated as a result of humus decomposition than is accounted for by crop consumption; some of the nitrogen is reassimilated by the microorganisms for their synthesizing activities, especially in the presence of roots and other plant residues, while some of it is lost in drainage waters and possibly some by processes of denitrification.

Changes in energy relationships of humus as a measure of its decomposition. Humus plays a leading part in the storage of energy of solar origin on the surface of the earth. The living plant transforms some of the solar energy into potential energy; a part of this is utilized by the bodies of men and animals, but the major part of the synthesized plant material is sooner or later returned to the soil, where it is decomposed; most of the energy present in these residues is liberated into space, and a part remains stored in the humus.

The energetics of humus can be used as a basis for measuring the rate of its transformation through the activities of microorganisms. Three different methods can be employed for this purpose (1200): 1. The differential method based upon the change in the combustion value of humus at the beginning and at the end of the decomposition period. 2. The indirect method, based upon the calculation of the energy liberated in the formation of products of metabolism, measured from carbon dioxide production and oxygen consumption. 3. The direct method of physical calorimetry based upon measurement of the heat produced during the process of decomposition. The production of heat in the process of humus decomposition was found to be (1200) a much more sensitive index than CO_2 evolution or changes in microbial population. When fresh soil is collected in the field and placed in an incubator, the rate of heat production is stimulated because of the increased supply of oxygen; the same is true of the rate of CO_2 evolution and development of microorganisms. After a few days the biological activity returns to a lower, more constant level (951).

Transformation of certain specific complexes in humus, as a measure of its decomposition. In view of the fact that humus is characterized by the presence of certain organic chemical substances, including nitrogenous compounds, lignins and lignin derivatives, polyuronides and pentosans, it is logical to expect that determinations of the disappearance of any one or more of these complexes, in the process of humus decomposition, would be used as a measure of the transformation of humus. Frequently only certain specific groups characteristic of some of these complexes were determined.

The decomposition of the nitrogenous constituents of humus can be followed by the reduction of total organic nitrogen or of certain products of acid hydrolysis of humus (611, 728). It thus becomes possible to determine whether the organic nitrogenous complexes decompose as a whole, or whether some of the constituent groups of the proteins in humus, such as the amides, the mono-amino or the di-amino acids, undergo preferential decomposition, under specific conditions.

The transformation of the lignin complexes in humus can be determined by measuring; 1. the residual acid lignin, 2. the formation of alkali-soluble and acid-precipitated complexes, these being equivalent to the "humic acids" or the α -humus fraction, or 3. the methoxyl content of the humus (566, 64, 765); the assumption is thereby made that the methoxyl content of lignin does not change in the process of decomposition (p. 121).

The transformation of the carbohydrates in humus as a result of its decomposition also can be followed by three different procedures: 1. by measuring the total reducing sugars produced on hydrolysis of the humus with dilute or concentrated acids; 2. by determining the pentosan content of the humus, using ordinary distillation with 12 per cent hydrochloric acid and measuring the furfural produced; 3. the analysis of the uronic acid content of the humus. These three methods enable one to obtain a fairly good insight into the nature of the carbohydrates of the humus and their transformation in the process of humus decomposition (823, 1111).

Influence of soil and environmental conditions upon humus decomposition. Among the various factors which influence the rapidity of humus decomposition, moisture, temperature, aeration, and reaction are most important (1071). Wollny (1301) was among the first to emphasize the importance of temperature and moisture upon the rapidity of humus decomposition, as measured by their influence upon the CO₂ content of the soil atmosphere. Under normal conditions, there was a marked increase in CO₂ evolution with increase in temperature up to a max-

imum of about 32°C.; above that temperature, decomposition rapidly declined (fig. 40). When the water content was diminished below the optimum, decomposition also declined.

Petersen (816) and others have further contributed toward the establishment of the fact that with an increase in soil temperature there

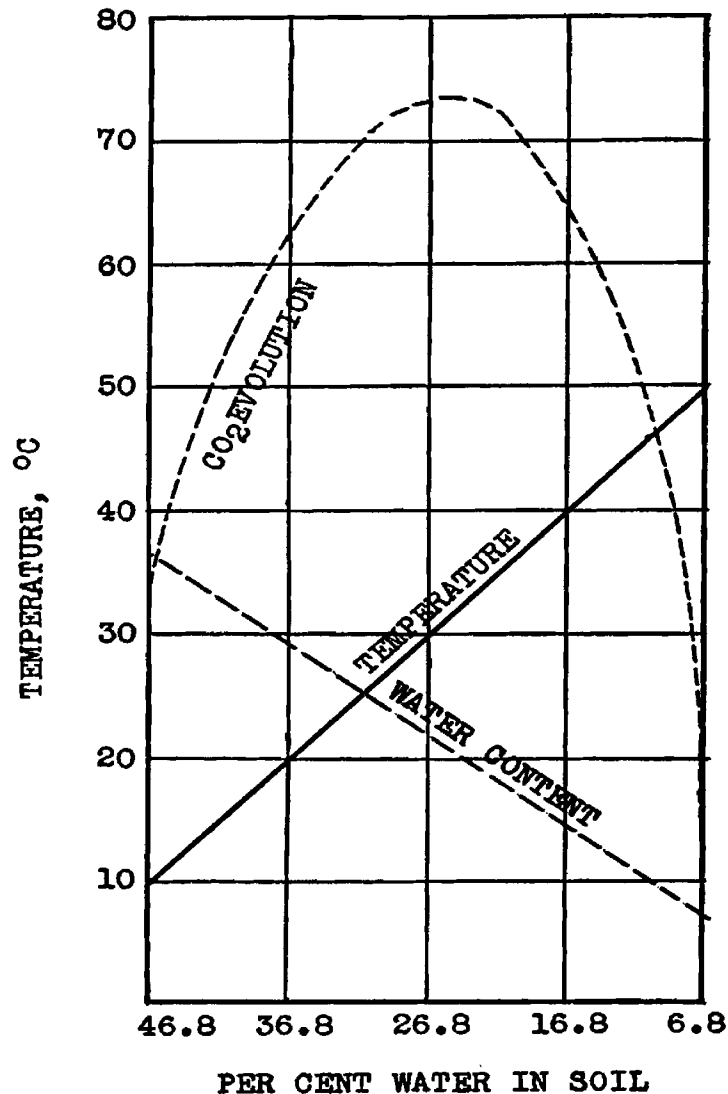


FIG. 40. Influence of temperature and moisture upon the decomposition of humus in soil, as measured by CO₂ content in soil atmosphere (Wollny).

is an increase in humus decomposition. A given amount of soil gave off the following amounts of CO₂, during 3 days, at different temperatures:

°C.	mg. of CO ₂
12.5	18.16
21.0	45.95
35.0	70.34

In the case of the organic matter in forest soils, most active decomposition of the fresh litter (birch leaves) was shown (581) to take place at 35°–37°C., whereas the humus of the soil or of those residues which had already undergone decomposition for 1 year was attacked most rapidly at 50°–60°C. The rate of decomposition of humus in peat depends to a large extent upon the moisture content, which in its turn controls the air supply and the nature and activities of microorganisms (1234). The most essential prerequisite for hastening the decomposition of humus in peat bogs is to bring about, first of all, drainage of the bogs. In the case of highmoor peats, additional treatments, such as liming or burning of the surface layer, also favor microbial activity (428). Various chemical treatments of peat also hasten its decomposition (1302, 290).

The influence of straw upon humus transformations (1001) is to be correlated particularly with the consumption of nitrogen by microorganisms; as a result of enhanced microbial development at the expense of the excess of available carbohydrates, the liberation of nitrogen is depressed. It is this factor rather than a reduction in the rate of humus decomposition that is responsible for stopping the accumulation of ammonia and nitrate, characteristic of decomposition in the absence of the straw.

Influence of lime and fertilizers upon the decomposition of humus. The influence of addition of calcium in the form of the oxide or carbonate, upon the soil, especially on the humus relationships in the soil, is threefold: 1. its effect upon the physical condition of the soil, rendering it a more favorable medium for plant nutrition; 2. its effect upon the reaction of the soil, making humus a more favorable substrate for the activities of the microorganisms and modifying the microbiological population decomposing the humus; 3. its effect upon the cation and anion balance in soil. The favorable effect of calcium in hastening the decomposition of the humus in soil is well established (38). A small amount of calcium exerts a sufficiently favorable influence upon plant growth so that the residues balance the loss of humus, whereas higher concentrations lead to losses of humus. According to Wollny (1300), Ca-humate is decomposed twice as rapidly as Ca-free humus.

Using the CO₂ content of the soil air as a measure of humus decomposition, Petersen (816) reported the following results:

Faintly acid soil	Untreated	57.2 gm. CO ₂ per 1 cubic meter
Faintly acid soil	$\frac{1}{2}$ per cent CaCO ₃	163.5 gm. CO ₂ per 1 cubic meter
Very acid soil	Untreated	55.6 gm. CO ₂ per 1 cubic meter
Very acid soil	1 per cent CaCO ₃	214.7 gm. CO ₂ per 1 cubic meter
Very acid soil	3 per cent CaCO ₃	334.3 gm. CO ₂ per 1 cubic meter

More recently König and Hasenbäumer (568) obtained the following results on the influence of CaCO₃ upon the decomposition of humus in a loam soil; in this experiment the amounts of CO₂ liberated from 4 kg. of soil in one day were recorded:

CaCO ₃ added, per cent....	0	0.04	0.10	0.20	0.40
CO ₂ per day, mg.....	181.3	223.6	308.4	416.4	455.4

Numerous other investigations (1199, 1239, 1091) pointed in the same general direction. A close correlation was found (1276) between the reaction of the soil and its respiratory and organic matter decomposing power. The addition of lime to acid soils greatly stimulated the production of CO₂, which could serve as a measure of the increase in organic matter decomposition.

It was at first believed (316, 702) that the addition of inorganic fertilizers to soil has a favorable effect upon humus decomposition. Where positive results were obtained, they were due largely to the confusion between fresh undecomposed plant residues and soil humus. More recently it has been definitely established that the decomposition of humus of only a wide carbon-nitrogen ratio is favored by the addition of inorganic fertilizers. Extreme illustrations of this phenomenon are found in the decomposition of straw and tree residues in composts and in soil, and in the decomposition of drained highmoor peats. In the case of humus in mineral soils or in lowmoor and sedimentary peats, however, the effect of nitrogen, phosphorus, or potash in hastening its decomposition is, in most cases, almost negligible. Kamerman and Klintworth (521a) have shown recently that while the carbon-nitrogen ratio of the soil humus remained almost unaffected by the addition of nitrogen fertilizer, the hydrolyzable nitrogen was markedly influenced. A definite relation was found between this form of nitrogen and nitrification. They suggested that the ratio between the total and hydrolyzable nitrogen can serve as a measure of the extent to which the soil has been affected by the addition of ammonium salts in the fertilizer.

Procedures for hastening humus decomposition. As a result of continued cultivation, without returning to the soil sufficient quantities of organic matter in the form of plant residues, stable manures, or green manures, the content of humus is reduced gradually. It has, therefore, become an established fact that, although humus may undergo but slow decomposition in peat bogs and gradually may accumulate there it does not persist for long in field and garden soils. When a soil is properly limed and well aerated, the humus is rapidly attacked and reduced in concentration. This indicates that one set of conditions, as encountered in peat bogs, favors the accumulation of humus, whereas another set of conditions, as found in normal cultivated soils, favors the slow and gradual decomposition of the humus (243).

When a virgin soil is brought under cultivation, a change takes place in its chemical properties. This is accompanied by marked changes in the chemical composition of its humus (24, 602, 806, 1120, 1293). The greatest effect is usually exerted by continuous fallowing, and a less effect, by a system involving crop rotation. Cultivation causes a reduction of the total humus content, which is accompanied by a reduction in total nitrogen. The α -fraction is destroyed more rapidly than the total humus, although the nitrogen content of this fraction remains the same (4.24–4.54 per cent), pointing to its uniformity. The pentosans are rapidly destroyed, but less rapidly than the cellulose, while the methyl pentosans are more resistant to decomposition. The decrease of hydrolyzable nitrogen is parallel to that of the total nitrogen. However, there is a certain change in the balance of the various forms of hydrolyzable nitrogen, the amide nitrogen increasing with decomposition and the mono-amino nitrogen decreasing (240).

Dehérain (210) recorded, from an analysis of the carbon content of soils, that plots left unmanured for a number of years lost over 50 per cent of their carbon. These results have been confirmed by a number of subsequent investigations (739). The reduction in humus is accompanied by a decline in soil fertility. Jenny (491) calculated that the loss of nitrogen during the first 20 years of cultivation is 25 per cent, during the second 20 years—10 per cent, and during the third 20 years—7 per cent. The gradual decline in fertility is shown in figure 41. The loss of organic matter from surface soils has frequently been found to be proportional to the extent of fallowing and cultivation (291a).

When a soil is fallowed, the total humus content is reduced compared to that of the same soil which receives stable manure or clover. This

reduction in content of humus was found to be accompanied by a considerable destruction of that part of the organic matter which can be readily oxidized by hydrogen peroxide. The ratios of carbon to nitrogen and that of nitrogen to humus are usually not affected to any marked extent by soil treatment (426). Similar observations were made in virgin soil supporting growth of cotton in Queensland;

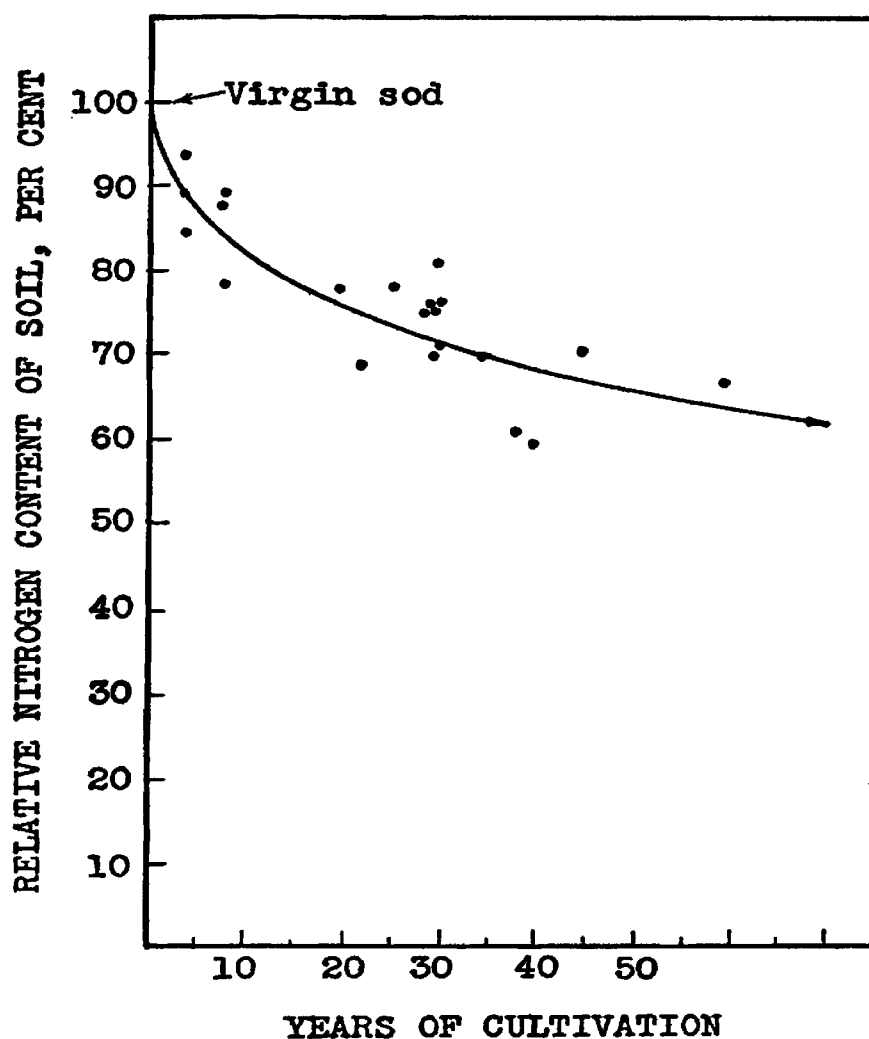


FIG. 41. Influence of cultivation period upon the decline of soil fertility under average farming practices in the Middle West. Curve showing decline in nitrogen level with years of cultivation (Jenny).

cultivation of the soil for 12 years resulted in loss of the structural organic matter, deterioration in permeability, and excessive accumulation of nitrate (1266a). These results have a very important bearing upon the susceptibility of the soils to erosion, whether by water, resulting in the formation of gullies and ravines, or by wind giving rise to dust storms. An abundance of organic matter in the soil is effective in controlling soil damage by such agencies.

When serozems are taken under cultivation, there is a very rapid loss of organic matter and nitrogen, Geltzer (346) having reported a loss of 53.3 per cent of the organic carbon (from 0.781 to 0.365 per cent) and 39.2 per cent of the organic nitrogen (from 0.097 to 0.059 per cent) in 3 years' cultivation. Together with the reduction in organic matter content there was a marked change in a number of the soil properties, including physical characteristics, moisture holding capacity, and influence of the soil on seed germination; these changes were accompanied by a decrease in biological activity. After the first period of loss, a certain equilibrium is established and further losses are less rapid.

It may become advisable to hasten the destruction of some of the humus in the soil, in order to liberate some of the nitrogen and other nutrients into forms available to higher plants. This can best be effected by increasing soil aeration through cultivation and drainage, and by adding lime and gypsum, or by applying certain special treatments, such as partial sterilization. The decrease in humus content following application of lime and gypsum may not always be accompanied by a decrease in the nitrogen content of the humus but sometimes even by an increase (1270).

Occasionally cultures of microorganisms which were believed to be active in decomposing organic residues were added to the soil, with the hope of hastening the rapidity of decomposition of the soil humus. In practically all cases, the expectations have failed to materialize; none of the various bacterial preparations, ranging from Caron's "alinit" to the more recent "soil-grow," "soil-life," etc., were effective in stimulating decomposition of soil humus or in favoring plant growth. The only exception to this general rule is inoculation of freshly drained peat bogs, provided through the addition of manure or composts (1198, 1058).

On the other hand, attempts have been made to develop "humus" preparations for improving the fertility of the soil or for increasing crop yields; these have invariably given results inadequate to justify their extensive use in agricultural practice. Most of these preparations have been derived from peat or from brown coal by treatment with an alkali (218), as shown later (p. 367).

Summary. Although "humic acids" and "humin" preparations obtained from peat or from soil humus have been found to be resistant to decomposition, claims made in the literature that soil humus is equally resistant to decomposition are not justified. In the process of preparation of various "humus" fractions, their chemical nature

has been so changed as to make them particularly resistant to microbial attack.

After plant residues, stable manure, or composts are added to the soil, they undergo rapid decomposition, as measured by the evolution of CO_2 and the disappearance of various organic constituents; however, the amount of nitrogen liberated in available forms depends largely upon the carbon-nitrogen ratio of the material. When large amounts of organic matter with a ratio wider than 20:1 are used, the soil is not in a condition to support active plant growth; nitrogen starvation will be observed as long as there is an excess of carbohydrates, since the microorganisms using these as sources of energy assimilate all the available nitrogen that would otherwise become available to the higher plants. When the organic matter has a narrow C:N ratio (<15:1), there is no tendency to restrict the supply of available nitrogen in the soil. Soil humus, which has a more or less constant low carbon-nitrogen ratio, supports a relatively low level of microbial activity, due to the resistance of the humus to rapid decomposition; decomposition of the soil humus is accompanied by the formation of ammonia, which is gradually transformed into nitrates.

The rate of decomposition and the amount of nitrogen liberated in an available form in a soil depend on the amount and kind of humus present in the soil or added to it, on the nature of the soil, and on the environmental conditions. The addition of fresh organic matter with a narrow C:N ratio, of about 15:1 to 10:1, stimulates the activities of the microorganisms and results in the liberation of a more abundant supply of CO_2 ; these changes are accompanied by a parallel liberation of the nitrogen as ammonia.

CHAPTER XV

PRESENCE IN HUMUS OF SPECIFIC SUBSTANCES WHICH HAVE AN INJURIOUS OR A BENEFICIAL EFFECT UPON GROWTH OF PLANTS, ANIMALS, AND MICROORGANISMS

“The death and decay of animal substances tend to resolve organized forms into chemical constituents. The fermentation and putrefication of organized substances in the free atmosphere are noxious processes; beneath the surface of the ground they are salutary operations. In this case the food of plants is prepared where it can be used.”—SIR HUMPHREY DAVY.

In addition to the rôle played by humus in soil processes and in plant nutrition, both as a source of mineral nutrients and by improving the physical condition of the soil, there are other influences upon plant growth, less closely defined and understood. Numerous observations have revealed the fact that humus contains substances, which are either injurious or favorable to the growth of higher plants. The exact chemical nature of these substances and the specificity of their action are still imperfectly understood, in the majority of cases. Some of them seem to be synthesized by microorganisms living in the soil, whereas others are liberated during the decomposition of plant residues or are formed as transformation products of these residues. It has been shown, for example, that many fungi living in the soil are able to excrete products which are distinctly injurious to plants, while other fungi may produce substances which have a direct stimulating effect upon plant growth. The soil absorbs all or some of these substances, which thus become a part of the humus complex. Humus thus influences in various ways the absorption of these specific substances by plant roots and modifies their effect upon plant development (672).

Organic compounds in soil injurious to plant growth. Poor development of higher plants in soil may occur as a result of unfavorable physical, chemical, and biological conditions, brought about through imperfect drainage and poor structure of soil, unfavorable reaction and excess of salt concentration, and presence of plant pathogenic bacteria and fungi. Furthermore, substances of an organic nature, which are directly injurious to plant growth, may be present in the soil. It has been suggested (167) that the favorable effect of artificial fertilizers upon plant nutrition is due largely to their neutralization of the in-

jurious influences of these substances. Schreiner and his associates succeeded in isolating from humus (p. 129) a series of organic compounds, such as vanillin, benzoic acid, various aldehydes, and dihydroxystearic acid, which, in culture solutions, proved to be injurious to plants, even in very low concentrations. These compounds exerted quite different effects upon growth of plants in soils: injury was apparent only at much greater concentrations of the specific compound; there was also a tendency for the latter to become decomposed by the numerous bacteria and fungi inhabiting the soil. It is now generally assumed that organic compounds which are capable of causing injury to plants are not present in abundance in the humus in a free state, but that they exist in combination with, or as a part of, other complexes, and are liberated only in the process of their chemical preparation; it is also believed that these complexes are constantly being formed and decomposed in the soil.

Of special interest in this connection is a substance, gliedine, produced during the decomposition of peat, which causes a specific disease of cereal plants, such as oats (466, 1050), and is capable of preventing the development of many other plants. This substance is soluble in alcohol and is carried over when the solvent is distilled; it is precipitated by copper. Even small amounts of it are capable of causing a highly toxic effect upon plant growth; this effect is also exerted upon sugar cane and other plants which cannot be grown upon the saw grass peat in Florida without the application of copper. Kwiecinski (600) suggested that the injurious effect of peaty material in soil upon oats is due to picoline and to xanthine. The addition of CuSO_4 results in a change in the colloidal dispersion of the humus and leads to more rapid liberation of the nitrogen. The toxic effect of water from high-moor peats, frequently observed (722a), may be due to the high content of ferrous and manganous compounds, soluble in water, and reported to be present in swamps (906a). Other "soil diseases" can be cured by manganese salts and town refuse (466).

In addition to the organic complexes found in certain drained peat soils, a number of other substances capable of producing a direct injurious effect upon plant growth are frequently encountered in certain soils. It is sufficient to mention the complex which produces mottle-leaf of citrus trees in California (154). Various other diseases, somewhat related to this one, also seem to be associated with certain organic compounds which are either synthesized under specific soil conditions by a number of bacteria or are formed by microorganisms during the

decomposition of some of the plant residues. The fact that chlorosis in corn plants which responded to the application of zinc sulfate could also be corrected by stable manure and leaf mold (68a) pointed to the presence in these forms of substances capable of correcting certain soil deficiencies.

In a study of the injurious influence of straw upon plant growth, Collison and Conn (183) came to the conclusion that two factors contribute to the inhibitive effects: 1. the influence of the energy yielding constituents in the straw which enable the soil microorganisms to reduce the supply of available nitrogen in the soil; 2. the presence in the straw of toxic substances which are directly injurious to plants. The fact, however, that this effect can be overcome by the addition of nitrogenous fertilizers, and that straw has no injurious effect upon the growth of leguminous plants (818a) tends to refute this theory. It has even been shown that the injurious effect of brown coal upon crops can be overcome by the addition of enough available nitrogen to reduce the ratio of carbon to nitrogen in the coal to 20:1 (944a).

The lack of mycorrhiza formation upon certain soils was shown (867a) to be due to unfavorable soil conditions brought about by the presence of inhibitory substances; this condition can be corrected by the addition of organic composts to the seed beds.

In the case of a number of plant diseases, commonly described under the heading of "soil sickness," especially those of cereal crops, the causes have been traced in many instances either to excess alkalinity or to excess acidity of soil. Sölmgen (1063) recorded that the phenomenon of "soil sickness" is usually associated with relatively high amounts of free "humic acid" in the soil; various salts modify their concentration in the soil and, for that reason, influence plant development favorably or unfavorably. However, "humic acid" preparations isolated from peat were shown to have practically no injurious effect upon plant growth, causing even less injury than citric acid (57). The variation in the chemical composition of plants grown on different soils and the poor palatability of forage from "sick" soils, which frequently have a high concentration of organic matter, was explained (1213a) by the direct assimilation by the plants of various organic substances from the soil.

Another group of substances, namely, the so-called bacterio-toxins, or substances which exert an injurious effect upon bacterial growth, has also been detected in the soil. Their nature and importance in controlling soil processes is still to be determined (364, 473); it has

been suggested (217a) that the phenomenon of "soil fatigue," frequently observed in old alfalfa fields is due to the production in the nodules of a specific bacteriophage, which diffuses into the soil rendering it an unsuitable medium for the growth of the legume; this condition persists until the bacteriophage has disappeared.

One may thus conclude that comparatively little is known concerning the formation or liberation in soil of organic complexes, through the direct or indirect activities of microorganisms, which modify the growth of higher plants in general or of certain plants in particular. The limited information thus far made available seems to point to some very important problems which still await solution.

Organic complexes in humus favorable to plant growth. At various periods, important specific functions have been ascribed to humus, as a result of its favorable action upon plant growth. On further study, the value of these functions was frequently found to be overestimated; however, in some cases the claims have been substantiated. With the development of our knowledge of vitamins and their function in animal nutrition, searches for vitamins in humus of soil and in composts, and attempts to establish their possible rôle in plant nutrition have been made. As a result of these studies, a number of new names were introduced for hypothetical substances said to have a highly favorable effect upon plant growth. It was found that animal manure added to soil exerted a favorable effect which could not be explained either by the introduction of nutrient elements or by improvement in the physical condition of the soil. This action was believed to be due to certain colloidal substances present in the manure.

Bottomley (135) has shown that treatment of peat with certain aerobic microorganisms favors the production of soluble "humates." This "bacterized peat" was found to possess, after sterilization, "growth stimulating" properties, which could not be accounted for by known plant nutrients. The growth of plants was stimulated by this material both in soil and in solution cultures. The treated peat was believed to contain specific organic substances (auximones) which were considered to be responsible for the stimulating effect; the action of these substances was looked upon as similar to that of vitamins. Mockeridge (714, 716) found that auximones favor the processes of nitrogen-fixation and nitrification; the growth-promoting influence of extracts of stable manures and leaf-mold was proportional to the degree of their decomposition; it was suggested that the substances are manufactured by various bacteria and fungi, but not by green plants. The transformation

of the nucleic acids to di-nucleotides, to purine, and to pyridine bases was believed to be responsible for this phenomenon. The phosphatides produced by germinating seeds of spruce and pine were found (695) to stimulate the development of mycorrhiza fungi.

Hilletzer (444) demonstrated that certain humus substances exert a specific effect upon plant development by increasing their root system. He agreed with the designation of the specific substance as "auximone." The plant-stimulating substances found in organic composts were characterized as being water-soluble, fairly stable in aqueous solutions, and active even in small concentrations (483a).

Bottomley's theory was not accepted by most of the subsequent investigators (701, 180, 1297). Clark and Rollen (180) stated that they could not confirm the aforementioned claims; the possibility was not eliminated that the action of these organic complexes may be similar to that of "bios" on yeast. Wolfe (1297) considered "auximones" as purely hypothetical complexes and totally unnecessary for normal growth of the plants. However, Ashby (56) demonstrated that, although organic matter was not essential for the normal growth of Lemna, it had a marked influence upon the rate of growth; this effect was shown (179) to be indirect, due to its influence upon the development of microorganisms in the nutrient medium. Olsen (790) suggested that wherever a favorable effect of organic matter upon plant growth was observed, it was due to the increase in the amount of iron available to the plants.

More recently a renewed interest became apparent in the specific action of organic composts, and of humus preparations in general, upon plant development. In some cases, definite claims have been made concerning the relation of this action to the presence and abundance of vitamin-like substances in humus. Nath (744) suggested that microorganisms act upon the organic matter of the soil and liberate certain active complexes which are absorbed by the plant roots; this results in the formation by the plant of substances which would not be produced otherwise. Seed from a crop grown in a soil which received farmyard manure was claimed (745) to be superior to seed obtained from a similar crop grown in a soil receiving no treatment or only mineral fertilizer. The seed produced from plants grown in the manure-treated soil had the best cropping value and was the most nutritious. This seed gave a higher germination and a thicker and better stand than seed from an unmanured plot or from a plot treated with inorganic fertilizers. It is further of interest to note that decom-

Even those investigators that denied the presence of any plant stimulating substance in soil organic matter had to admit (179) that, although green plants grow, remain healthy, and reproduce without any organic matter or bacteria, still certain types of organic substances, especially in the presence of bacteria, may markedly affect the constitution of the plant. The rôle of microorganisms present in animal manures and in composts in synthesizing the accessory substances for the plant was thus again emphasized. This hypothetical plant growth promoting substance, which was believed to occur in humus and in organic manures, was designated as "phytamin" (41); it was further suggested that the microorganisms in the manures synthesize these substances, the plant being presumably unable to produce them. The favorable effects of leguminous plants upon non-legumes may be at least partly due to the phytamins synthesized by the former (764). A number of other specific effects which are exerted by the soil upon plant growth are associated with the influences of certain organic substances which are produced in the soil through biological processes (277a). The nature of root excretions (7) and of their effect on plant development is also still undetermined. ✓

The presence in peat, in coal and in oil of substances which exert a hormone-like effect upon plants was believed (54) to be responsible for the stimulating action upon plant development frequently reported for coal. The possible relation of the plant growth promoting substances to hormones excreted by the animals has been further suggested in a number of recent investigations. The growth regulating factors, which are designated in the case of men and animals as "hormones" and "vitamins," have their counterparts in plants and are known as "auxins" or "phyto-hormones." Auxin-a, $C_{18}H_{32}O_5$, contains one carboxyl group, three alcoholic hydroxyls, one double bond, and one carbon ring; auxin-b is $C_{18}H_{30}O_4$; hetero-auxin is β -indolyl acetic acid, and originates by bacterial decomposition of tryptophane and was first found in urine. In the case of an abnormal intestinal flora, large quantities of this compound may be found in the urine (558). It has been definitely established that these specific hormones influence plant growth in a number of ways. Female sex hormones were shown (959) to stimulate the growth of hyacinths and tomatoes. Another hormone said to initiate root development has been described under the name "rhizocaline" (1267, 1154). The formation of similar plant growth regulating hormones by microorganisms has also been definitely established (145). The "bios" question or formation of microbial stimu-

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lants is closely related to that of specific hormones or vitamins. Bios I, identified as meso-inosite, was described by Kögl (558), and bios II, equivalent to the "penthatenic acid," was designated as "biotin." The growth promoting substance of *Phycomyces*, identified as B1, is distinct from bios (960a). The formation and accumulation of growth-promoting substances and hormones in humus and their importance in plant nutrition may still be considered as subjects for speculation (671a). As a result of these studies (41), a relationship was believed to exist between phytamins, vitamins, and hormones, circulating from the soil to the plant and animal, and back to the soil.

The preparation of composts from plant residues and from peat, leading to an enrichment in the plant-stimulating substances or "auximones" (917) has received considerable attention, with anticipation of their use in practical agriculture. These preparations were usually designated as "humogen" and "bacterized peat" (1214). In most cases, peat was inoculated with certain bacteria belonging to the group of the so-called "decay" organisms, and the compost was allowed to remain for 7 to 10 days, under favorable moisture and temperature conditions. The peat was then sterilized with steam, allowed to cool, and subsequently inoculated with cultures of *Azotobacter* and *Bact. radicicola*. After several days' incubation, the compost was ready for use. Claims were put forth that by this process the nitrogen content of the peat was increased from 1.26 to 4 per cent, and that this "bacterized" peat favors extensive root development (177). Numerous humus preparations have also been made from brown coal. It was also claimed (641) that these preparations have a favorable effect upon plant growth; it was believed that the humus affected the permeability of the plasma membrane of the plant cells, favoring the absorption of nutrients. It has been shown (p. 367), however, that most of these assumptions were not justified. To what extent humus serves as an agent for the absorption of various injurious substances in the soil, as well as for the catalysis of certain important transformations in the soil, such as fixation of nitrogen (878), still awaits further study.

In addition to the aforementioned participation of humus in various processes of plant nutrition, there are other important influences which humus exerts upon plant growth in soils and in solution cultures, as well as in lakes, in rivers, and in seas. Of these, its rôle in keeping iron in solution is of great significance. At neutral or slightly alkaline reactions, inorganic iron is precipitated as hydrate or phosphate and becomes quite unavailable to plants growing in culture solutions or in

sandy soils, poor in humus. Certain plants may, therefore, become chlorotic under such conditions. Humus can form compounds with iron which render this element available to plants at even neutral and somewhat alkaline reactions. This is also true of the effect of humus upon the availability of iron for the growth of microorganisms, as the nitrogen-fixing *Azotobacter* (163).

The high productive capacity of seas in coastal regions, as compared with waters well removed from the influence of terrestrial waters, has been ascribed to the iron contained in forms available to plants in the humus complexes removed from land by drainage waters (360). It was suggested that the organic iron compounds are consumed by the algae and, when these die and decompose, they are precipitated as inorganic ferri-compounds.

Whether humus plays a similar function in the assimilation of manganese, zinc, and other rare metals still remains to be determined.

Curative effects of organic complexes in humus upon animals and man. Various peat formations and limans high in organic complexes are utilized for balneological purposes. A number of theories have been proposed to explain the specific curative effects. Winckel (1291) found that peat and peat extracts possess strong catalytic properties, which are comparable with the catalase found in certain mineral waters (936). Kobert and Triller (556) claimed that the curative effects are due to the astringent properties exerted by some of the peat constituents on the red blood corpuscles. The question has often been raised as to what extent the tannin content of the peat can be used as a measure of the specific effects, which were believed to be due largely to the organic complexes. The therapeutic effect has also been ascribed to the presence of iron, titanium, and other minerals, as well as to the absorbing properties of the peat, as measured by the absorption of methylene blue and salts (943); this was comparable to the action of pure medicinal coal (1070). The thermal properties of peat, which are characterized (1070) by a high heat capacity, low heat conductivity, very low heat connection, and strong heat radiation, were also believed to contribute to the curative action upon certain disease conditions.

Artificial curative muds have been prepared by allowing a mixture of clay, fresh organic matter in a green state, minerals, namely sulfates and chlorides, undergo decomposition under water (922a).

Effect of organic compounds in humus upon the growth of injurious microorganisms. Organic residues in soil and their decomposition products also contain substances which have specific effects upon the nu-

merous fungi and bacteria which are pathogenic upon plants and animals and which are able to lead a saprophytic existence in the soil. The effect upon the pathogens may be favorable, as shown by the extensive development of plant disease producing organisms in humus-rich greenhouse soils; it may also be injurious. The specific nature of the destructive effect has not been established as yet; in some cases, it seems to be due to a phenomenon which is of the nature of a bacteriophage or bacteriolytic substance; in other instances, it prevents the development of the pathogenic microorganisms or in other ways modifies their growth. It was found, for example, that extracts of natural humus added to cultures of *Pythium* favor oospore production, which does not take place otherwise; synthetic humus had no such effect (860). To this group of phenomena belong the observations (1263) concerning the production by *Trichoderma lignorum* of a substance which has a destructive effect upon the plant parasite *Rhizoctonia solani*. The antagonistic action of various soil organisms upon others is treated in detail elsewhere (1225). The beneficial effect of green manuring in controlling potato scab has been ascribed (708a) to the competitive action between the soil saprophytes and the pathogens. The control of other plant (cereals) diseases in soil by the use of stable or green manures may be due to similar causes.

CHAPTER XVI

UTILIZATION OF VARIOUS FORMS OF HUMUS FOR AGRICULTURAL AND INDUSTRIAL PURPOSES

“Der Grund der Nützlichkeit, der nach Zwecken fragt, der offene Feind der Wissenschaft ist, die nach Gründen fragt.”—LIEBIG.

Humus, with its immense stores of carbon and nitrogen in organic combinations, may be considered to represent one of the most important sources of available energy in nature. Untold generations of plants, ranging from the smallest algae to the largest sequoias, accumulated these extensive deposits of potential energy during millions of years. Part of this energy has been liberated by animals feeding upon the plants, and part by microorganisms, through their processes of decomposition; still another part has accumulated as potential energy, in the soil humus, in peat, in coal, and in oil. In addition to the practically inexhaustible sources of energy, humus in its various forms represents tremendous accumulations of both carbon and nitrogen. Carbon is essential for both animal and plant life and the atmospheric supply is very limited; the nitrogen in humus comprises most of the fixed nitrogen present on this planet.

Humus has been utilized by man for thousands of years for various purposes, largely agricultural, and more recently as a source of fuel. Its utilization in agricultural economy and industry has reached the maximum in recent years. The availability of an abundance of humus has led to wastefulness; continuous cultivation of soils without provision for adequate return of organic matter has resulted in rapid disappearance of the humus. However, just as man has come to recognize the necessity of conserving the forest and land resources, he will soon be forced to adopt stricter policies of conservation of humus in the soil. When the supply of free land, to which many fled leaving exhausted soils behind, came to an end, most countries were forced to adopt a policy of strict land conservation. Although the resources of peat, coal, and oil still seem to be unlimited, they will soon disappear at the present rate of exploitation, and a policy of conservation will be required, unless in the meanwhile new sources of energy are discovered.

Agricultural utilization of humus. By far the most important utili-

zation of humus in the world today is found in agriculture. It plays an important rôle in mineral soils, such as fields, gardens, orchards, and pastures, and in soils with a special humus horizon, such as forest soils and heath soils, as well as in soils predominantly organic in nature, such as drained peats. Humus serves three particularly important purposes in the soil: 1. it creates a more favorable physical medium for plant growth; 2. it retards the removal of important plant nutrients, especially from mineral soils; 3. it supplies to the plants a continuous stream of the necessary nutrients during its decomposition by microbial agencies. Among the recent investigators who have emphasized the importance to plant growth of the carbon dioxide liberated in the decomposition of soil organic matter, may be mentioned Lundegårdh (657), Reinau (872), and others. Lemmermann (621) found that more carbon dioxide may come from the soil than the plants require.

In an effective system of soil economy there are practices through which an attempt is made to compensate for the losses of humus through decomposition, by the addition of various organic materials. Neither loss nor accumulation should predominate except in special cases. When the supply of humus becomes depleted, impoverishment of the soil results; when the supply of humus increases too rapidly, as in certain raw humus forest soils, the rate of growth of the trees may be considerably reduced. In order to uphold or improve the fertility of the soil, the mere introduction into the soil of available nitrogen, phosphorus, and potassium does not suffice; organic matter has to be added in the form of stable manures, composts, and green manures (663a).

Problems of humus formation and humus conservation are involved in the agricultural utilization of stable manures and other farm residues, of sewage disposal products, and of other waste materials of plant and animal origin, whether they are used directly or after preliminary composting. Knowledge of the chemical composition of these residues and waste materials, of the changes taking place during the processes of their decomposition, and of the nature of the humus product, aids in the preparation of useful substances, with the least loss and the most effective conservation of the valuable elements essential for plant nutrition.

The preparation of special composts for the growth of the cultivated mushroom represents a special case of humus utilization. The medium is prepared by a process of composting under conditions of favorable temperature, moisture, and aeration. Either horse manure, consisting

of the animal droppings and the stable bedding, or plant residues to which certain nutrients in the form of inorganic salts are added, can be used for the preparation of the compost. The compost must contain the nutrients essential for growth of the mushroom and it must not favor active development of the common bacteria and fungi, which would compete with the mushroom for the constituents of the compost or otherwise create an unfavorable medium for the mushroom. With the replacement of horses by machines, the need for artificial composts as substitutes for manure becomes greater. When horse manure was commonly used and the growth of the mushrooms was more of an art than a science, one could obtain good yields with little actual knowledge of the processes involved, either in the composting or in the nutrition of the mushroom. But even with the use of stable manure, it became established that where a certain amount of available nitrogen was added to a manure which was particularly free from urine, or where straw was added to a manure high in excreta, yields would be so affected that a profitable crop could be obtained, whereas there would have been poor development in the absence of treatment. With the introduction of composts prepared exclusively from plant residues, it becomes essential to know the chemical composition of the plant material and the rapidity and extent of its decomposition, since materials of different composition require different treatments and periods of composting (p. 191).

The effective use of peat soils in agriculture also requires the application of knowledge of the chemical nature of the peat and of the processes associated with its decomposition. Lowmoor peats and sedimentary peats should be treated entirely differently from highmoor peats. The requirements of specific crops must be considered, of course. For the growth of certain crops, for example, if the soil is more acid than pH 4.5, the addition of lime is essential; if it is more alkaline than pH 7.0, the use of sulfur is frequently recommended (393). The addition of CuSO_4 to many peat types has favored the crop growth, for reasons already discussed. In some cases the surface layer of the bog is burned in order to increase fertility, especially when the surface is covered with undecomposed sphagnum. This practice is usually recommended only when mineral fertilizers and lime are too expensive to be applied to the drained bog.

There are numerous other applications of humus to processes connected directly or indirectly with agriculture, some of which will be cited later. It may be recalled in passing, that fresh composts of animal

manure or plant residues have been commonly used in hotbeds, the heat generated during the processes of decomposition being sufficient to keep the temperature of the beds at a point favorable for plant development.

In view of the resistance of humus to rapid decomposition by microorganisms, numerous attempts have been made to hasten its decomposition. Liming of acid soils and cultivation are probably the most economic and most widely used methods for effecting this change. All attempts to inoculate the soil either with specific cultures of bacteria, fungi, or actinomyces, or with special extracts of beetle larvae, of manure, or soil have thus far failed to advance the decomposition process. Partial sterilization of soil, which is usually brought about by heating or by treatment with volatile antiseptics, accelerates the decomposition of humus complexes in soil. However, the primary object of such treatment is to destroy plant parasites living in the soil and not to hasten humus decomposition.

Humus as a fuel. While humus in soil and in composts and to a considerable extent that in peat is utilized principally for agricultural purposes, the humus in coal and some of the peat humus are employed for industrial uses. The carbon content of plant residues increases during decomposition, as a result of the destruction of the cellulose and other carbohydrates, which are low in carbon, and of the accumulation of lignin and protein, which are high in carbon. The increase in carbon concentration continued even when the microbiological processes were superseded by purely chemical changes, as when the ancient peat bogs became covered by heavy layers of silt and sand, and were subjected to high pressure and temperatures. As one proceeds from peat to brown coal, then to bituminous coal, and finally to anthracite, whether or not these coals have been formed *in situ* (autochthonous) or from residues brought in by wind and water (allochthonous), one finds an increase in carbon content and in calorific value, as shown in table 52. The higher the carbon content and the lower the oxygen content of the material, the greater is the heat of combustion. The humus types which have accumulated as coal and peat during untold generations thus represent excellent sources of fuel. They have been used extensively for this purpose during recent years and they will be used for many years to come as the most important sources of fuel, either directly, or after their conversion to coke and gas and all their accompanying by-products.

This is not the place to consider the abundance and distribution

of peat and coal deposits in the world, their heat values, and the numerous problems connected with their utilization; these are discussed in detail in numerous special treatises already referred to (p. 282). It suffices to mention here that coal and peat are the most important sources of fuel in the world today, and probably exceed both wood and petroleum in the amount of total available energy. Peat has been used extensively previous to the development of the coal resources and is still used as a source of fuel in Russia, Ireland, and elsewhere. Brown coal, or lignite, and bituminous coal exceed both peat and anthracite coal in abundance and distribution; anthracite and bituminous coals are the most valuable forms of coal. The total world reserves of coal are estimated at about 7,500,000,000,000 metric tons, and the world annual production is about 1,350,000,000 tons.

In addition to serving as direct sources of fuel, peat and various types of coal are used for providing electric power, gas, and coke and for producing a number of derivatives, such as coal tar, pitch, paraffin hydrocarbons, benzol, toluol, dyes, various medicines, ammonium sulfate, and montan wax.

Use of humus in technique and industry. Because of the specific colloidal properties of humus, certain types are particularly valuable in some industries. It may be sufficient to mention their use in storage batteries and in ceramics. In the preparation of batteries, use is made of the "humic acid" fraction of humus, or that part of the humus which is soluble in alkalis and is precipitated by acids. Humus for this purpose is obtained from coal, peat, and composts, as well as by boiling a sugar solution with acids or by the oxidation of phenols (1102). The addition of such preparations to the battery plates lengthens the period of their serviceability, by preventing the particles of spongy lead from cohering and becoming inactive.

In the preparation of the negative plates of the lead acid type of storage batteries, the alkali-soluble portion of the humus is precipitated by sulfuric acid and the precipitate is added to the lead paste, so as to have about 0.5 per cent of the humus fraction in the lead oxide. The humus fraction may also be incorporated or deposited in the pores of the lead-oxide pan, before or after it is applied to the grid, or in the pores of the material on the plate itself, before or after it has been charged. Only a certain specific constituent of humus, or even of the "humic acid" fraction, is active, and, since the amount of this constituent varies in different humus preparations, it is natural that different types of humus should give different results. In several patents, an

attempt has been made to cover all humus preparations that have ever been described as well as the various "humic acids."

Since humus preparations make kaolin more fluid and plastic, they have been used in ceramics, especially in clay casting. In an aqueous medium, humus spreads over the surface of the kaolin and causes a greater dispersion of the particles, which protects them against the precipitating action of cations. In alkali solutions, humus forms alkali humates, which, like a soap, reduce the surface tension at the interface between the liquid and the kaolin; the humate is adsorbed and forms, as an emulsoid, a protective coating over the particles. The kaolin suspension is thus transformed into a pseudo-emulsion which acts as a true emulsion; such preparations can be used with a high concentration of particles and these are much less sensitive to the precipitating action of electrolytes than is untreated kaolin. The concentrated pseudo-emulsion of clay particles is the ceramic casting mass. The dispersion of the particles and the stabilization of the dispersed condition by the humus, which are hastened by the action of hydroxyl-ions, are responsible for the fact that the constituents of the mass possess increased mobility; the mass is thus transformed, at the time of casting, into a material of lower liquid content (1072). Tannin and extracts of straw also increase the fluidity of clay and diminish the amount of water needed to produce a mass sufficiently plastic for molding (9).

Various forms of humus, notably a type of coal designated as Cassel brown, have found application in the preparation of certain dyes (717).

Composts of manure are also used in industry to produce a continuous source of heat or of carbon dioxide, or both. This can be illustrated by the process of manufacture of lead carbonate by the "Dutch Process." Lead buckles are placed in earthen pots partially filled with a dilute solution (2 per cent) of acetic acid. The pots are covered and placed in trays in a pit, then covered with tanbark and built up in alternate tiers to a height of 80-100 feet. The process lasts for 100 to 120 days. The temperature gradually rises to 70°C., then drops to 55°C. The acetic acid is volatilized, forming lead acetate, while the CO₂ produced during the decomposition changes the lead acetate to lead carbonate. The moisture content of tanbark is about 50-55 per cent. If the materials are too wet the process results in the production of butyric acid. The process is carried out largely by thermophilic bacteria (365). The heat and carbon dioxide given off from the compost gradually transform the lead into lead bicarbonate. Another illustration is found in the protecting action of organic matter against freezing

of accumulated water in valves of oil tanks during the winter; quantities of manure or compost are placed around the pipes, to act both as insulating material and to supply sufficient heat to prevent freezing. These are but a few illustrations of the applications of humus and of the practical use of microorganisms as agents of decomposition of plant residues (see also 1246).

Humus as a fertilizer. Various attempts have been made to use humus, directly or after treatment with certain chemical reagents or subsequent to the addition of bacterial cultures (177), for fertilizer purposes and for soil improvement (400). The primary purpose of the chemical or biological treatments of the humus was either to render it more readily decomposable, accelerating the rate of liberation of its carbon as CO_2 and its nitrogen as ammonia (833), or to enrich it in certain so-called plant-stimulating substances, called "auximones" (p. 354), which are assumed to be similar to animal vitamins. In most cases these attempts have proved unsuccessful.

Among the numerous preparations which have been introduced at different times, are substances which have been labelled with the following names:

Alfano humus	Huminal
Bacterized peat	Biomoor
Humus-silicic acid	Biohumus
Humus carbolineum	Sperkit
Humogen	Granol
Humusom	Delassol
Humuform	Nettolin
Humunit	Phosphohumus

Most of these were preparations of peat, of plant composts, or of brown coal, altered by certain physical (heating, freezing) or chemical reagents (acids, alkalies); in many cases, the substances were supplemented with fertilizer nutrients or disinfecting agents. Nettolin, for example, was shown (704) to consist of 60 per cent humus, 30 per cent lime, 3 per cent soluble nitrogen, 2 per cent soluble P_2O_5 , 4 per cent potash, and some wood-tar as disinfectant. The preparation of such materials was based upon recognition of the importance of humus in soil processes (811). Numerous patents have been granted to cover the modification of peat by chemical or physical treatment which presumably make its constituent elements more readily available for plant growth; other patents are concerned with the addition to peat of inorganic salts which increase its immediate fertilizing value. No at-

tention whatsoever was paid in these patents to the botanical or chemical composition of the peat or to the degree of its decomposition. In some cases, the treatment was so vigorous as to change considerably its chemical and biological properties.

At best, these preparations have only limited application, and most of them have proved to be practically worthless. The use of some can be recommended, but only after very careful testing (1126). The favorable effects which have been observed occasionally, have been shown to be due to the mineral constituents of the preparation (330), to its amphoteric properties, or to the absorption of complexes which are injurious to plant growth (641).

Recently, considerable attention has been paid to the absorption of ammonia by peat (830a). Several procedures have been used to effect the absorption, one of which is outlined here (236, 237): lowmoor or transition peat was treated with dilute acid (2 per cent HCl, H₃PO₄, etc.) and then with water; the washed peat was dried until it contained from 22 to 50 per cent moisture and was then saturated with gaseous ammonia. The excess NH₃ was removed by warm air or neutralized with H₃PO₄. The ammonium-saturated humus is said to dissolve slowly in cold water and to contain 5 per cent or more nitrogen. When the peat was first freed of absorbed bases, the nitrogen content was increased to 6 per cent. Ammoniated peat was found to be superior to mineral nitrogen and had a better residual effect. Peat extracts which were acidified with phosphoric acid and then ammoniated, yielded a preparation which contained 5–7 per cent nitrogen and 22–26 per cent total P₂O₅ (humophos, phosphohumate).

The favorable effect exerted upon plant growth by the addition to the soil of brown coal (641, 545), either in powdered form or after saturation with ammonia, or after nitration and saturation with ammonia, has been ascribed to the content of "humic acids" in the coal. This effect was also believed (545) to be due to changes in the physical properties of the soil, such as increases in the soil temperature and water-holding capacity and modification of the soil structure, as well as to certain chemical and biological properties, such as those associated with increased liberation of CO₂. Some (421) ascribed the favorable action of coal to its nitrogen content. Lieske (641) has shown that this nitrogen is unavailable for plant growth; however, coal may influence the absorption of nitrogen. Lieske suggested that the "humic acid" components of coal affect the cell membranes of plants. Brown coal and its "humic acid" derivatives were also believed (906c) to have

a highly stimulating effect upon the fixation of nitrogen by bacteria; this phenomenon was explained by the catalytic absorption of the nitrogen by coal, whereby the bacteria were assisted in the fixation process. This and numerous other hypothetical assumptions require confirmation and further study.

Some coals (as brown coal dust) may have an injurious effect upon plant growth by reason of their high acidity (pH 4.5) and their reducing properties (755). The injurious effect resulting from the addition of large quantities of coal has been ascribed (559) to the acidity produced by the sulfuric acid which is formed during the oxidation of the sulfur compounds in the coal; it may also be due to the reducing properties of the coal and to a decrease in the wetability of the soil. This effect partly disappears when the coal is treated with ammonia. This treatment renders the humus more soluble and enriches it at the same time in available nitrogen. It is still to be determined whether the favorable effects of such preparations upon plant growth (545) are due to the ammonia present, to the humus itself, or to some specific property of the latter.

Crowther and Brenchley (195) have demonstrated, for example, that the effect exerted by ammonium humate upon plant growth is not greater than the equivalent amount of ammonia used in the form of ammonium sulfate. Negative results concerning the specific effect of humus preparations upon plant growth, aside from any incorporated fertilizing materials, were also obtained by other investigators (81, 623, 1109).

Occasionally, various humus preparations, such as iron humates, are prepared for certain specific purposes. These preparations can be obtained by: 1. precipitating a neutralized NaOH extract of soil, peat, compost, or brown coal with an aqueous solution of salts of ferrous or ferric iron; 2. by shaking a "humic acid" preparation with FeCl_3 ; 3. by shaking a "humic acid" preparation with an alcoholic solution of FeCl_3 (462). It was found (562) that the amount of iron which combines with the humic acid varies, but may be as high as 10 per cent. When the humate was washed with hot water until there was no test for iron with potassium ferrocyanide, constant results were obtained. It was suggested that 1 atom of iron combines with 1 molecule of humic acid. The presence of iron, especially in the ferrous state was found to accelerate the oxidation of humic acid (see also 527, 532, 721, 749, 770, 893, 1059).

Use of peat and other forms of humus in fertilizer mixtures, as bedding

and for packing purposes. Various forms of humus, especially lowmoor peat, are used in the fertilizer industry, because of their high moisture-holding capacity. The nitrogen of the peat itself may be as high as 3 to 4 per cent; the inclusion of this nitrogen in the figures for the plant nutrients contained in the fertilizer is not justified, since an erroneous impression is left concerning its availability. The use of peat as a filler or as an actual fertilizer carrier, as with calcium cyanamide and ammonium salts, is fully justified. Lowmoor and other peats are also effectively used on lawns and golf greens in cases where it is desirable to increase the moisture-holding capacity of the soils through raising the organic matter contents. By treating peat with ammonia gas, under pressure and at high temperature, the nitrogen content is increased considerably; however, this nitrogen is only partly available for plant utilization and a large portion becomes a part of the resistant complex.

Certain forms of peat, especially the acid highmoor or sphagnum types, are used extensively as absorbents, especially for moisture and bases. Such peats are ideal absorbents for urine and for free ammonia and are therefore used in stables as litter. This yields a type of manure which can be handled readily, and in the case of cow manure, which has a high moisture content, it can even be dried and subsequently shipped long distances; such manure has found application as a top-dressing for lawns and for golf greens. Acid peats are also used in composts with insoluble phosphates in order to increase the solubility of the latter (262).

Sphagnum peat serves as an ideal packing agent for fruit, since by its absorption of the free moisture it prevents fungus development. Problems pertaining to handling of peat are beyond the scope of this treatise (923, 403, 454, 1124).

CHAPTER XVII

SOIL HUMUS AND THE SCIENCE OF PEDOLOGY

"Soil characteristics have a definite relationship to the forces of the environment, consisting mainly of climatic and vegetative forces."

—K. F. MARBUT.

The rôle of organic matter in the formation of soils was well appreciated even in ancient times. It received more definite consideration with the recognition of the soil as a natural body, produced as a result of natural agencies, primarily climate and vegetation. From the time of the Romans until the middle of the 18th century, the term "humus" was frequently used to designate the soil as a whole. Probably with this idea in mind, it was recently suggested (387) that the science of the soil should be called *humology*.

With the development of our knowledge of the chemistry of plant and animal residues, their decomposition in the soil, and the formation of dark colored organic complexes, the term became more limited in its application, referring only to the organic fraction of the soil. However, the importance of humus in characterizing the soil and the essential part which it is known to play in soil processes are so well recognized, that the very conception of the soil as a surface layer of the earth has been based, even in modern times, upon the presence of organic substances in it or upon it. It is sufficient to cite the ideas of two of the greatest students of the genesis and chemical nature of soils: Sprengel (1075) defined the soil as "a changed mass of material derived from minerals and containing the decomposition products of plants and animals"; fifty years later, Dokutchaiev (228) spoke of the soil as "the layer of material lying on the surface of the earth or near it, which has been changed by natural processes, under the influences of water, air and living and dead organic matter."

The processes of soil formation are highly complicated and are a result of the interaction of various factors, especially the nature of parent material, topography (805), climate (1052), vegetation (1160), and microbiological activities. The transformation of the plant and animal residues, leading to the formation of humus, and the weathering of the inorganic rock constituents are two of the most important processes

in soil formation; they give rise to substances which interact with the formation of new compounds; the movement of the ground waters also plays an important rôle in the dissolution, and translocation and subsequent deposition of the soil constituents. Soil formation is thus a result not only of decomposition and disintegration, but also of synthesis and accumulation (350). The complex organic and organic-inorganic compounds characterize the soil and differentiate it from other layers of the earth's crust.

Rôle of humus in soil formation. The influence of humus substances upon the process of rock weathering has received much consideration (82, 477). Humus formation and transformations bring about the chemical dissolution of some of the rock constituents in two distinct ways: 1. carbon dioxide, liberated from humus through microbial or chemical agents, acts as a dissolving agent; 2. the humus complexes take part in rock disintegration, through their capacity of exchanging or adsorbing cations. Although it is recognized by pedologists and geologists that the weathering of rocks is primarily brought about by water, through hydrolysis, the presence of carbon dioxide in the water results in a decided increase in the hydrogen-ion concentration, whereby the process of weathering is hastened. This effect of humus has also been ascribed to the action of its constituent "humic acid" complexes (768). Blanck (122) found, however, that the weathering action is not due to the organic constituents of the humus as such, but to the sulfuric and nitric acids which are formed as a result of its decomposition. Ramann's gray-earth theory, which ascribed to the "humic acids" the kaolin-producing effect of humus upon rocks and soils, was shown to be limited in its application; the process was found to be due to the sulfuric acid produced during oxidation of the H_2S which is liberated in the decomposition of the humus proteins. The rôle of humus compounds in the removal of bases from soil (492, 620) is also due in part at least, to the adsorption of the bases by the mobile constituents of the humus, as in podsol formation (766). Humus further transforms the lifeless mineral residues formed during rock weathering into a favorable medium for the growth of both plants and microorganisms, so that the soil becomes a living system. Humus can thus be considered as an essential and characteristic constituent of the soil, and its function in the formation and transformation of the latter is of the greatest importance (800).

The nature and decomposition of the organic residues in the soil play an important rôle not only in the formation of the soil as a whole,

but also in determining the specific major and even minor soil types. Differences which characterize and differentiate one type of soil from another are not only those associated with the inorganic constituents, but are also differences in the humus brought about through climatic effects which determine the nature of the vegetation and the course of decomposition of the plant residues. It has also been shown (299, 366) that one soil may change into another, as a result of a change in the type of decomposition of the organic matter, following a change in the nature of the vegetation, in the aeration of the soil, and in the reaction.

The rôle of humus in soil formation has been given careful consideration by the Russian pedologists, who have contributed both theoretical and factual evidence towards establishing the nature of profile formation in the process of soil development, as influenced by physico-geographical conditions. The characteristics of soil structure and morphology, used as a basis for soil classification, pointed to distinct differences in the decomposition processes, to which organic residues are subjected in various soil types. This is brought out in a striking manner, in a comparison of the chemical nature of the humus in two of the most common and characteristic soil types, the chernozems and podsols. It is also apparent in other soil formations, such as purely organic soils (peats), on the one hand, and gray desert soils (serozems), on the other. An attempt has even been made to explain the formation of the first two soil types by establishing chemical differences in the humus constituents, which were believed to have played an important part in their development. These considerations led to the assumption that the major portion of the humus in chernozem soils is composed of slightly soluble or completely insoluble "humic" and "ulmic" acids, whereas the humus of podsols consists chiefly of water-soluble "crenic" and "apocrenic" acids. In spite of the fact that the empirical nature of the various formulae for these "acids" was recognized and the fact that their very existence as chemical entities was frequently questioned, considerable weight was attached to their importance in the development of the soils.

According to Glinka (350), information concerning the humus is essential for an understanding of the origin and nature of the soil profile. It is not sufficient to determine merely the quantity of humus present in a given soil, but it is also important to know its chemical composition. Dokutchaiev (228) has previously assumed that the nature of humus cannot be the same in all soil formations. Various attempts have been

made to justify this assumption but they have not led to any definite conclusions. This is due largely to a lack of adequate methods for distinguishing and characterizing the chemical nature of humus in various soil types. The mere demonstration and isolation of certain chemical substances from a soil are not sufficient to characterize chemically a type of humus which has been formed under different climatic and geographic conditions; it is more important to study the chemical composition of the humus as a whole.

Kossovitch (576-8) suggested that the transformations of inorganic nitrogen in the soil into organic compounds takes place until the nitrogen content of humus approaches that of cells of fungi and bacteria. When this point is reached, the process of mineralization of nitrogen, namely, its transformation from organic into inorganic compounds, begins to predominate. When soils are subjected to intensive cultivation, without the addition of fresh organic substances, there is a gradual decrease in the humus content; this is accompanied by an enrichment of the residual humus in nitrogen. Humus of lower soil horizons is usually richer in nitrogen than is humus of the surface layers. Humus in mineral soils is distinct in chemical composition from that in peats, the latter being poorer in nitrogen. A definite relationship has been shown to exist (65) between the nature of the organic matter in the soil, its reaction, and the degree of its base saturation. The more acid the soil and the less it is saturated with bases, the lower is the nitrogen content of the humus and the wider is its C:N ratio. With increasing concentration of humus, the nitrogen content diminishes.

Remezov (875) emphasized the importance of humus in the processes of formation of different soil types. "Under the action of the biological world and the subsequent development of the process of humus-formation," rocks, which had undergone a process of preliminary weathering, gave rise to soil. Since the nature of the humus is not the same in the different climatic zones, soils formed in these zones differed in nature, even at the very beginning of the process of their formation. The function of humus in the formation of the various soil types was summarized as follows: 1. In the serozem or gray soil zone, the soils contain a small quantity of organic matter and the climate is characterized by low rainfall and high evaporation. 2. The chestnut zone is characterized by a higher rainfall and lower evaporation, hence an increase in humus content. 3. Soils of the chernozem zone are characterized by a large mass of organic matter, with humus formation reaching a maximum; a decrease in the humus forming proc-

esses is accompanied by an increase in degradation and podsolization, giving rise to podsols. 4. In the zone of chernozem-like soils there are relatively high precipitation and poor soil aeration; this condition results in limited decomposition of the plant residues and humus accumulation. The meadow-swampy soils may become changed to podsols or solods, depending upon the summer evaporation, leaching, etc. 5. When humus forming processes predominate, as a result of low evaporation and abundant rainfall, a cover of meadow or forest vegetation results, finally leading to peat-bog formation.

Not only the concentration of humus, but also its chemical nature, differ in various types of soil (1150a). By utilizing a differential method of chemical analysis of soil humus (1241), Remezov (876) has shown that definite differences exist in the humus occurring in specific soil types; this can be traced directly to the chemical nature of the humus produced under the different conditions.

As an indication of the differences in chemical composition of the humus in various soils, it may be sufficient to call attention to the variations in carbon-nitrogen ratios of the humus (36). Although it has been shown that the C:N ratio is more or less constant in the organic matter of the soil, considerable variation has often been reported, first by Hilgard (437-8) and more recently by Leighty and Shorey (617). The latter did not seem to find any specific soil condition associated with this variation. Hilgard, however, believed that the differences could be ascribed to the soil and climatic conditions; soils of arid regions were shown to contain nearly three and one-half times as much nitrogen in the humus as soils of humid regions (443, 931). Hilgard's conclusions were questioned by subsequent investigators (642); they were confirmed, however, by Remezov (877). The narrowest C:N ratio was found in the soils of the serozem zone, the average being 4.5:1; on proceeding northward, to regions of lower temperature and greater precipitation, the ratio is wider, so that in the chestnut zone it is on the average 6.8:1, while in the chernozems it is at a maximum of 10:1; further north this ratio is narrower again, being 8.0:1 in the gray-forest-steppe zone, and finally 6.8:1 in the podsols. In peat formations the ratio is wider. A definite relationship was thus shown to exist between the C:N ratio and the climate. In soils of climates favoring the most rapid and complete decomposition of the organic residues, there are the least amount of organic matter and the narrowest C:N ratio (serozems). In the chernozem region, the climatic conditions favor accumulation of organic matter, resulting in a wider ratio, with less

nitrogen in the humus. Further north, where the soils have a higher moisture content and are deficient in calcium, the content of organic matter is lower, and the C:N ratio is narrower.

There is also considerable variation in the C:N ratio within each soil zone: the chernozem zone of the Ukraine gave a C:N of 7.6:1; that of Central Russia, 11.4:1; and that of Siberia 13.6:1, i.e. going eastward with an increase in the continental nature of the climate, the C:N ratio widens. The climatic factors, particularly precipitation and temperature, elevation, and the activity of microorganisms are of considerable importance in determining the degree of variation of the ratios of carbon to nitrogen in the humus in any soil zone.

Humus and the soil profile. The soil profile is composed of layers or horizons, each of which is characterized by a certain concentration of humus with specific physical and chemical properties. The upper layer of the profile is usually darkest in color, because of the abundance of humus; the color is generally lighter in the deeper layers where the humus content is lower. In the podsols, below the light gray A horizon there may be a dark accumulation horizon, where the humus has not been formed in place as in the upper layer, but has been washed down and deposited. Frequently in its movement from the A horizon, humus accumulates in spots well below the surface.

The abundance (126) and nature of humus characterize not only the color of the soil (156), but also its structure and morphology. Humus not only imparts to the soil black, brown, and gray colors, but also modifies the soil coloration caused by iron and manganese compounds. The final color is determined principally by two factors (1194): 1. the physical and chemical properties of the humus, and 2. the nature of the mineral constituents; the same amount of humus darkens a gray soil much deeper than a brown or a red soil. In dry regions the humus content is not the dominant factor in determining the soil color (654, 1002).

Although the importance of humus in soil-forming processes is now generally admitted even for mineral soils, some soils are primarily organic in nature or particularly characterized by their humus content. Three of the six major classes of soil established by Dokutchaiiev are directly characterized by their humus formations: 1. the continental humus soils (light gray, gray forest, chernozem, chestnut colored, and brown alkali soils), 2. the continental bog soils, and 3. the typical bog soils. Further development of these ideas has found expression in Glinka's discussion of the origin of soil types. This can best be

summarized by considering the abundance and nature of humus in the ectodynamomorphic soils:

1. Soils developed under high moisture conditions: the organic substances are readily decomposed and, as a result, the soils are low in humus; this leads to the liberation of salts, which are leached out, thus giving rise to laterites.

2. Soils developed under average moisture conditions: the moisture content and temperature are sufficiently high to prevent the accumulation of large amounts of unstable humus compounds; the humus is not completely decomposed, with the results that the bases and sesquioxides are removed, giving rise to podsol, gray forest soils, and brown soils.

3. Soils developed under moderate moisture conditions: a rich grass vegetation develops on these soils, but the organic substances do not decompose rapidly enough to prevent an abundant accumulation of humus, especially the unstable compounds, giving rise to chernozems.

4. Soils developed under low moisture conditions: because of the limited supply of moisture, the vegetation is not so well developed as in the previous group, with the result that the humus content is limited; this leads to the formation of chestnut soils and steppes.

5. Soils developed under excessive moisture conditions: when the soil is saturated with water, rapid decomposition of the plant residues is prevented and peat soils are formed.

6. Soils developed under conditions of periodic excessive moisture, which give rise to alkali soils: the rôle of humus in the formation of these soils is not clearly defined.

The foregoing system of classification, although stressing the importance and participation of humus in the soil-forming processes, is too broad and vague. It does not consider sufficiently the relations between organic matter formation and decomposition (719), nor the nature of the humus itself.

Just as the geologist formerly considered the soil to be merely a mass of *débris* overlying the native rock, so does the pedologist at present consider the humus horizon to be a mere mass of plant residues in various stages of decomposition, but having little to do directly with the soil itself, although this horizon is probably the most important in the soil as far as soil processes and plant growth are concerned. Such a surface humus layer as that which exists in forest soils is frequently not even considered as a part of the soil, although it is agreed that it contributes to the soil as a result of its decomposition; it is rather con-

sidered as merely supplying the organic substances essential for the process of eluviation. When considered at all, the humus layer is usually designated as A_0 , while the entire eluvial horizon is designated as A , being subdivided into A_1 , A_2 , A_3 , etc. The A_0 , or humus, layer contributes to the process of eluviation, not only by supplying the disintegration products of the organic residues or the various humus fractions, but also by liberating CO_2 , as well as nitric and sulfuric acids, which interact with the soil minerals producing marked changes in their composition and in their translocation in the soil profile. The humus complexes interact with the inorganic soil constituents in the A horizon, especially with the sesquioxides of iron and aluminum, as well as with the phosphates and silicates, and accelerate their downward movement in the percolating waters, in the process of leaching. Tamm (1133) has shown that a process of de-silication is brought about as a result of the displacement of SiO_2 by certain humus complexes. The leached materials, notably the sesquioxides and humus, are deposited in the B horizon (illuvial)—the horizon of accumulation; this soil layer becomes enriched in bases and in colloids, both inorganic and organic. There is considerable difference, however, in the rate of accumulation of the different materials in the B horizon, depending upon the nature of the soil, organic residues, rate of decomposition, and climate. In general, the nature of both the A and B horizons, which chiefly characterize the soil profile, is found to depend largely upon climatic conditions.

From the point of view of abundance and nature of humus, four soils can now be recognized and characterized:

1. Soils predominantly organic in nature. These are formed under conditions of excessive moisture content and largely under bog conditions. They are considered in detail elsewhere, under peats (p. 259).

2. Podsol, brown forest, red, and yellow soils. These show a rapid drop in humus content from the surface to a depth of 15 cm.; the percentage of organic matter becomes very low at shallow depth (673). Soils in temperate regions with a cool, humid climate are podsolized. Podsol is frequently identified with forest soils, especially coniferous forests, but they are also found under other types of vegetation, giving rise to heath podsol, meadow podsol, peat podsol, podsol-gley soils, etc. Although these soils have been discussed in detail under forest soils, consideration is given to them here, from the pedological point of view.

3. Prairie soils, chernozems, chestnut brown and brown grassland

soils. These soils are formed in relatively dry climates, under an abundant development of grassland vegetation (steppe, prairie); they are rich in humus, which penetrates to a great depth, 1 meter or more, gradually changing to the underlying subsoil.

4. Gray soils, serozems, chestnut soils (arid soils). These soils are formed under the influence of a very dry climate and with limited precipitation; the humus content is very low, and its rôle in the formation of these soils is questionable, although it no doubt plays an important part in their fertility.

In the various profile descriptions, the degree of decomposition of the humus and its structure are usually characterized by such vague terms as "moderately decomposed," "fibrous," and "peat-like"; various color gradations are recognized, such as "gray," "gray-brown," and "chocolate-brown." Descriptions based on these terms are of only limited value, since they vary with the interpretation of the individual observer. Even such well-accepted terms as "mild humus," "acid humus," and "moder" fail to typify accurately the organic matter with regard to mode of origin or morphology.

Origin and nature of the podsol profile. The podsol profile is very typical and does not vary greatly in its principal characteristics, even under a variety of conditions. Within the major group are found a number of gradations and variations. The profile of this soil type consists of three or four genetic horizons: 1. The horizon where the humus is formed and may even accumulate; this is spoken of as the A_1 or A_0 horizon. 2. This is followed by the eluvial horizon (A_2), where the humus is removed; this layer of soil is light gray, gray, or dark gray in color and is bleached. 3. Below this is the illuvial horizon (B) where the humus is deposited; the soil is yellow or brown in color, usually deeper at the top and gradually blending into the parent material at the bottom; in some cases it is colored uniformly, but in others it has an uneven distribution of ortstein, of fen concretions, or of fen layers; the color of this horizon depends on the content of humus and iron oxide; it varies in thickness from a few centimeters to several meters. 4. The parent material or C horizon.

A sharp line of demarkation in humus content is found between horizons A_1 and A_2 , which is characteristic of the podsol profile. Table 63 shows the abundance of humus in two podsols and the rate of its decomposition, as measured by the course of CO_2 evolution and by nitrate accumulation. The humus in the B horizon is found to be much more resistant to decomposition than that of the A horizons.

humus being completely soluble in ammonia. The A_1 horizon is 5 to 30 cm. thick and consists usually of moist raw humus or peat. 3. Humus podsol, with the A_1 consisting of peat or moist raw humus.

The last type of podsol is further subdivided into four subtypes: (a) humus podsol with considerable enrichment in the B horizon and no

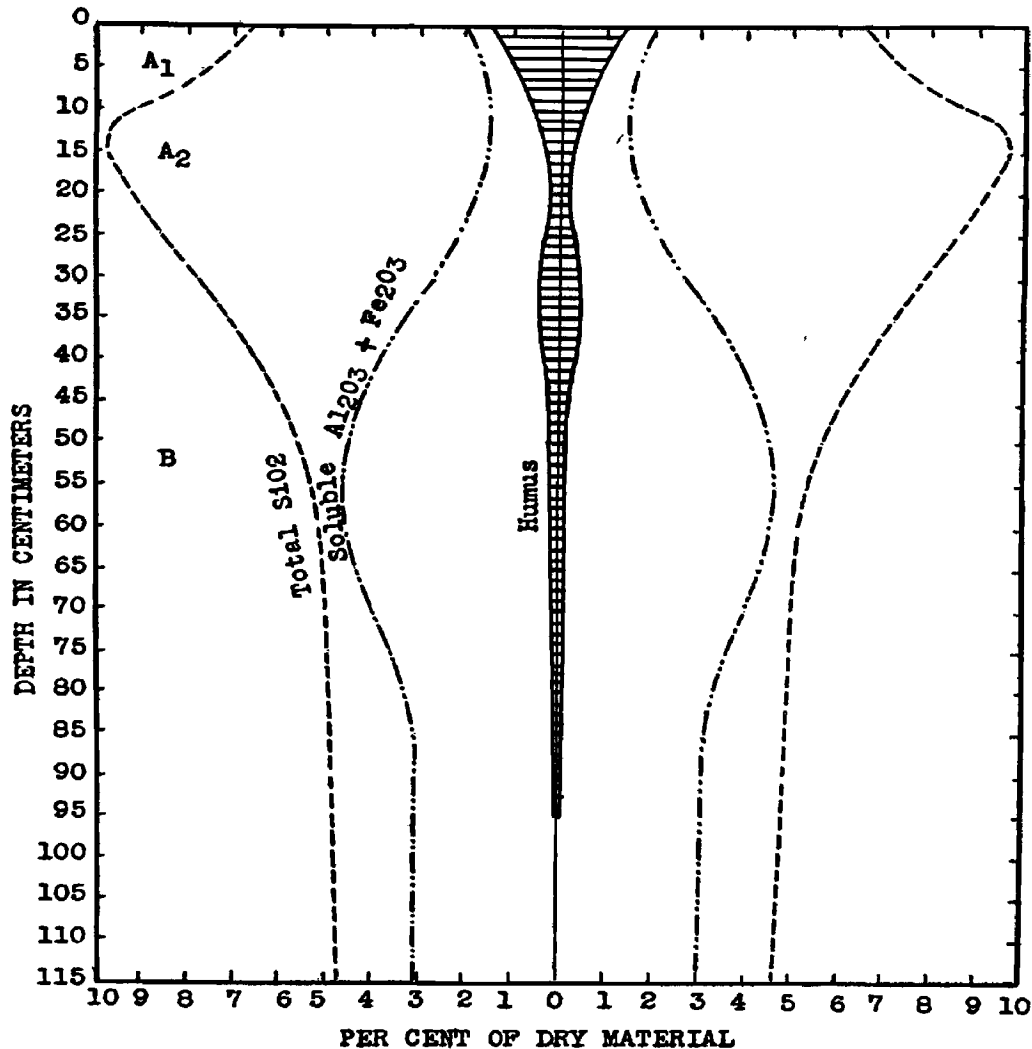


FIG. 42. Distribution of humus in a podsol profile. Schematic representation (Neustruiev).

ortstein formation; (b) humus podsol with ortstein formation; (c) humus podsol with a weak enrichment in the B horizon, the A_1 horizon being less than 30 cm. thick; (d) same as (c), with the A_1 horizon being more than 30 cm. thick.

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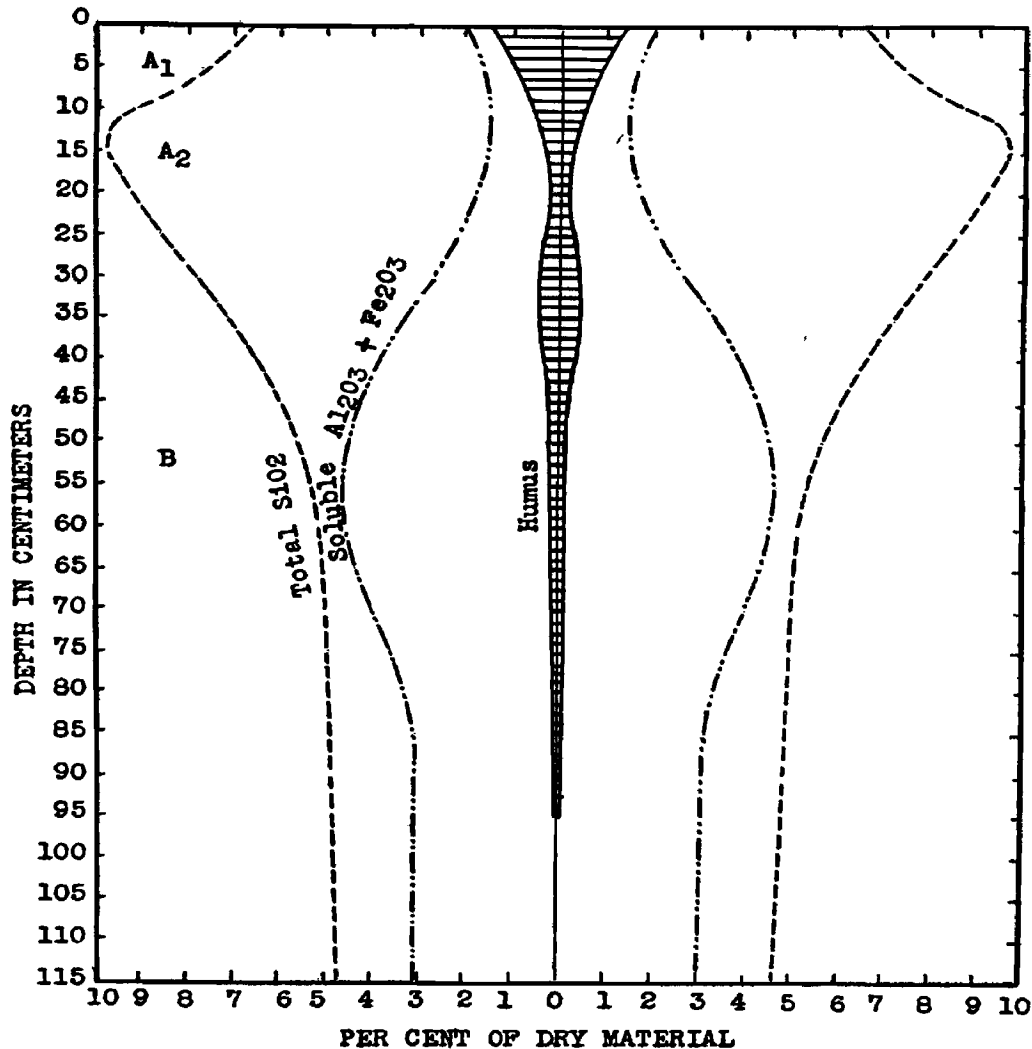


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In attempting to differentiate between the various humus complexes responsible for this process, however, they were misled by the older terminology of the "humic acids," whereby the humus was differentiated into insoluble "humins" and "ulmins," slowly soluble "humic acids" and "ulmic acids," and readily soluble "crenic acid" and "apocrenic acid." They believed that the humus in horizon A_1 is largely characterized by "humic" and "ulmic" acids, and that in the A_2 horizon the "crenic acids" (unsaturated or partly neutralized by bases) predominate, the latter being more readily removed by water. The lack of justification for this terminology becomes clear when one considers the evidence previously submitted.

These conceptions led to numerous speculations which were based upon unreliable experimental evidence. One may cite the ideas of Williams (1285), in order to illustrate the nature of the confusion. "Crenic acids" were believed to be formed as a result of decomposition of forest litter by fungi; these hypothetical acids were assumed to react with carbonates, first with calcium carbonate, then with carbonates of iron and manganese, liberating CO_2 , and giving calcium, iron, and manganese "crenates"; the latter being soluble in water were carried downward, thus changing the color of the soil horizon to whitish or gray, causing the disintegration of the alumino-silicate complexes and forming "aluminum crenate"; the podsolized horizon is supposed to be free of bacteria, "because of the acid medium due to the crenic acid," and free of fungi, "because the crenic acid is a waste product of the fungi."

Similar hypothetical ideas were expressed by various other pedologists, with the prevalent conception that "humic acid" represents the dark colored substances, and "crenic acid," the light-colored humus compounds, the accumulation of the latter being a characteristic part of the whole process of podsolization. However, Neustruiev (760-1) and others raised a protest against this general application of the conception of the rôle of organic acids in the process of soil formation, by pointing out that the properties and the very existence of the "crenic acid" are hypothetical. Aarnio (4) definitely established the fact that the nature of the humus, its relative concentration, and the nature of the sesquioxides are of great importance in influencing the removal of the latter and in determining their subsequent precipitation.

Humus is also considered to be of great importance in "gley" formation (12); the process is believed to involve the reduction of iron under anaerobic conditions. In podsol formation the organic sub-

stances dissolve the iron and aluminum, and remove both, whereas in gley formation, reduction predominates and only iron is removed.

Grassland and prairie soils. The Russian term "chernozem," or "black earth," is frequently applied to all the grassland or prairie soils. Several hypotheses have been proposed to explain their origin: 1. aqueous or sea origin, 2. swampy or peat origin, 3. origin from surface vegetation, 4. loess origin.

Pallas (228) stated in 1799, in discussing the formation of the Southern Steppes in Russia, that this valley was at one time either a measureless reed swamp or had been frequently covered by the sea, under the surface of which mud rich in salts was deposited; following the recession of the sea, the plant residues in this mud underwent decomposition, finally giving rise to the thick layers of black soil. Some investigators accepted the theory that chernozems were formed from the sea bottom, the nitrogenous complexes originating from the aqueous plants and animals; others claimed that the area was covered by large lowmoor peat bogs, which gave rise to black soils upon drying; the latter were thus believed to have originated from inner lakes and bogs. Some of the early chemists, including Hermann (422), suggested that "chernozem" or "humus" originated from the decomposition of plant roots, leaves, and other plant residues; it is the humus which gives to the soil its characteristic color; the conclusion was reached that chernozem is nothing but a mixture of sand and clay with varying quantities of humus. The last idea was accepted and formulated in detail by Rupprecht (924). He emphasized the rôle of the steppe vegetation in the formation of this soil type, with the movement of some of the soluble constituents of the surface vegetation into the lower soil layers. This theory was accepted and further developed by Dokutchaiiev (228), with the result that chernozem formation is now regarded as a product of a surface autochthonous vegetation, which was of a steppe and not of a forest nature. The occurrence of humus in the lower layers was explained either by the decomposition of roots or by the washing down of some of the organic constituents from the surface layer (950).

The conception of Rupprecht (924) that humus occurrence in lower layers was due to the mechanical removal of some of the decomposed plant constituents from the upper into the lower soil horizons was soon confused by Kostytchev (579), who made two new suggestions; namely, 1. that humus complexes are insoluble and hence could not possibly have a direct effect upon the mineral soil constituents; and 2. that only one of the products, ammonia, which is able to dissolve certain of the humus

compounds, takes part in their transfer. As a result of these ideas, the ammonia-soluble substances were considered to be largely responsible for the distribution of humus compounds in the soil. The transformation of the soluble humus compounds into insoluble forms was explained by Kostytchev as due to the loss of the ammonia, through its oxidation to nitrate, and to the precipitation of the organic compounds by interaction with salts of calcium, magnesium, and iron.

These theories were submitted to experimental test by Barakov (66), who studied the movement of humus compounds in artificial soils consisting of varying mixtures of clay, sand, and CaCO_3 ; these investigations led to the conclusion that humus can be distributed in soil both mechanically and in the ammonia-soluble form. Kostytchev later changed (580) his ideas concerning the accumulation of humus in the lower soil layers, suggesting that humus is not brought there in solution but is formed in place through the decomposition of plant remains, especially roots. While disclaiming the possibility of mechanical and chemical movement of humus substances in the soil, he admitted the possibility of biological movement, such as through the agency of fungi, which play an essential rôle in the formation of dark colored substances in the soil.

Levakovski (635), Slezkin (1045), and Kravkov (587) emphasized the importance of the rôle of water in carrying various constituents of the "humified" plant residues downward into the soil layers. It was believed that the water extracts subsequently interacted chemically with the iron and aluminum in the soil. Calcium was at first considered to render the humus more soluble and more readily transferred. Slezkin suggested, however, that calcium preserves the humus against further decomposition by microorganisms, and fixes it in the soil. According to Kravkov, the absorption and fixation of organic complexes in the soil depend largely upon the calcium content of the soil; since a certain amount of calcium can saturate only a definite amount of humus, a given soil becomes saturated with humus to the extent of its calcium content. Each type of soil has, therefore, a specific degree of saturation with humus; soils poor in organic matter, as well as soils very rich in organic matter, may be totally unable to absorb and fix humus further (121).

The generally accepted theory concerning the development of chernozem soils is that of Dokutchaiev (228). According to his theory, the humus in these soils resulted from a grass vegetation; the temperature and moisture of the steppes and prairies favor abundant growth of

grasses, but not rapid decomposition of the organic residues. The highest humus content of these soils in Russia was shown to occur in the center of a broad grassland belt, the contents becoming progressively lower in the soils to the north and south. The successive parallel belts were designated as *iso-humus belts*. Dokutchaiiev constructed a schematic soil map of the chernozem region of European Russia, which

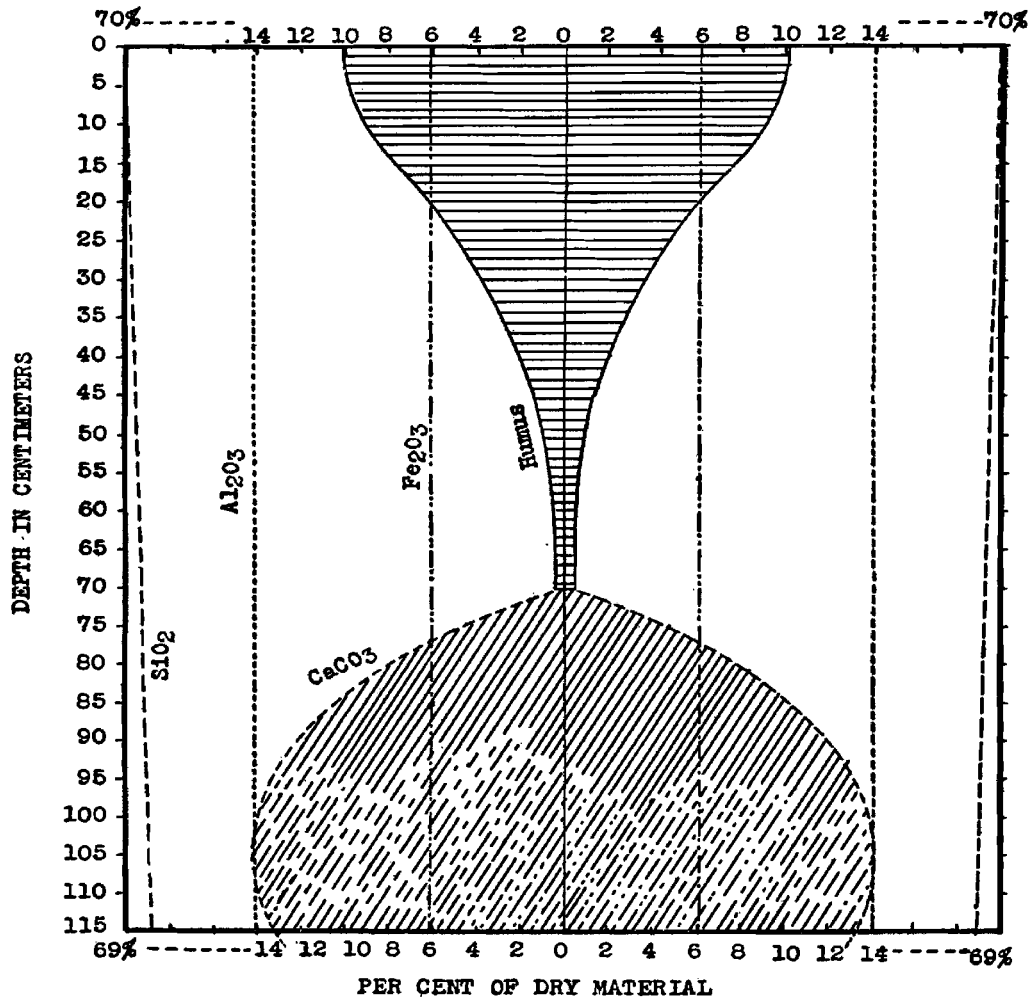


FIG. 43. Distribution of humus in a chernozem profile. Schematic representation (Neustruiev).

traced the distribution of chernozem soils with similar humus contents, showing the *iso-humus zones*.

The characteristics of the chernozem soils were summarized by Kostytchev as follows:

1. These soils have a relatively high organic matter content which gives them their black color.

2. The organic matter is not present in the same concentration in the various soil layers, but diminishes with depth; there is no sharp line of demarkation, however, between the dark surface soil and the light-colored subsoil.

3. The organic substances of chernozem soils, other than roots, are amorphous in nature; a microscopic examination shows only that they are of plant origin, coming principally from grass plants.

4. Since the soil does not show any regular layer structure, one cannot consider that these humus formations are water deposits.

5. These results indicate definitely that the chernozem soils were formed *in situ* from such plants as are still growing upon the soils and under conditions which are still dominating at the present time.

The continuous annual growth of plants, both on and below the surface, is accompanied by a gradual decomposition of the plant residues. Whenever humus accumulation takes place, the process of decomposition must be slower than that of accumulation of the plant residues. Kostytchev (581) calculated that the total quantity of humus accumulating in a soil is determined not so much by the absolute amount of plant residues added annually and by the absolute rate of decomposition of these residues, as by the relative amount of humus which can be decomposed in the soil in a given area within a year. These results led Kostytchev to question the existence of iso-humus zones.

Ordinarily, the humus horizon (A_1 - A_2) of chernozem soils is about 50 to 200 cm. thick. Different types of soil vary in gradation of color from the A_1 to the A_2 horizon, as well as in structure. Frequently, at a depth of 200 to 400 cm., faintly developed humus horizons are found associated with accumulations of lime and gypsum (F horizon); this phenomenon, however, is not of frequent occurrence and has not been observed in the soils of the United States (Marbut).¹

The humus content of the black soils is generally between 6 and 10 per cent, but it can be less than 4 per cent, especially over sandy subsoils, or as high as 20 per cent or more. In summarizing the analyses of 50 typical chernozem soils, Kossovitsch (577) reported a humus content of 2.27 to 19.77 per cent, with a nitrogen content of 0.14 to 1.00 per cent; the concentration of nitrogen in the humus was calculated as 4.1 to 8.2 per cent, with an average of 4.85 per cent. The humus figures were based on determinations of total organic carbon; the common factor, 1.724 was used. The average C:N ratio of these soils

¹ Personal communication.

was found to be 11.96. In the case of chestnut-brown soils, the maximum humus content was about 5 per cent, and usually only 3 to 4.5 per cent.

There is considerable variation in the humus content of soils of the same type. The variation from the mean of the individual samples was shown to range from 5.8 to 19.5 per cent (221). The texture of the soil, as well as its nitrogen content, also influences the relative abun-

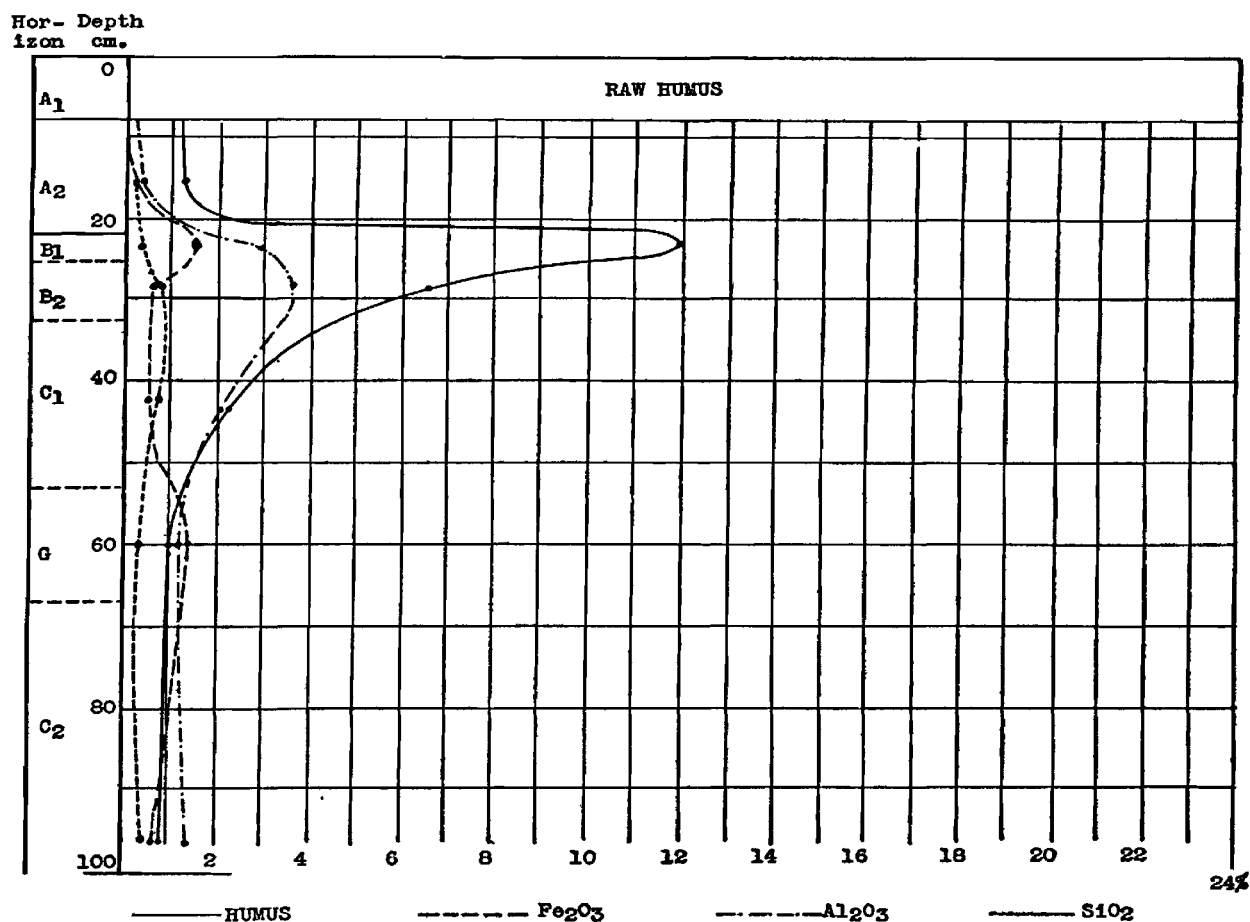


FIG. 44. Distribution of humus and other colloids in the profile of an iron-humus podsol (Tamm).

dance of humus (1024-6). By using the hygroscopic coefficient as a measure of texture, a definite relationship was established (930) between the texture and the nitrogen content of the soil, as shown in figure 32. The amount of precipitation is of considerable importance in this connection.

The absorbing complex in chernozem soils is saturated with bases, namely, calcium and magnesium (341). This determines some of the

characteristic properties of these soils: (a) the constancy of the absorbing complex which is highly resistant to the decomposing and dissolving action of water; (b) the capacity of both the zeolitic and humic constituents of the absorbing complex to attain a maximum; (c) the lack of compacted illuvial horizons in these soils.

Neither the abundance of humus nor its nature is uniform in different soils; it undergoes various changes in composition, primarily as a result of climatic conditions, vegetation, soil texture, and reaction. The processes of transformation of humus and the interaction between humus and the inorganic constituents may change entirely the characteristics of the soil and lead to a change of one type into another. It is sufficient to call attention to the changes produced when a black soil is transformed into a forest soil, or a semi-swamp bog into a podsol, under the influence of aeration.

Humus in saline and in alkali soils. A decrease in soil moisture, under certain specific climatic and topographic conditions, results in the accumulation of soluble salts and alkali carbonates, with the result that calcium and magnesium are gradually replaced by sodium in the adsorbing complex. The humus part of the complex is also gradually reduced, in contrast with the changes in chernozems, and its place taken by alumino-silicates (341). Saline soils (solontchaks) are thus produced, followed by the formation of alkali soils (solonetz), when the clay and humus are mainly saturated with sodium. The abundance and distribution of the humus in these soils depend largely upon their geographical location and chemical composition. The abundance of humus in a profile of a Siberian saline soil is reported by Glinka (350) as follows:

DEPTH OF SOIL	HUMUS CONTENT	LOSS ON IGNITION	CARBONATE AS CO ₂
<i>cm.</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
0-8	6.85	10.68	1.24
10-17	1.89	4.41	3.48
45-58	1.41	4.34	1.44
125-138	1.87	4.06	0.08

The reduction of humus content with an increase in depth is gradual. There is also a variety of gradual changes from the saline to the surrounding non-saline soils. These transition soils have been termed salinized soils; they are high in carbonate and the humus is not distrib-

uted uniformly in them, but changes abruptly, as shown for a Siberian soil as follows:

DEPTH OF SOIL	HUMUS CONTENT	LOSS ON IGNITION
<i>cm.</i>	<i>per cent</i>	<i>per cent</i>
5-20	13.90	16.18
35-45	2.60	7.52
65-75	0.57	9.57

In the case of the alkali soils (solonetz), the concentration of humus may be high at the surface, as shown by Glinka for a Tobolsk soil:

HORIZON	DEPTH OF SOIL	HUMUS CONTENT	LOSS ON IGNITION
	<i>cm.</i>	<i>per cent</i>	<i>per cent</i>
A ₁	0-5	13.67	15.83
A ₂	12-14	8.91	10.24
B ₁	14-20	6.51	7.90
B ₂	40-50	1.14	3.87
C	85-95	0.73	3.50

Chestnut and gray desert soils (serozems). The chestnut soils adjoin the chernozems, either to the south of the latter, as in Russia, or to the west, as in the United States. They are light brown to dark brown in color and are rich in carbonates, without containing, however, any sodium in their adsorbing complex. They contain, according to Glinka, 3.5-4.5 per cent humus in the surface layer; there is a rapid decrease of humus content with depth, so that at 35-45 cm. it is only 0.94 per cent.

The gray desert soils, or serozems, are formed under conditions of dry and continental climate, with hot summers, cold winters, and absence of precipitation in the summer. The high summer temperatures and constant winds dry out the soil extremely. The limited vegetation leaves comparatively little residual material, which is itself rapidly decomposed. The organic matter content of these soils is usually very low, from 1.5 to 0.2 per cent or even less. The serozems are formed in Russia to the south of the chestnut soils, with lower humidity and warmer climate. Less abundant vegetation and more rapid decomposition lead to the accumulation of less humus.

Many of the gray soils, as those found in Turkestan, were at first considered to be of loess origin. It was later shown, however, that the

processes of soil formation are here similar to those active in other soils. Whatever contribution the loess made, was limited to the original formations which gave rise to the material. The analyses of a typical serozem given by Glinka is shown here:

DEPTH OF SOIL	HUMUS CONTENT	CARBONATE AS CO ₂	LOSS ON IGNITION
<i>cm.</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
0-3	2.00	4.93	3.68
13-26	0.45	6.72	2.04
50-60	0.26	8.92	1.67
103-110	0.22	10.74	1.56
172-180	0.13	8.52	1.33

Frequently, higher concentrations of organic matter are found in the chestnut soils than those reported in the foregoing. The following results for three soil profiles in Hungary, were cited by Sigmond (1029):

HORIZON	DEPTH OF SOIL	HUMUS CONTENT	CARBONATE AS CO ₂
	<i>cm.</i>	<i>per cent</i>	<i>per cent</i>
A ₁	0-22	4.83-5.96	0.46- 5.86
A ₂	40-80	2.59-5.42	2.11-10.89
A ₃	50-120	2.50-2.77	6.62- 7.10
C	150	0.54	16.78

There is no accumulation horizon in the chestnut soils. Water-soluble salts are limited and occur in the deeper layers. The gray desert soils can be looked upon as transition forms to the saline and alkali soils.

A number of other soil types are recognized, intermediary between the chestnuts and serozems, such as the brown soils, as well as between the serozems and the saline soils; namely, the gray-brown, light, and white soils (233).

Humus in laterites. The process of formation of red-colored subtropical soils or laterites has still been insufficiently studied. It is assumed to be the reverse of that which takes place in the formation of podsoles. The humus-zeolite complex is totally decomposed. The A horizon consists of sesquioxides, while the mono- and di-valent bases and the SiO₂ have been leached out in the alkaline medium; this horizon adjoins the C horizon and is imposed upon by the B₁ and B₂ horizons; the latter is the uppermost and consists chiefly of sesquioxides. The

humus content of the upper 5 cm. in the laterites has been reported to range from 0.8 to 1.7 per cent. Even this limited amount of humus plays an important part in the movement and deposition of the iron in a manner similar to the processes taking place in podsol formation, although in an opposite direction (123).

The rôle of humus in hardpan formation. The terms "pan" and "ortstein" are applied to the hard compact layer of a soil, formed during the process of podsolization or solodization, at a depth of 25 cm. or more below the surface. Several types of pan are recognized: iron and aluminum pans, formed by the precipitation of humus and ferric sols, together with some clay and alumina, in acid soils; pans are also formed in alkali soils under arid conditions, as a result of flooding.

Ramann (855) defined "pan" as a layer of soil cemented together by humus; since podsoles are chiefly sandy soils, pan is a humus sandstone. According to Albert (19), however, compounds of aluminum, iron, and phosphorus form the cementing substances of the sand grains. Three types of ortstein were distinguished: 1. brown soils, a mass rich in humus and not cemented together; 2. true ortstein, a hard, rock-like material, dark brown to black, with a medium content of humus; 3. dark brown ortstein, very hard and containing a small amount of humus. Van Bemmelen (90) designated as ortstein, the cementing of sand particles with a colloidal complex consisting of humus, silicic acid, aluminum and iron oxides, and clay particles; small quantities of calcium, magnesium, sodium and phosphates are absorbed in this complex. Tamm (1133) considered ortsteins as unweathered material cemented with iron (limonite) and humus; the humus-rich ortsteins are soft and the iron-rich are hard (1).

P. E. Müller (737) explained the process of ortstein formation as follows: The organic matter in the surface layer of soil is rich in "humic acids" and in "humic acid salts"; these dissolve the bases, such as iron oxides; the solution is leached downward and, upon coming in contact with more bases, forms a precipitate of an insoluble basic humate. Müller distinguished three types of ortstein formation: 1. that formed by elluviation, giving rise to the clay ortstein and peat-like ortstein; 2. that formed by absorption, consisting of a humus ortstein rich in iron and a humus poor in iron; 3. that formed by concretion, consisting largely of iron ortstein.

Mayer (484) came to the conclusion that, in ortstein formation, the binder consists of colloidal humates of iron and aluminum and of silicates. The relationship of humus to this process was described as

follows: The colloidal humates are formed from plant residues in the surface layer of the soil; they are partly dissolved and, in leaching downward, take up more iron and finally become precipitated. The hardness of the ortstein depends less on the absolute amount of the colloidal binder than upon the manner of binding. The processes of iron removal and of iron precipitation were also presented as follows: In the absence of oxygen, the iron is reduced to the ferrous form, which reacts with some of the humus constituents to give ferro-compounds (668); these dissolve and are leached downward; in the lower layer, the ferromates are oxidized to ferri-humates, which are insoluble and become precipitated, binding the sand grains together.

In contrast to Mayer, who considered the reactions of transfer of iron as purely chemical in nature, Hornberger (461) suggested that microorganisms play an important rôle in the process; the organisms were believed to oxidize the ferrous compounds to ferric hydroxide, using the humus complex as a source of energy.

Rather (919) suggested that the reactions involved in ortstein formation are purely colloidal. The iron and aluminum which form the cementing substances in the ortstein, originate in the upper soil horizons; they are formed in the process of weathering, as a result of the action of "humic acids," are dissolved as colloidal salts, and are carried downward. As a result of evaporation of the solution or because of the presence of electrolytes, such as CaCO_3 , the iron and aluminum are precipitated as colloidal gel; colloidal humus compounds exert a protective action upon the iron and aluminum colloids. This process is possible only when the surface layers of soil are free from calcium, which would coagulate the iron and aluminum colloids and prevent the formation of free "humic acids" or readily soluble humus compounds. Aarnio (5) also concluded that, even if inorganic electrolytes play a certain part in the precipitation of the sesquioxides, one is justified in concluding that in humid regions the reactions of the humic substances are most important in this soil-forming process.

According to Morison (726), the concentration of humus in the pan is even more characteristic than that of iron. The formation of pan was shown to be dependent upon several factors: 1. the formation of an acid humus layer; 2. the removal of the soluble calcium from the underlying layer; 3. the production of humus sols; 4. the exertion by these sols of a protective action upon the inorganic colloids of $\text{Fe}(\text{OH})_3$, $\text{Al}(\text{OH})_3$, and silicic acid; 5. the deposition of these removed materials at a certain depth of soil; 6. the coagulation of the removed sols.

Chemical nature of humus in the soil profile. Sufficient evidence has been submitted previously to demonstrate that definite differences exist in the chemical nature of the humus in the different soil profiles, as well as in the different horizons of the same profile. The fact that there are marked chemical differences can be indicated even by the characteristics of the humus extract obtained with dilute alkali solutions. Dobrovolski (226) employed ammonium carbonate: the A_1 horizon gave a dark brown extract, which, on acidification, yielded a black precipitate and a reddish yellow filtrate; the A_2 horizon gave a reddish yellow extract, but no precipitate was formed on acidification; when $CuSO_4$ was added to this solution, a dirty green color was obtained, which led to the conclusion that the bleached horizon (A_2) contained no "humic acid," but only "crenic acid." Here as well, the unfortunate use of specific names to designate substances presumably different conceals the true nature of the conditions. Although there is no doubt that the black precipitate obtained on acidification of the alkali extract of the A_1 horizon is predominantly a humus complex, probably ligno-protein substances, one cannot say with as much justification that the Cu-compound from the A_2 extract is an organic complex at all; it may as likely have been an inorganic compound, such as Cu-silicate or Cu-Al-silicate, with a slight admixture of organic matter.

Khainsky (542) found that a solution of sodium carbonate extracts the lowest relative portion of the humus from chernozem soils, more from podsols, and most, amounting to practically all of the humus, from chestnut soils. When the soils which have been treated first with Na_2CO_3 are subsequently extracted with NaOH solutions, a considerable amount of humus is removed from the chernozems, less from the podsols, and practically none from the chestnut soils. Even a hot NaOH solution, however, still leaves a large part of the humus in the chernozem soils. This phenomenon was considered as sufficient evidence that humus in different soils occurs in different stages of decomposition, the humus of the chestnut soils being the most completely decomposed and that of the chernozems the least. An attempt to separate the organic constituents of the humus, by the use of the methods of Schreiner and Shorey, led Khainsky to the following conclusions: the chernozem soil is characterized by the presence of complex organic substances formed as a result of condensation and carbonization; podsols are characterized by the presence of substances which are more readily soluble; and the humus in chestnut soils consists of complexes representing stages of still further decomposition.

A more logical system, based upon the proximate analysis of the humus in different soil types, was proposed by Remezov (876). He found that, in serozem soils, the organic matter is free from cellulose and hemicellulose, the proteins predominate, and the lignin is low, thus explaining the low base exchange capacity; the nitrogen is probably present largely as bacterial cell substance. In the case of chestnut soils formed under conditions of greater humidity and cooler climate, the cellulose is absent, but hemicelluloses are present; the lignin complex is more abundant than the protein, in a ratio of 40:24; these soils have a higher base exchange capacity. In the case of the chernozems, the colloidal organic complexes are coagulated by calcium and magnesium, impeding their removal by water or microbial decomposition, so that as much as 18 per cent organic matter accumulates; there is a greater increase in the lignin complex (from 40 to 54 per cent), a slight increase in protein (from 24 to 27 per cent), and a decrease in hemicellulose; this phenomenon explains the high base exchange capacity of these soils. To the north, the chernozems become degraded, with the entrance of the H-ion into the soil-adsorbing complex, which increases the solubility of the soil organic matter, resulting in its removal; the soil is gradually changed to a podsol. In the gray forest-steppe soil type and finally in the podsol types, the lignin complex is gradually lost and to a less extent the protein and hemicellulose groups, with a decrease in the content of adsorbed bases.

A further study (1223) of different soil types led to the conclusion that humus varies markedly in chemical composition (table 19).

Humus in podsols is characterized by an abundance of cellulose and hemicellulose and a low protein content. As a result of deficiency of bases in these soils, the two major constituents of the humus—the lignin and the protein—are readily dispersed in water and carried to the lower horizons, where they are precipitated, in the presence of greater base concentration. One need not assume the existence of “humic acids” and “crenic acids” in order to explain the movement of specific organic complexes in the process of podsolization. This process can be much better understood when consideration is given to the specific chemical constituents of the soil humus.

The humus of the chernozems is characterized by a narrower carbon-nitrogen ratio, which is nearly 10:1; by a high content of lignin and protein; and by a lower amount of both cellulose and hemicellulose. The humus in these soils is fixed because of the abundance of the bases. The humus in chestnut soils approaches that of the chernozems in its

chemical composition; it stands midway between these and the serozems. In view of the fact, however, that only one soil of this type was analyzed, no broad conclusions can be drawn. The humus of the sero-

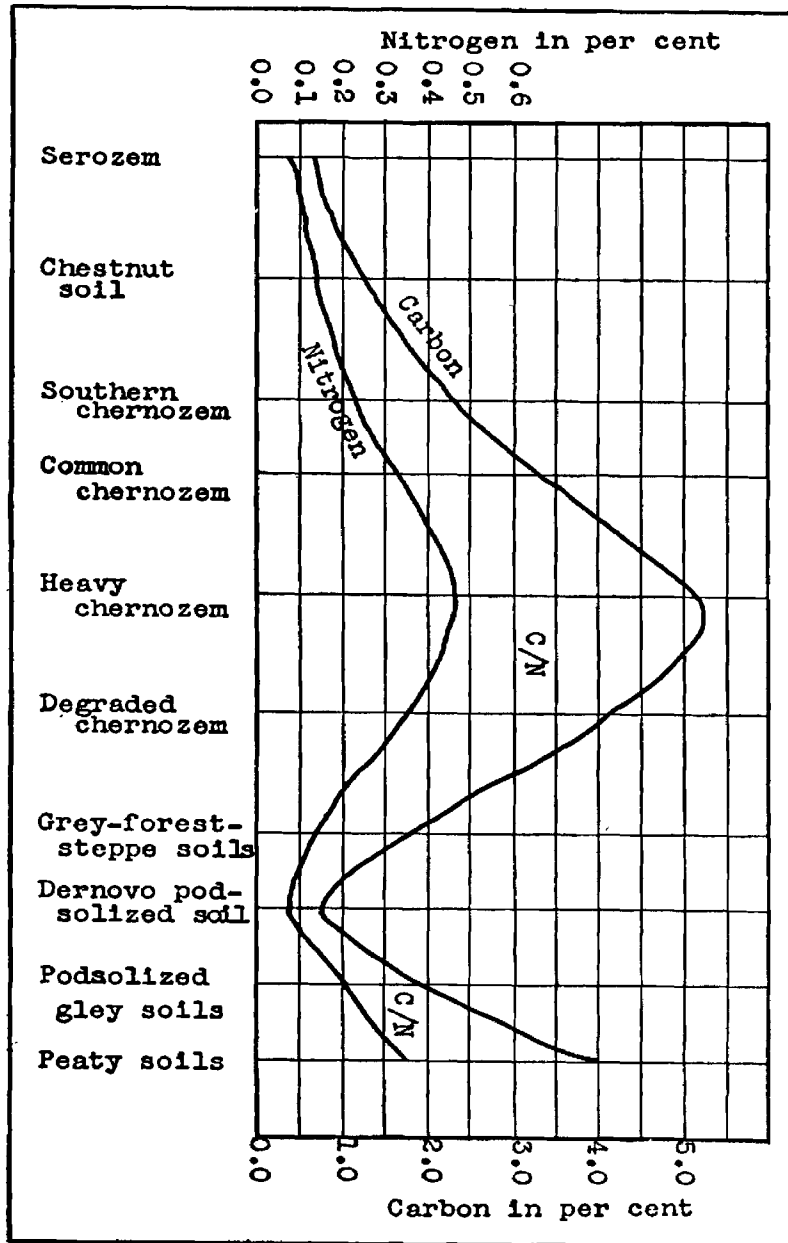


FIG. 45. Schematic representation of the changes in C/N ratio in different soil types of U. S. S. R. (Remezov).

zem is characterized by a narrow carbon-nitrogen ratio of about 6.0:1. This is explained by the relatively high protein content of this type of humus. Cellulose is completely absent. Hemicelluloses are either

absent or present in very low concentrations. Lignins are present, but in somewhat lower amounts than in chernozems.

As one proceeds from the podsols to the serozems, the following changes are evident in the chemical composition of the humus: 1. disappearance of the cellulose and hemicellulose, due to conditions more favorable to rapid decomposition; 2. an increase in the nitrogen content of the humus, resulting from the synthesizing activities of the microorganisms, accompanying the reduction of the carbohydrates; 3. narrowing of the C:N ratio, explained by the preceding two phenomena; 4. a gradual decrease in the relative lignin content, due to its more rapid decomposition. There are several other phenomena to be considered in this connection, such as the mobility in the podsols of the lignins and their derivatives and of the proteins, by reason of the fact that they are not fixed in the base-deficient soil; in the case of chernozems these complexes are fixed; in the serozems, they are slowly decomposed, especially the lignins. Considerable variation was found among soils belonging to the same general type.

Kudriavzeva (596) found that the various forms of nitrogen are different in podsols and in chernozem soils. In the latter, the nitrogen compounds are more resistant to decomposition, are less readily extracted with alkali solution, and are less readily hydrolyzed with acids. Under aerobic conditions, these compounds tend to be in a more readily decomposable state than under anaerobic conditions. Alexander and Byers (22) also emphasized the variation in chemical nature of the humus in different soil types, as brought out by the carbon-nitrogen ratios. This is illustrated in figure 45.

Summary. Humus plays an essential part in the various processes of soil formation. This has been definitely recognized by pedologists, who have frequently used the abundance and nature of humus as a basis for soil classification. The available evidence at the present time, however, is limited largely to a knowledge of the total humus content of the soil. Comparatively little is known as yet of the chemical nature of the humus in different soil types or of the function of the different humus constituents in the formation of the soil profile, or to what extent these constituents are responsible for certain soil characteristics.

OUTLOOK

HUMUS AS AN ORGANIC SYSTEM

The study of humus, including not only its chemical nature, but also its formation, decomposition, and importance in soil processes, in plant nutrition, and in industrial utilization, involves many specific problems which are closely concerned with various phases of plant and animal life. The physicist, the chemist, the botanist, and the microbiologist can all contribute to the solution of the numerous complicated problems involved in the formation and utilization of humus.

The soil is influenced in numerous ways by the humus content. Such physical characteristics of the soil as its structure, texture, moisture holding capacity, and temperature, are modified by the presence and abundance of humus. As a result of the various chemical and physicochemical reactions between humus and the inorganic constituents, the acidity of the soil, its colloidal condition and its base exchange capacity are greatly affected. A considerable amount of the important elements, carbon, nitrogen, phosphorus, sulfur, and iron remain stored up in the soil humus for considerable periods of time. During decomposition of the humus, these elements become liberated as CO_2 , NH_3 , PO_4 , SO_4 , and, being available for plant growth, influence soil fertility. Because of its high combustion value, humus is an excellent source of fuel; many deposits of economic importance have accumulated in aquatic environments and where the amounts of bases and mineral nutrients are insufficient to favor decomposition.

Knowledge of the abundance and chemical nature of humus, of its variation in composition under different conditions of formation and transformation, and of the changes that it undergoes as a result of treatment is extremely important in determining the value of a given soil for crop production. This is true especially of soils rich in humus, such as forest soils, in which the natural humus type determines the system of forest management.

The importance of humus in human economy seldom receives sufficient emphasis. Suffice to say that it probably represents the most important source of human wealth on this planet. Nature has stored in and upon the earth, in the form of humus, the source of a vast amount

of readily available energy, a large part of the carbon needed for life processes, and most of the combined nitrogen, so much needed for plant growth.

The study of humus thus involves problems in various fields of science: 1. in chemistry, embracing the chemical composition of humus and its numerous constituents, the interaction of the organic with the inorganic soil complexes, and the chemical characteristics of humus in relation to the chemical composition of the plant and animal residues from which it originated; 2. in physics and physical chemistry, including an investigation of the relationship of humus to those soil properties which influence plant development; 3. in microbiology, dealing, on the one hand, with the formation of humus, and on the other with its decomposition; 4. in soil fertility and plant physiology, concerning the liberation of the nutrient elements contained in the humus, and the direct relationships of humus to plant nutrition. Aside from these, numerous special problems arise in studying the utilization of humus both for agricultural and industrial purposes.

Humus can thus be considered as a natural body, related to: 1. the soil or the surface weathered layer of the earth, to which it gives characteristic properties and in the formation of which it plays a prominent rôle; 2. the majority of plants which have their roots in the humus, from which they derive directly or indirectly a large part of their nutrients and to which they continuously contribute, and 3. the majority of microorganisms, which find in humus a natural habitat, from which they derive their energy and nutrients and in the formation and transformation of which they exert the dominant influence.

APPENDIX

METHODS OF ANALYSIS OF HUMUS AND OF CERTAIN HUMUS CONSTITUENTS

In the various problems dealing with fertility and classification of soils, as well as in the study of certain chemical and microbiological processes, it may become necessary to determine the total organic matter content of the soil and the abundance of certain organic fractions or constituents of humus. A more detailed chemical analysis of the humus may further contribute to a better understanding of the processes of decomposition of the plant residues in composts, in peat bogs, and in soil, as well as of the reactivity of humus with inorganic soil constituents and of the processes of decomposition of humus, which lead to the liberation of the plant nutrients in available forms.

Numerous methods have been proposed for the determination of the total organic matter, or humus, and of the "humified" portion of the organic matter in soils, peats, and composts. No attempt will be made here to describe or even to enumerate all these methods. Only those that have found extensive use, at one time or another, will be mentioned or briefly discussed.

I. DETERMINATION OF TOTAL HUMUS

Five distinct methods are available for determining total humus:

1. Determination by the loss on ignition or related procedures.
2. The determination of total carbon, by one of the dry or wet combustion methods; a conversion factor is used in calculating the total amount of organic matter.
3. Complete oxidation of the organic matter with a strong oxidizing agent, such as 30 per cent hydrogen peroxide or other peroxide.
4. The calculation of the quantity of organic matter from the determined amount of total nitrogen.
5. Measurement of the amount of oxygen consumed in the process of humus oxidation.

The results obtained by these different methods are not always alike; frequently they vary considerably. Each of these methods has certain advantages as well as certain distinct limitations.

1. *Loss on ignition.* The oldest and most common method for determining the amount of organic matter in soils involves the ignition of a weighed amount of oven-dried soil, until all the organic matter has been destroyed, cooling the sample, and weighing it; the loss in weight is usually assumed to represent the amount of organic matter (1282, 693, 449). This method was criticized long ago by Mulder (735), who stated that the loss in weight on ignition includes also a considerable amount of chemically combined water not driven off during the preliminary drying of the soil. It is now well established that the water present in the soil colloids and in the clay minerals (water of constitution), as well as the water of hydrated minerals (water of crystallization) of the zeolite type are included in the loss on ignition. Some attempts have, therefore, been made (140) to distinguish between the loss on ignition due to organic matter and that due to the dehydration of some of the inorganic soil constituents.

The determination of the organic matter content of mineral soils by the loss on ignition is, therefore, at best only an approximation. This is especially true of soils containing a large amount of clay and calcium carbonate. In the case of surface soils, results obtained by this method were found to be from 35 to 120 per cent higher than the actual organic matter content of the soil as calculated from the organic carbon; in the case of clay subsoils, the discrepancy may even be considerably larger. Couture (196) condemned this method as not giving any reliable information concerning the humus content of the soil. However, the method is useful for determining the organic matter content of composts, peats and surface layers of forest soils.

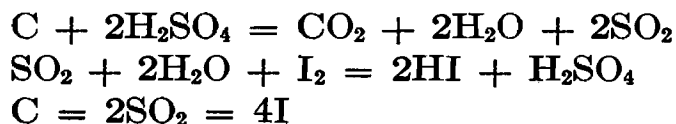
Rather (863) suggested that the hydrated mineral matter be removed from the soil by repeated treatments with a mixture of dilute hydrochloric and hydrofluoric acids; the soil is then washed with water, and the organic matter determined by ignition. The amount of organic matter lost in the process of leaching and treatment with acid was found to be small. This method was used by Read and Ridgell (869) for a series of soils with very satisfactory results. Alexander and Byers (22) compared this method with the combustion and hydrogen peroxide methods and found that it gives higher results in most cases. They believed, however, that the method is most satisfactory for determining the true organic matter content of the soil, although it is time consuming. It cannot be recommended for routine analyses, but only for special studies of the organic matter-carbon relationships.

Bouyoucos (140) suggested a method which consists in distilling

Various types of apparatus, to be used for dry and wet combustion, have been described (353, 320, 134, 411, 449). The absorption of the CO₂ in a potash bulb has been criticized (1181), largely because of the error involved in recording a small increase in weight of a large piece of apparatus. The CO₂ liberated during the combustion may be absorbed in standard barium hydroxide solution, which is titrated back with standard oxalic acid solution. The accuracy of the wet combustion method was determined by Gortner (353), who obtained a recovery of 101.8 per cent.

Another procedure for the determination of carbon by wet combustion consists in using a mixture of KMnO₄ and sulfuric acid (1238, 743). A set of KOH bulbs containing a 1:1 solution of KOH and a soda-lime tube serve to remove all the CO₂ from the entering air. A small portion of the soil or solution to be analyzed is placed in the combustion flask and 2.5 gm. KMnO₄ added. Suction is applied and 50 cc. concentrated H₂SO₄ slowly admitted through a separatory funnel during which time the system is continuously aerated. The solution is then heated to boiling and the aeration continued with heating for about three hours. This period of time has been found to be sufficient for the complete combustion of the carbon and the removal of the carbon dioxide. The CO₂ is absorbed in Truog towers or in a series of large glass test-tubes of about 70 cc. capacity, each containing 25 cc. of 0.05 *N* Ba(OH)₂ solution. At the end of the determination, the Ba(OH)₂ is titrated with 0.05 *N* oxalic acid, with phenolphthalein as an indicator. This method is especially convenient for the determination of carbon in liquids or in soils containing very small amounts of organic matter. Couture (196) also states that the most convenient method of carbon determination in soil consists in the oxidation of the organic matter with permanganate and sulfuric acid.

Robinson and his associates (905) suggested a combination of the carbon and nitrogen determinations in the Kjeldahl digestion method. The carbon determination was based upon the following reactions:

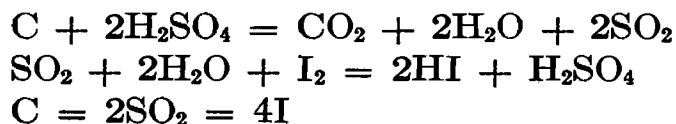


The gaseous products are passed through standard iodine solution, and the excess iodine is titrated back with standard sodium thiosulfate solution. One cubic centimeter of *N*/1 solution = 3 mg. carbon. The results are multiplied by 1.116, in order to correct for the percentage

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of organic carbon. No correction for inorganic carbon was found necessary (834). A comparative study of the dry and wet combustion methods has recently been made by the organic carbon committee of the International Society of Soil Science (1942); the dry combustion methods gave concordant results, while in the wet determinations, the recoveries of carbon varied with the details of the technique.

The micro-determination of total carbon and carbonate carbon in soil was described by Nicloux (763). Other modifications of the combustion method are referred to later.

3. *Peroxide method.* Coppentrath (189), as well as May and Gile (682), have shown that the decomposition of hydrogen peroxide in soil, as measured by the oxygen liberated, is nearly proportional to the amount of organic matter present in the soil. König and his associates (568-9) demonstrated that 60 to 90 per cent of the total carbon of soil organic matter is changed to carbon dioxide by treatment with hydrogen peroxide in an alkaline solution. Peterson (817) digested the soil with a dilute solution of hydrogen peroxide until constant weight was attained; by comparing the loss in weight by this method with the amount of organic matter found by direct combustion, the conclusion was reached that hydrogen peroxide oxidized about 90 per cent of the organic matter.

Robinson (406) suggested the use of 15 per cent hydrogen peroxide for the destruction of the organic matter in the soil. About 1 gm. of soil or 0.2 gm. of peat is introduced into a 250-cc. beaker; 10 cc. of water and 10 cc. of 30 per cent H_2O_2 are then added. If the reaction is not very vigorous, the beaker is placed in a boiling water bath and digested until gas formation ceases. The process is usually completed in one hour. The contents are filtered through a Gooch crucible, and the residue is washed, dried, and weighed. The filtrate is evaporated, ignited, and weighed, and the weight of ash is added to that of the residual soil; the combined weight represents the soil free from organic matter.

The hydrogen peroxide method was found to give lower results than the combustion method, for 22 of 26 soils, the difference being considerable in some cases. This method offers no advantage over the combustion method and is not applicable to soils containing more than 2-3 per cent calcium carbonate or to soils containing more than a trace of manganese dioxide or chromium sesquioxide. Furthermore, the hydrogen peroxide does not remove all the carbon compounds from the soil. If the organic matter, as determined by the carbon content of

the residue after the hydrogen peroxide digestion, is added to that found by this treatment, a fairly accurate figure for the total organic matter is obtained; however, this procedure makes the method too tedious and complicated. Soils rich in carbonate must be treated first with hydrochloric acid and the excess then removed; this may result in some loss of organic matter.

The use of hypobromite for the quantitative determination of the soil organic matter (1177) is also open to similar criticisms. Soil organic matter can also be oxidized with sodium peroxide (Na_2O_2), in the presence of magnesia powder (808) and the CO_2 liberated from the fused mass and measured; this method is known as the bomb method and was found to give quite satisfactory results in many cases; it is useful when great accuracy is not needed and when a large number of determinations are to be made.

4. *Total nitrogen of soil as a measure of the humus content.* It has frequently been suggested that the amount of humus in soil be calculated from the nitrogen determined by the Kjeldahl method. The factor commonly used for making such calculations was $N \times 20$. The assumption is thereby made that the carbon content of humus is constant and that the ratio between the carbon and nitrogen is also more or less constant. However, in view of the fact that this ratio varies considerably, this method has very limited value.

5. *Rapid titration methods.* Several methods based upon the consumption of oxygen from a standard solution of a strong oxidizing agent have been proposed for making a rapid determination of the humus contained in soils and in peats (960). Chromic acid, in the presence of concentrated sulfuric acid is commonly used; heating at $165^\circ\text{--}175^\circ\text{C}$., for a few minutes, is required for the digestion. The residual chromic acid is titrated with a standard solution of ferrous ammonium sulfate, diphenylamine being used as an indicator. Degtjareff (207) suggested that the digestion be carried out in a sulfuric acid bath, at 165°C ., for 10 minutes; by adding a little hydrogen peroxide to the oxidizing mixture, the use of heat could be omitted; however, this modification was found (1244) to introduce a considerable error.

The foregoing method has been variously modified (1167). Three reagents are commonly used: (1) 0.4 *N* solution of CrO_3 , obtained by dissolving 40 gm. of $\text{K}_2\text{Cr}_2\text{O}_7$ or 32 gm. CrO_3 in 1 liter of water; 1 liter of concentrated sulfuric acid (sp. gr. 1.84) is then added to the chromic acid solution. (2) 0.2 *N* solution of ferrous ammonium sulfate, ob-

tained by dissolving 80 gm. of the salt in a liter of water containing 20 cc. of concentrated H_2SO_4 ; the solution is standardized with 0.1 *N* $KMnO_4$ solution; 1 cc. of this solution corresponds to 0.6 mg. of carbon or to 1.034 mg. of humus. (3) 0.5 gm. diphenylamine, dissolved in 100 cc. concentrated H_2SO_4 + 20 cc. water, is used as an indicator.

In carrying out the determination, from 0.3 to 0.5 gm. portions of oven-dry soil or 1 to 2 gm. portions of sandy soil are placed in 100-cc. Erlenmeyer flasks; 10 cc. of the chromic acid solution are added and the flasks covered with small funnels, which act as condensers. The flasks are placed on a hot plate, the contents allowed to reach the boiling point, and kept moderately boiling for exactly 5 minutes. The flasks are allowed to cool, and the contents are transferred to 400-cc. beakers with about 250 cc. of distilled water. Care is taken to rinse into the beaker any material adhering to the funnel. Ten drops of the indicator are added, and the solution is titrated with the ferrous ammonium sulfate reagent, until the violet-blue color of the solution just changes to a gray-green, which changes, on standing, to a deep green. By subtracting the titration figure from that of the control (10 cc. chromic acid solution) and multiplying by 0.6, the carbon content of the amount of soil used for the determination is obtained. A comparative study of this method with that of the wet and dry combustion procedures was made (1226, 1202, 1174, 194a) with highly satisfactory results.

This method can also be used for determining the organic matter content of solutions. A 10-cc. portion of the solution (the amount depending upon the content of organic matter) is placed in a 100-cc. flask; 10 cc. of 0.45 *N* CrO_3 dissolved in concentrated H_2SO_4 (sp. gr. 1.84), 0.1 gm. Ag_2SO_4 , and a pinch of ignited soil are added. The solution is boiled for 5 minutes and titrated with 0.2 *N* ferrous ammonium sulfate solution, in the presence of diphenylamine as an indicator. One cubic centimeter of the 0.2 *N* solution corresponds to 1.6 mg. of oxygen needed for the oxidation of 0.6 mg. of oxidizable carbon and is equivalent to 5.3 calories.

II. DETERMINATION OF SPECIFIC HUMUS CONSTITUENTS

A number of methods are available for the study of various chemical constituents of humus (561); these range from the methods adopted by Schreiner and Shorey for the isolation of definite organic compounds to the numerous methods of determination of such vague preparations as "humus," "matière noire," "humic acid," "humic matter," and the

“humified portion” of the organic matter in soils, peats, and composts (1013). Very little can be said in favor of the determinations for these last preparations, or for alkali extraction methods, or for oxidation of humus with various agents. A number of specific reagents, such as pyridine and acetyl-bromide, have also been used for distinguishing certain humus fractions, such as “decomposed” and “undecomposed” humus (834); the decomposed humus was separated into irreversibly coagulated and reversibly coagulated humus; the first is insoluble in alkalies, representing mild humus, and is neutral or alkaline in reaction, consisting of Mg-, Ca-, Fe-, and Al-humates; the second is colloiddally soluble in alkalies, is highly dispersed, has a protective action and a high water-holding capacity, and represents hydrogen- or alkali-humates (raw-humus).

III. PROXIMATE ANALYSIS OF HUMUS

Keppeler (537) proposed, in 1920, a method of separation of peat into several fractions, by treatment with 72 per cent sulfuric acid. The total carbohydrates were thus hydrolyzed and their amount was determined by the reducing sugar content; by measuring the amount of pentose in the latter, the carbohydrate group could be further separated into the pentosans and hexosans; the amount of the unhydrolyzed residue, which consists largely of lignin, was considered to indicate the extent of decomposition of the peat.

A somewhat more detailed system of analysis of peat was proposed by Oden and Lindberg (784). The powdered dry material was extracted for 6–8 hours with ether, giving a group of fats, waxes, and resins. After ether extraction, the residue was treated in the autoclave with 300 cc. of a 1 *N* H₂SO₃ solution, with the result that lignin and a certain amount of pentosans were brought into solution. One- to two-gram portions of residue were then extracted with 300 cc. of 2 *N* NH₄OH solution, for 3–4 days, followed by 3–5 hours in the autoclave, yielding a solution of “humic acids”; since these contain also pectic substances, a furfural determination was made on a portion of the solution. The residue was now treated with Schweizer’s reagent, giving a solution of cellulose, which was precipitated by alcohol and washed with acid and distilled water. This method of analysis is open to severe criticism, for the following reasons: (a) it does not take into consideration the highly important nitrogenous constituents of the humus; (b) the water-soluble substances and the hemicelluloses are not accounted for; (c) an abnormally high “lignin” fraction is ob-

tained which consists of real lignin to only a limited extent; (d) the "humic acid" obtained by this method is indefinite in composition.

Only slight importance can be attached to the methods employed in foodstuff analysis when applied to humus (201). This system of analysis, which records the ash, fat, crude fiber, nitrogen-free extract, and crude protein, tells but little of the chemical composition of the organic materials.

Groszkopf (373) analyzed the humus of forest soil as follows: the cellulose was determined by the Cross and Bevan method, the pentosans by the furfural method, and the lignin-humus complex by the Willstätter method; this complex was divided, on treatment with acetyl bromide, into lignin which dissolved in this reagent, and "pure humus" which was left undissolved. Similar procedures were used by Maliutin (671) for analysis of peat.

In 1928, Waksman and Stevens (1240) proposed a system of humus analysis which accounts for 85 to 98 per cent of the constituents of the humus in composts and peat, in the form of definite chemical groups. Two 5-gm. portions of material are first extracted with sulfuric ether in Soxhlets, for 16 to 24 hours; the soluble portion is determined by evaporating the ether and drying the residue in weighing bottles until constant weight is attained (*a*). The residues are then treated with cold distilled water for 24 hours; aliquot portions of the extracts are evaporated to dryness in weighed evaporating dishes on a water bath, dried, weighed, ignited, and reweighed, thus giving the water-soluble organic matter and ash (*b*); other portions are used for the determination of total nitrogen, and of nitrates and reducing sugars if desired. The residues from (*b*) are treated with hot water for 1 hour on a steaming water bath, and the extracts analyzed for soluble organic matter and nitrogen (*c*). This is followed by two or three treatments with 100-cc. portions of boiling 95 per cent alcohol; the filtered solutions are combined and evaporated, in weighed dishes, to constant weight (*d*).

To the residues from (*d*), 100- to 150-cc. portions of a 2 per cent solution of hydrochloric acid are added and the flasks heated to 100°C. in flowing steam for 5 hours. The hot extracts (*e*) are filtered through papers previously dried and weighed; the residues are washed upon the filter and treated with distilled water until free from acid. The combined filtrate and washings are analyzed for total reducing sugar, aliquot portions of the solutions neutralized with 40 per cent NaOH solution being used. The reducing sugar is multiplied by 0.9 and reported as hemicellulose. This figure, although frequently much larger

than the total pentosan, determined as furfural, represents only a minimum amount of hemicellulose present, and is considerably lower than the total organic matter made soluble by the hot dilute hydrochloric acid; this is due to the fact that various substances, such as pectins, gums, and other polyuronides, methyl pentosans, and certain glucosides, do not give 100 per cent reducing substance upon hydrolysis, whereas certain plant materials, like mosses, contain polysaccharides which are hydrolyzed only after prolonged boiling with dilute acids.

The residues (*f*) left on the paper after the last treatment, are dried for 24 hours at 70°C. and weighed. In the case of sphagnum moss or young sphagnum peat, the material must be washed with alcohol and ether, to give a properly dried product. Two 1-gm. portions of each sample of the dry residues are treated with 10 cc. of 80 per cent sulfuric acid, in the cold, for 2 to 3 hours. If the material does not mix well with the acid, it must be broken with a glass stirring rod. One hundred fifty cubic centimeters of distilled water are then added and the material boiled for 5 hours under a reflux condenser or autoclaved for 1 hour at one atmosphere pressure. The extracts (*g*) are filtered either through weighed Gooch crucibles or through small dried and weighed quantitative filter papers. The residues (*h*) are washed thoroughly with distilled water, dried at 70°C., and weighed. Two of the residues are ignited to determine the ash, and the other portions are used for the determination of total nitrogen. The ash and protein content (total nitrogen $\times 6.25$) are subtracted from the total weight of the residue, to give the lignin content of a 1-gm. portion of the material left after the treatment with dilute hydrochloric acid. When multiplied by the weight of these portions (*f*) the lignin content of the original 5 gm. of material is obtained. The solution and filtrate (*g*) from the H_2SO_4 treatment are analyzed for sugar, after first neutralizing an aliquot portion with 40 per cent NaOH solution. The reducing sugar multiplied by 0.9 gives the cellulose content of 1 gm. of material left after the dilute HCl treatment. This figure multiplied by the weight of the HCl residues (*f*) gives the cellulose content of the original 5 gm. of material.

This system of analysis can be supplemented by several other determinations to give a more complete picture of the chemical nature of the specific humus formation. These include: 1. the pentosan content, by the furfuraldehyde method, of the total material and of the hydrochloric acid hydrolyzate; 2. the uronic acid content of the total

material (p. 164); 3. extraction of the material, especially in the case of peats, with ether and alcohol after the dilute acid treatment (22, 1168).

Thiessen and Johnson (1153) proposed a method of peat analysis based upon the procedures commonly employed by the wood chemist. This method has a number of limitations, chief among which is the fact that two of the most important groups of organic complexes in the peat are not accounted for, namely, the nitrogenous constituents and the hemicelluloses; further, the chemical nature of the preparations obtained by the use of various reagents is not known and the results, therefore, become of doubtful value.

Waksman and Stevens later (1241) modified their original method to be applied also to the study of humus in mineral soils. Here as well, the various constituents of the humus are determined directly and not by difference in weight. The soil is first analyzed, for moisture, organic carbon, and total nitrogen. Two 100-gm. portions of the air-dry soil are extracted in Soxhlets, for 12 to 24 hours. This is followed by extraction with hot 95 per cent alcohol, for 1 to 2 hours, on a boiling water bath. The residual soil is treated with hot water, followed by a 2 per cent hydrochloric acid solution, for 5 hours at 100°C. (the hot water extraction may be omitted because of the low concentration of the fraction extracted and its indefinite nature). The acid extract is filtered and the residue washed with distilled water; the filtrate and washings are combined and made up to volume; aliquot portions are used for the determination of reducing sugar, total nitrogen, and ammonia. The total organic matter brought into solution can be calculated from the carbon content in an aliquot portion of the extract. The hemicellulose and amide content of the humus are calculated from the sugar and ammonia. The soil treated with hydrochloric or with sulfuric acid usually gives a solution rich in iron and aluminum, which interferes with accurate sugar determinations. After neutralization, the precipitate formed is filtered off, and the residue washed; the sugar is determined in the filtrate.

Aliquot portions (20–50 gm.) of the residue, after the hydrochloric acid treatment, are placed in beakers, and 20 to 30 cc. of 80 per cent sulfuric acid solution added; the acid is allowed to act upon the soil for 2–3 hours in the cold; the mixture is then diluted with 15 volumes of water (300 to 450 cc.) and boiled for 2 to 5 hours. This results in complete hydrolysis of the cellulose occurring in the soil and its transformation into glucose; the determination of the reducing sugar serves

as an index of the cellulose content of the soil. The residue from the sulfuric acid treatment is washed with water, dried, weighed, and analyzed for total carbon and nitrogen. This residual portion of the humus consists entirely of: (a) lignin and its transformation products, and (b) various synthesized microbial complexes, including certain organic nitrogen compounds. If one assumes that the distribution of the nitrogen in the organic complexes in the soil is the same as the distribution in native plant and animal proteins, one can calculate the amount of nitrogenous substance in the residual material by multiplying the amount of nitrogen found by the factor 6.25. By subtracting from the total carbon found in the residue, the carbon of the nitrogenous complex, assuming that the latter contains 50 per cent carbon, and allowing 62 per cent carbon in the "lignin" complex, one can calculate the amount of "lignin" in the residue, as well as in the original soil. The following formula may be used for this purpose:

$$\text{Per cent of "lignin" in humus complex in soil} = \frac{a \times 100}{A} - \frac{b \times 100}{S}$$

when a = carbon content in the sulfuric acid residue, calculated on the basis of the total original sample of soil, A = total carbon content of the soil, b = protein in the sulfuric acid residue, obtained by multiplying the nitrogen content of the residue by 6.25; this is then calculated for the whole sample, S = total organic matter in the soil, as determined from the organic carbon.

It may prove desirable to subdivide this "lignin" fraction further; for this purpose one can use special reagents, such as acetyl-bromide, ascertain its solubility in ammonium hydroxide solution, or otherwise characterize the material.

This method was modified by Kamerman and Klintworth (521a). The soil was treated for 2 hours in the cold, with 80 per cent sulfuric acid, diluted with $1\frac{1}{2}$ volumes of water and digested over night on a water bath. The hydrolyzate was analyzed for total carbon and ammoniacal nitrogen. The ratio of total carbon to hydrolyzable carbon was found to be quite constant, having a value of 2:1. However, the ratio of total nitrogen to hydrolyzable nitrogen was not constant and was found to be influenced by the addition of nitrogen fertilizer.

Pichard (822) proposed another method of analysis of humus in peat, composts, and soil. The material is first extracted with ether, to remove the fats, and with a mixture of alcohol and benzol, to remove the resins. The residue is treated with hot water, followed by extraction with 2 per cent ammonia water, at 60°C in a closed vessel, in the

absence of oxygen; in the case of calcareous material, this treatment is preceded by extraction with 2 per cent HCl, at 15°C. The residual soil or compost is now hydrolyzed with dilute hydrochloric acid, to remove the hemicelluloses; this is followed by phenol which dissolves the lignin and leaves the cellulose. The pentosans are determined on a separate sample, as well as on the hydrochloric acid hydrolyzate and on the ammoniacal extract.

IV. DETERMINATION OF SPECIFIC CHEMICAL COMPOUNDS OR CHARACTERISTIC CHEMICAL GROUPS IN HUMUS

Among the chemical groups or compounds that can be determined in humus, the following may be mentioned here:

1. Proteins and their derivatives. The total protein in humus is best calculated from the total nitrogen content by the use of the factor 6.25. Various forms of humus may be submitted to acid hydrolysis, and the hydrolyzed products analyzed by the method of Van Slyke, Kossel, and Kutscher (575) or by any other convenient procedure (612, 728, 876).

2. Lignins. The presence of lignin in humus can be determined in four different ways: (*a*) treatment with 42 per cent hydrochloric acid, with 70–80 per cent sulfuric acid, or with a mixture of hydrochloric and sulfuric acids; the ash and the nitrogen in the residue must be accounted for; (*b*) extracting the lignin with alkali solutions under pressure and precipitating with a mineral acid; the hemicelluloses must be hydrolyzed with hot acid and the nitrogen accounted for; (*c*) extracting the lignin with various solvents, such as phenol, methyl glycol, etc.; (*d*) methoxyl determination (819, 820). Each of these methods has certain limitations; for quantitative purposes, the first and the last are probably most reliable. But the use of even these two methods is not free from criticism. It has been shown (445, 776), for example, that during treatment of plant material with mineral acids, certain carbohydrates, especially pentosans and levulans or levulose-containing carbohydrates (cane sugar) are resinified, giving lignin-like complexes, to the extent of 10 to 35 per cent of the carbohydrate. They are different from true lignins in that they are free from methoxyl, although they can also be methylated up to 12 per cent methoxyl. The last method (*d*) is open to criticism, since the methoxyl content of lignin changes during decomposition of the plant material (1237).

3. Hemicelluloses. Among these substances there are several groups of compounds which may be readily detected: (*a*) the pentosans, for

the determination of which the furfuraldehyde method is convenient; the uronic acids content must be determined separately; (b) the polyuronides, determined by treatment with 12 per cent HCl (406) and measurement of the CO₂ which is liberated; (c) various specific hexosans, such as mannans and galactans each of which requires a special method of procedure for its estimation.

4. Cellulose. Cellulose can be determined in humus by several methods, as mentioned previously.

V. METHODS OF STUDYING HUMUS DECOMPOSITION

A number of methods are available for measuring the rate of humus decomposition in soils and in composts. These are based upon the following processes: (a) liberation of carbon as CO₂, (b) the consumption of oxygen during the process of decomposition, (c) the measurement of the heat of reaction, (d) the liberation of nitrogen in an available form, as ammonia and nitrate. A detailed description of these methods is found elsewhere (1225).

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Sans Tache



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